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Effect of ZrO_2 on conductivity of PVC–PMMA–$LiBF_4$–DBP polymer electrolytes

S RAJENDRAN* and T UMA
Department of Physics, Alagappa University, Karaikudi 630 003, India

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Abstract. The preparation and characterization of composite polymer electrolytes of PVC–PMMA–$LiBF_4$–DBP for different concentrations of ZrO_2 have been investigated. FTIR studies indicate complex formation between the polymers, salt and plasticizer. The electrical conductivity values measured by a.c. impedance spectroscopy is found to depend upon the ZrO_2 concentration. The temperature dependence of the conductivity of the polymer films seems to obey the VTF relation. The conductivity values are presented and results discussed.

Keywords. Polymer electrolyte; PVC/PMMA blend; FTIR; impedance studies; plasticizer; inorganic filler.

1. Introduction

The addition of inert-phase particles (known as second phase or dispersoids) such as Al_2O_3, SiO_2, Fe_2O_3, ZrO_2, fly ash, etc to an ionic conductor (known as first-phase host materials) such as LiI, AgI, AgBr, AgCl, CaF_2, CuCl, etc has been reported to result in an increase in the conductivity value by one to three orders of magnitude. The resulting electrolytes are known as composite solid electrolytes and the increase in conductivity has been found to depend upon the concentration and particle size of the inert phase. The increase in conductivity is generally attributed either to the formation of a new kinetic path via a thin interphase layer along the interface itself, or to a concentration enhancement due to space charges in the sub interface region (Liang 1973; MacCallum and Vincent 1987, 1989; Maier 1989; Wagner 1989). Composite electrolytes containing a polymer–salt complex with a second inert phase are now being investigated (Wieczorek *et al* 1989; Capeano *et al* 1991; Croce *et al* 1991; Kumar *et al* 1993; Munichandraiah *et al* 1993; Sun *et al* 1999). Polymer electrolytes are of considerable interest for application in many electrochemical devices such as cellular telephones, smart credit cards, etc (Armand 1994; Aihara *et al* 1997). However, their low conductivity restricts their use in solid state batteries and electrochemical display devices. Plasticizers are added to polymer electrolytes to improve their mechanical and thermal properties, whereas the addition of dispersed second-phase particle is generally used to enhance their conductivity value (Kelly *et al* 1984, 1985; Ito *et al* 1987; Przyluski and Wieczorek 1989). Alamgir and Abraham (1993) studied poly(vinyl chloride) PVC based polymer electrolyte system plasticized by ethylene carbonate and propylene carbonate. Recently Sukeshine *et al* (1996) reported the transport and electrochemical characteristics of plasticized PVC based solid electrolyte systems. Appetecchi *et al* (1995) studied the kinetics and stability of the lithium electrode in poly (methyl methacrylate)-based gel electrolytes. Rhoo *et al* (1997) reported the ionic conductivity of plasticized PVC/PMMA blend polymer electrolytes.

In an attempt to look for good lithium ion conducting polymer electrolytes, we have investigated hybrid polymer electrolyte PVC–PMMA–$LiBF_4$–DBP with different concentrations of ZrO_2 and the effect of addition of ZrO_2 on the conductivity of the polymer electrolytes.

2. Experimental

The electrolytes were prepared from PVC (Aldrich, average molecular weight $1{\cdot}5 \times 10^5$) and PMMA (Aldrich, average molecular weight $1{\cdot}7 \times 10^5$) which were dried at 100°C under vacuum for 10 h. $LiBF_4$ (Aldrich) was dried at 70°C under vacuum for 24 h and DBP (dibutyl phthalate) (Aldrich) was used without further purification. Appropriate quantities of PVC, PMMA and $LiBF_4$ (table 1) were dissolved by adding in sequence to THF (tetrahydrofuran). After incorporating the required amount of plasticizer (DBP), inorganic filler (ZrO_2 powder) was suspended in the solution and stirred for about 24 h before the electrolyte films were cast on finely polished Teflon supports. The films formed were again dried in a vacuum oven at 323 K with a pressure of 10^{-3} torr for 24 h. FTIR studies were made using a Perkin Elmer Paragon Model

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*Author for correspondence

Table 1. Conductivity values of PVC–PMMA–$LiBF_4$–DBP–ZrO_2 polymer complexes (PVC–PMMA–$LiBF_4$–DBP (7·5–17·5–5–70 mole%)).

