JOURNAL OF MATERIALS SCIENCE **39** (2004) 2901 – 2904

Characterization of PVC-ZrO$_2$ composite polymer electrolytes

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Lithium ion conducting polymer electrolytes have been attracting attention due to their potential for application in high energy density lithium rechargeable batteries as well as a variety of all solid-state electrochemical devices [1–3]. Researchers have strived to achieve the combination of high ionic conductivity, good electrochemical and thermal stability, as well as good mechanical properties.

Alamgir and Abraham [4] studied poly (vinyl chloride) (PVC)-based polymer electrolyte systems plasticized by ethylene carbonate and propylene carbonate. The transport and electrochemical characteristics of plasticized PVC-based solid electrolyte systems were reported [5]. Recently, Ramesh and Arof [6] reported the electrical conductivity studies of poly (vinylchloride)-based electrolytes with double salt system. It has been shown that the conductivity of the double salt system can be improved by γ-irradiation and using double plasticizers.

Our recent work [7] has investigated the effect of ZrO$_2$ on conductivity of PVC-LiX (X = LiAsF$_6$) polymer electrolytes. In this work, we reported the ionic conductivity, structural and thermal studies of polymer electrolytes based on PVC and Li$_2$SO$_4$ as lithium salt, with and without the presence of different concentrations (5–15 wt%) of dispersed ZrO$_2$ ceramic powder.

The electrolytes were prepared from PVC (Aldrich, average molecular weight 1.5×10^5) and Li$_2$SO$_4$ (Aldrich) that were dried by heating under vacuum at 100 and 70 °C for 12 and 24 h respectively. DBP (dibutyl phthalate) (Aldrich) was used without further purification. Appropriate quantities of PVC and Li$_2$SO$_4$ (Table II), were dissolved by adding in sequence to THF (tetrahydrofuran). After incorporating the required amount of plasticizer (DBP), inorganic filler (ZrO$_2$) (particle size = 21.5 μm) 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 0.13 Pa for 24 h. The electrical conductivity of the polymer films was determined by impedance spectroscopy using a Keithley 3330 LCZ meter. The data were collected in the frequency range of 40 Hz–100 kHz and for temperatures in the range 304–373 K. The X-ray diffraction patterns of the samples were recorded using a computer controlled Jeol JDX 8030, X-ray diffractometer system (CECRI, Karaikudi.) with Ni filtered copper K alpha radiation (wavelength, λ = 0.15418 nm) and θ–2θ coupling mode. FTIR measurements were made in the range 4000–400 cm^{-1} using a Perkin-Elmer-Paragon 500 Grating IR spectrometer. The simultaneous thermal analysis systems of thermal analyzer model STA 1500, PL Thermal Sciences, (UK), were used in the present study.

Fig. 1 shows the X-ray diffraction patterns of pure PVC, Li$_2$SO$_4$, ZrO$_2$ and samples with 0, 5, 10, and 15 wt% of ZrO$_2$ to polymer complexes. The degree of crystallinity is calculated for the films shown in Fig. 1e–g as 4.4, 10.3 and 6.4 respectively. The maximum conductivity value (1.02×10^{-7} S cm^{-1}) is obtained for the film shown in Fig. 1d in accordance with low percentage of crystallinity (4.4%) compared to other films. It is observed from Fig. 1e–g that all the peaks pertaining to Li$_2$SO$_4$ are absent. Therefore, it is confirmed that complexation has taken place in the amorphous phase.

The infrared spectra would be sensitive both in situations where complexation has occurred in crystalline or amorphous phase. IR spectra were recorded in the transmittance mode. Fig. 2a shows the bands more characteristic of the spectrum in the region of 600–700 cm^{-1}, corresponding to C—Cl stretching vibrations. For pure PVC, a very strong absorption band is observed at about 1654 cm^{-1} corresponding to C═C stretching vibrations. This band is broadened, but at the same position in PVC, the band is shifted to polymer complexes (Fig. 2e–h). In PVC, the CH$_2$ deformation and CH-rocking vibration stretching frequency gives rise to an intense, a very strong and a sharp peak at 1339 and 1259 cm^{-1}. The intensity of the two medium CH$_2$ deformation vibration bands observed at 1489 and 1436 cm^{-1} in PVC. The two peaks are shifted to lower frequency {1433 and 1426 cm^{-1} (Fig. 2e and f)}. This suggests that the Li$^+$ ion may be located on the vinyl chloride of the polymer chain—[CH$_2$-CHCl-]$_n$. The 961 and 956 cm^{-1} bands are assigned to the weak trans CH wagging and the 669