Sample	Weight ratio of ZrO_2 to PVC–PMMA–$LiBF_4$–DBP	s values ($\times 10^{-3}$ S cm^{-1})					
		304 K	328 K	338 K	348 K	358 K	373 K
F1	0	0·005	0·008	0·010	0·011	0·012	0·013
F2	5	0·923	1·442	1·538	1·648	4·877	19·618
F3	10	2·227	2·688	2·957	3·550	25·132	27·927
F4	15	2·391	2·922	3·287	3·757	31·940	40·651
F5	20	0·607	0·835	1·043	1·192	1·481	1·517

500 spectrometer in the 4000–400 cm^{-1} region. Conductivity measurements were carried out using a Keithley 3330 LCZ meter in the frequency range 40 Hz–100 kHz.

3. Results and discussion

3.1 *FTIR spectroscopic studies*

IR spectra were recorded in the transmittance mode. IR spectra of the starting materials PVC, PMMA, $LiBF_4$, DBP, ZrO_2 and polymer complexes are shown in figure 1. The absorption peaks of PVC (2360, 1717, 1684, 1436, 1259, 669 and 418 cm^{-1}), PMMA (1458, 840, 750, 668 and 441 cm^{-1}), $LiBF_4$ (3563, 1633, 1083 and 521 cm^{-1}), DBP (1728, 1074, 1038 and 798 cm^{-1}) and ZrO_2 (1634 and 412 cm^{-1}) get shifted in the polymer complexes. The vibrational bands of PVC (1339 and 961 cm^{-1}), PMMA (3446, 1384, 1149 and 990 cm^{-1}), $LiBF_4$ (1305 and 521 cm^{-1}), DBP (3435, 1599, 1578, 1385, 1120 and 963 cm^{-1}) and ZrO_2 (3400, 2283, 1122 and 500 cm^{-1}) are found to be absent in the polymer complexes. The band at 1734 cm^{-1} of PVC is replaced by two peaks at 1720 and 1731 cm^{-1} in the polymer complexes. The peaks at 1654, 1339, 1259, 961 and 600 cm^{-1} are assigned to C=C stretching, CH_2 deformation, CH-rocking, *trans* CH wagging and *cis* CH wagging vibrations, respectively in PVC. The peaks at 2927 and 1734 cm^{-1} are assigned to C–H stretching and C=O stretching vibrations, respectively in PMMA. The peaks at 1599 and 798 cm^{-1} have been assigned to C=C stretching and C–H deformation in DBP. The peaks at 2958, 1731, 1453 and 1257 cm^{-1} have been assigned to C–H stretching, C=O stretching, –O–CH_3 stretching and C–Cl stretching vibrations, respectively in the polymer electrolyte systems (Vien *et al* 1991). From the above analysis, the complex formation has been confirmed.

3.2 *Conductivity measurements*

Complex impedance diagram of the electrolyte film PVC–PMMA–$LiBF_4$–DBP–ZrO_2 (film F3) at 304 K is shown in figure 2. From table 1, it is observed that as temperature increases, the conductivity increases and this behaviour is in agreement with theory (Armand *et al* 1979).

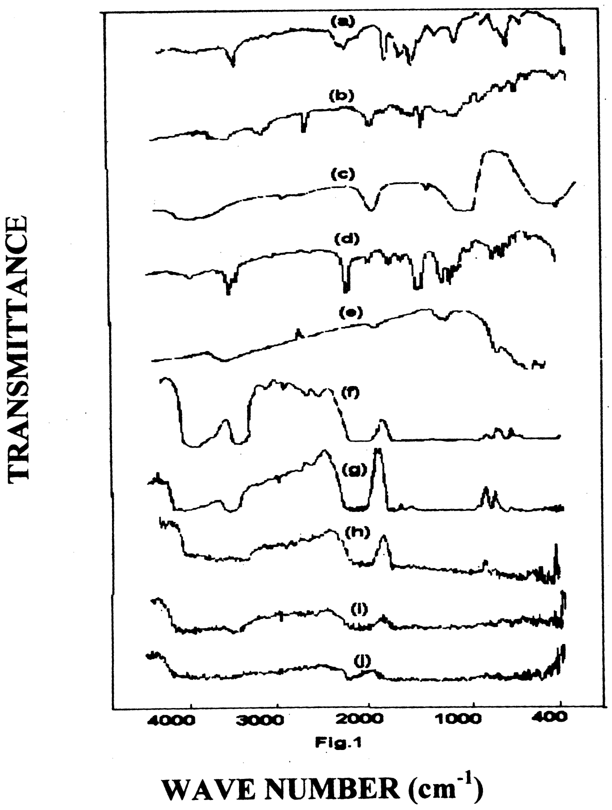

Figure 1. FTIR plots for PVC, PMMA, $LiBF_4$, DBP, ZrO_2 and the complexes: (**a**) PVC: (**b**) PMMA: (**c**) $LiBF_4$: (**d**) DBP: (**e**) ZrO_2: polymer complexes with: (**f**) 0, (**g**) 5, (**h**) 10, (**i**) 15, (**j**) 20 weight ratio of ZrO_2 to PVC–PMMA–$LiBF_4$–DBP.

The temperature dependence of electrical conductivities of the polymer blends is shown in figure 3. The overall features of the Arrhenius plot are quite similar for the electrolyte systems that no linear dependence could be obtained seems to suggest that ion conduction follows the Williams–Landel–Ferry (WLF) mechanism (Williams *et al* 1955). In other words, the non-linearity indicates that ion transport in polymer electrolytes is dependent on polymer segmental motion (Okamoto *et al* 1993). Thus, the result may be more effectively represented by the empirical Vogel–Tamman–Fulcher (VTF) equation (Vogel 1922; Fulcher 1925; Tamman and Hesse 1926):

$$s = AT^{-1/2} \exp[-B/T-T_g],$$

where A and B are constants and T_g the reference temperature taken as the glass transition temperature here. Constant A in VTF equation is related to the number of charge carriers in the electrolyte system and constant B is related to the activation energy of ion transport associated with the configurational entropy of the polymer chains. The temperature dependence of ionic conductivity suggests that the ion moves through the plasticizer-rich phase. Because the conducting medium, i.e. plasticizer-rich phase, involves the plasticizer, the salt and PMMA, the characteristics of the viscous matrix are brought out. The conductivity values for PVC–PMMA–$LiBF_4$–DBP–ZrO_2 systems are found in the range 10^{-4}–10^{-3} S cm^{-1} at 304 K which are comparable to the values reported by Rhoo *et al* (1997) for various PVC/PMMA blends at 293 K.

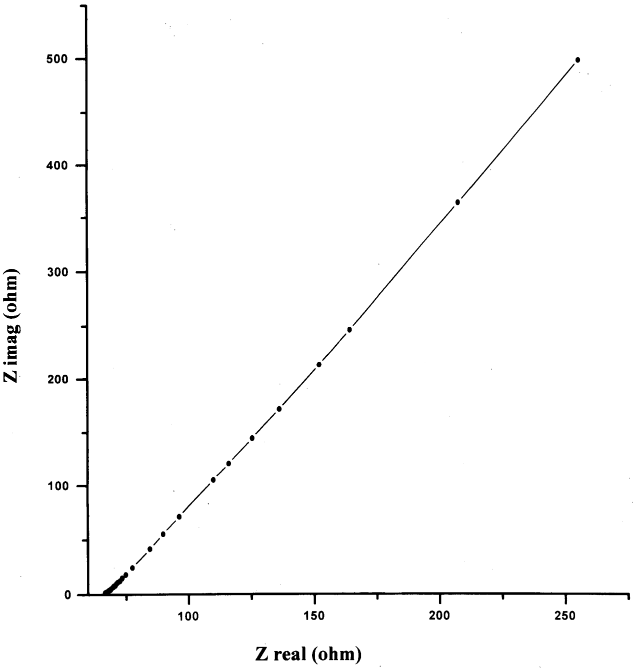

Figure 2. Impedance diagram of polymer electrolytes with 15 weight ratio of ZrO_2 to PVC–PMMA–$LiBF_4$–DBP at 304 K.