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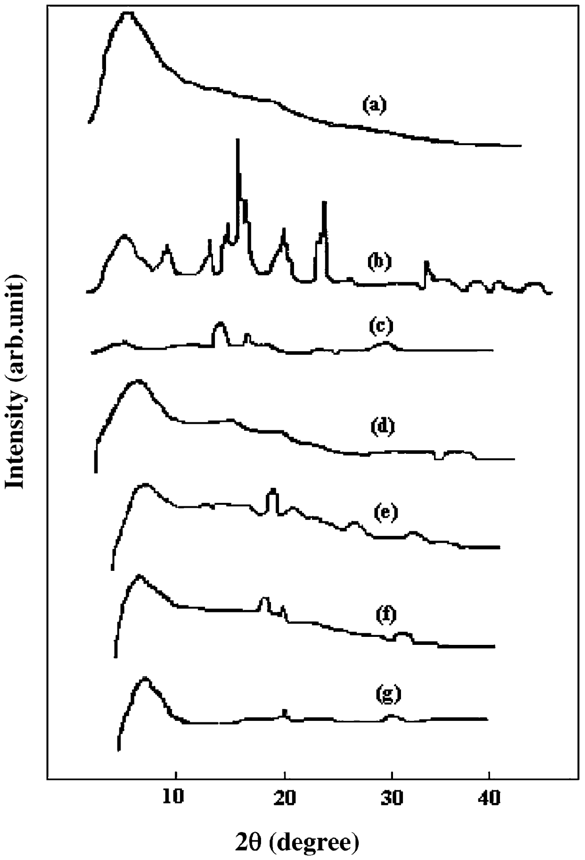

Figure 1 XRD patterns for PVC, Li_2SO_4, ZrO_2 and the complexes: (a) PVC, (b) Li_2SO_4, (c) ZrO_2, (d) 0, (e) 5, (f) 10 and (g) 15 weight ratio of ZrO_2 to PVC-Li_2SO_4-DBP.

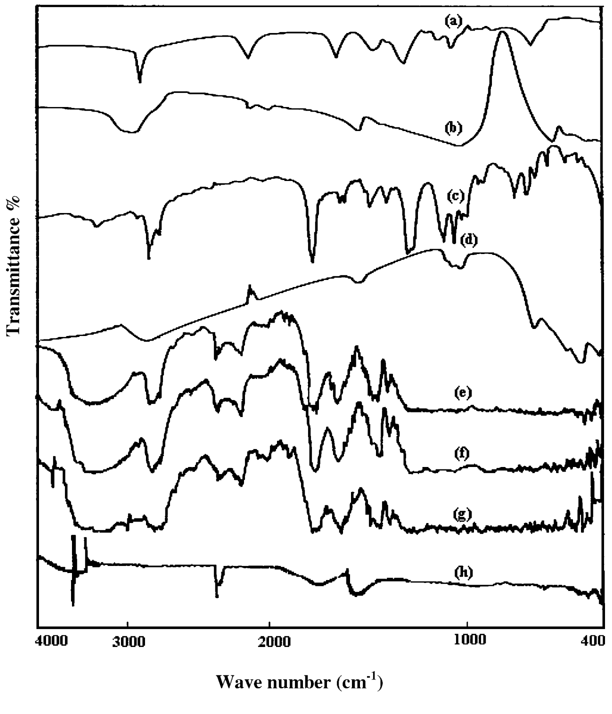

Figure 2 FTIR plots of PVC, Li_2SO_4, DBP, ZrO_2 and the complexes: (a) PVC, (b) Li_2SO_4, (c) DBP, (d) ZrO_2 polymer complexes with (e) 0, (f) 5, (g) 10, (h) 15 weight ratio of ZrO_2 to PVC-Li_2SO_4-DBP.

and 660 cm^{-1} bands are assigned to the cis CH wag vibration in pure PVC. If a vinyl group is conjugated to a trans CH═CH group, the CH wag vibrations of the two groups can interact also.

Further, the absorption peaks of PVC (1717, 1559, 1099 and 418 cm^{-1}), Li_2SO_4 (3529 and 1618 cm^{-1}), DBP (2961, 1728 and 1465 cm^{-1}) and ZrO_2 (1634 and 417 cm^{-1}) get shifted in the polymer complexes. The vibrational bands of PVC (1339, 1240, 1125, 956, 760 and 660 cm^{-1}), Li_2SO_4 (1112 and 642 cm^{-1}), DBP (3435, 1385, 1120, 963, 743 and 651 cm^{-1}) and ZrO_2 (3400, 2283, 1122, 745 and 500 cm^{-1}) are absent in the polymer complexes. Further, a new peak 2123 cm^{-1} is observed in the polymer complex [8]. From the above analysis, the complex formation has been confirmed.

DTA/TGA curves of PVC-Li_2SO_4-DBP-ZrO_2 polymer complexes of different compositions are shown in Fig. 3. The film is found to be stable up to a temperature of ∼180 °C. However, the weight loss is estimated as 23% at a temperature of ∼200 °C from the TGA graph (Fig. 3a). The weight losses for the film S2 [5 weight ratio of ZrO_2 to PVC-Li_2SO_4-DBP (25-5-70 mol%)] are calculated as 11 and 15% at 100 and 140 °C respectively from the TGA curve (Fig. 3b). A broad exothermic peak is observed above ∼142 °C in the DTA curve (Fig. 3c). Two endothermic peaks are observed at ∼28 and ∼29 °C respectively (Fig. 3c and d). In the TGA curve, the weight decreases gradually above ∼142 °C (Fig. 3d), concurrent with sample decomposition.

Weight loss data are compiled in Table I. Conductivity for the film S3 [10 weight ratio of ZrO_2 to PVC-Li_2SO_4-DBP (25-5-70 mol%)] is found to be 1.02×10^{-8} S cm^{-1} at 304 K (Table II). This value is found to be higher compared to the values of other films. Therefore, it is concluded that film S3 is superior compared to other films from the conductivity point of view.

From the TGA curves, it is found that films S1 and S2 (Fig. 3a and b) show thermal dehydration. Films S3 and S4 (Fig. 3c and d) exhibit a high thermal stability. The decomposition temperatures for the films S3 and S4 are found as 148 and 142 °C respectively. Hence film S3 reveals maximum thermal stability among the five films. The weight losses for the films S3 and S4 (10 and 15 weight ratio of ZrO_2 to PVC-Li_2SO_4-DBP (25-5-70 mol%)) are found as 7.2 and 8.9% at 100 °C (Table I). This may be understood in terms of the much smaller fractions, which lead to complex reaction path with varied amount of smaller distribution of polymeric backbones.

The conductivity values for PVC-Li_2SO_4-DBP-ZrO_2 system found in the range 10^{-10}–10^{-7} S cm^{-1} at 304 K respectively, which are comparable to the values reported by others [5, 6]. From Table II, it is observed that as the temperature increases, the conductivity values are also found to increase and this behavior is in agreement

TABLE I Conductivity values of PVC-Li_2SO_4-DBP-ZrO_2 polymer electrolytes

Sample	wt% of ZrO_2 to PVC-Li_2SO_4-DBP	From TGA graph weight loss% 100 °C	140 °C
S1	0	∼6.5	∼8
S2	5	∼11	∼15
S3	10	∼7.2	∼8.0
S4	15	∼8.9	∼9.9