The effect of addition of ZrO_2 to the polymer complex on its conductivity value has been studied. Figure 4 shows the variation of conductivity with ZrO_2 concentration at 304 K. The conductivity increases with the concentration of ZrO_2 and shows a maximum value of $2{\cdot}391 \times 10^{-3}$ S cm^{-1} corresponding to the sample with a 15 weight ratio of ZrO_2 to polymer complex. The conductivity of the polymer electrolyte systems bereft of ZrO_2 is found to be $4{\cdot}65 \times 10^{-6}$ S cm^{-1} at 304 K. The maximum value in conductivity vs composition behaviour observed in figure 4 may be attributed to be due to a dispersed second-phase effect as well as to an increase in amorphicity of the polymer electrolyte. The initial rise in conductivity (figure 4) is due to the availability of conducting ions supplied by the PVC–PMMA–$LiBF_4$–DBP–ZrO_2 polymer complexes.

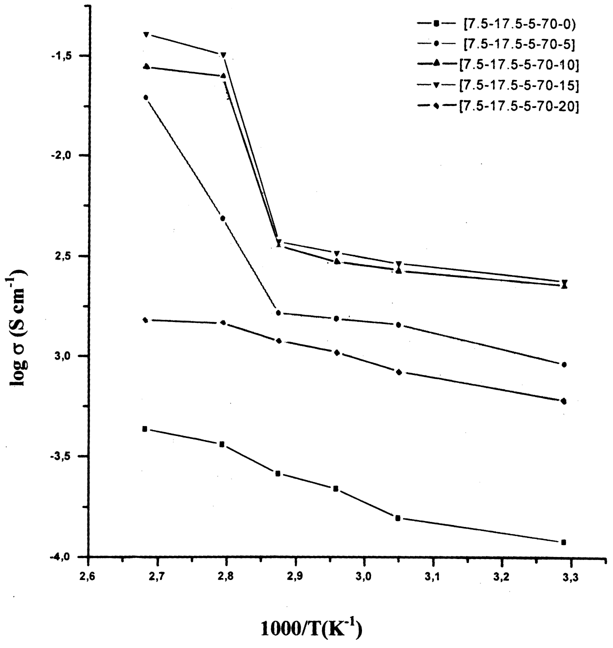

Figure 3. Arrhenius plot of log conductivity against reciprocal temperature for PVC–PMMA–$LiBF_4$–DBP–ZrO_2 polymer complexes.

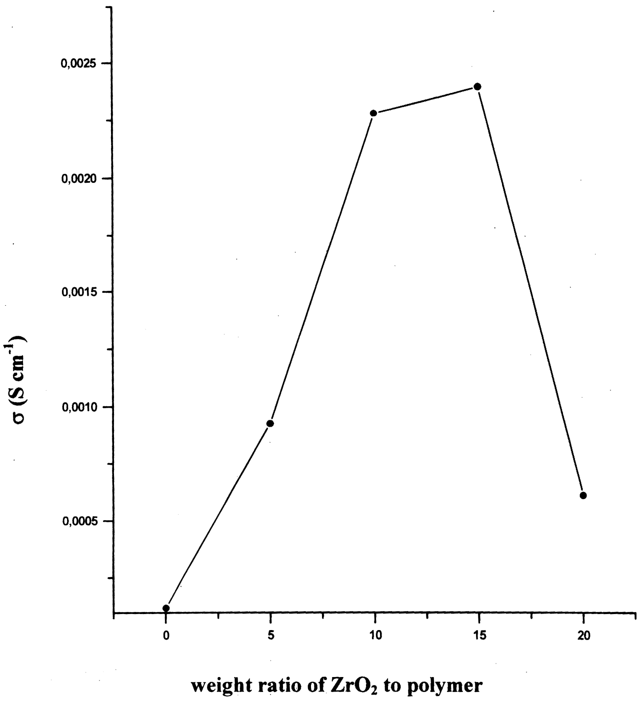

Figure 4. Variation of room temperature conductivity of PVC–PMMA–$LiBF_4$–DBP–ZrO_2 as a function of ZrO_2 concentration.

In the region of high ZrO_2 concentration (20 wt%), it is found that the conductivity decreases.

4. Conclusions

On the basis of different experimental measurements on PVC–PMMA–$LiBF_4$–DBP–ZrO_2 polymer electrolytes, the following conclusions are drawn:

(I) The complex formation in PVC–PMMA–$LiBF_4$–DBP–ZrO_2 system has been confirmed from FTIR studies.
(II) Conductivity increases and then dips with the addition of ZrO_2. The maximum value of conductivity obtained is $2{\cdot}391 \times 10^{-3}$ S cm^{-1} for samples with a 15 weight ratio of ZrO_2 to the PVC–PMMA–$LiBF_4$–DBP polymer electrolyte system.

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