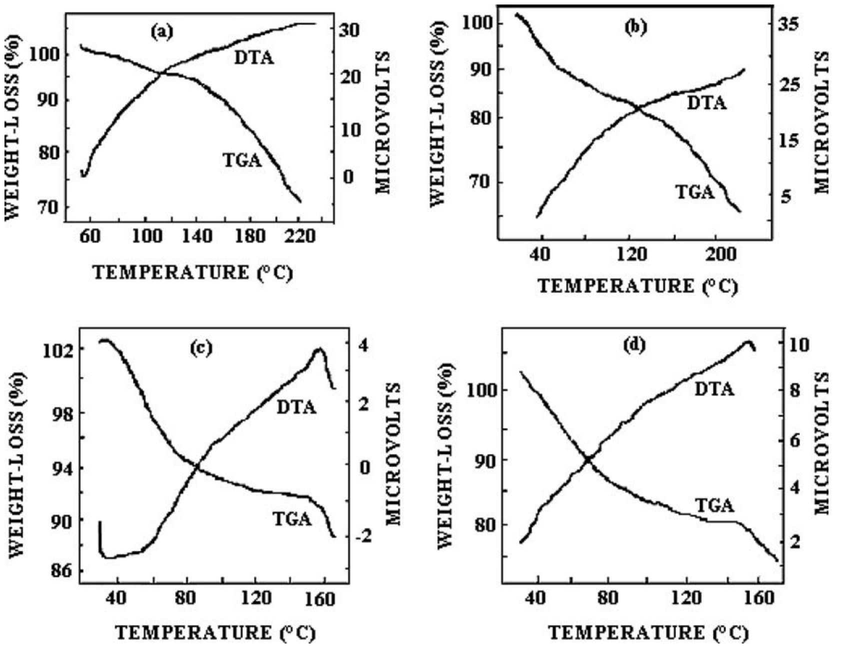

Figure 3 DTA and TGA scans of polymer complexes with: 0, (b) 5, (c) 10 and 15 weight ratio of ZrO_2 to PVC-Li_2SO_4-DBP (25-5-70 mol%).

with theory [9]. As the temperature increases, the polymer can expand easily and produce free volume. This leads to an increase in a mobility and segmental mobility that will assist ion transport and virtually compensate for the retarding effect of the ion clouds.

The temperature dependence of electrical conductivity (log σ vs. 1/T) for different compositions is shown in Fig. 4, and it seems to obey the Vogel-Tamman-Fulcher (VTF) relation [10]. The experimental data follow the Arrhenius equation:

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

where A and B are constants and T_g is a reference temperature. Constant A in the VTF equation is related to the number of charge carriers in the electrolyte system, and constant B in the VTF equation is related to the activation energy of ion transport associated with the configurational entropy of the polymer chains.

The effect of addition of ZrO_2 to the polymer complex on its conductivity value has been studied. Fig. 5 shows the variation of conductivity with ZrO_2 concentration in the temperature range 304–373 K. The conductivity increases with the concentration of ZrO_2 and shows a maximum value of 1.02×10^{-7} S cm^{-1} corresponding to the sample with a 10 wt% of ZrO_2 to polymer complex. The conductivity of the polymer electrolyte systems bereft of ZrO_2 is found to be 0.03×10^{-8} S cm^{-1} at 304 K. The initial rise in conductivity is due to the availability of conducting ions supplied by the PVC-Li_2SO_4-DBP-ZrO_2 polymer complexes. In the region of high ZrO_2 concentration (15 wt%), it is found that the conductivity decreases.

However the conductivity does not continue to rise indefinitely, with increasing concentration of ZrO_2. In fact it falls once an optimum concentration of ZrO_2 is crossed. This behavior is a direct consequence of high concentrations of the ceramic filler, which leads to well-defined crystallite regions. Further this optimum concentration, ZrO_2 particles tend to impede ionic movement by acting as mere insulators.

On the basis of different experimental measurements on PVC-Li_2SO_4-DBP-ZrO_2 polymer electrolytes, the following conclusions are drawn:

- When the complex films are completely or closely amorphous, the conductivity is found to be the maximum, as shown by their X-ray diffraction pattern. The peaks corresponding to lithium salts are reduced in intensity or absent in the polymer complexes. This indicates the absence of excess salt in the polymer complex films.
- The complex formation in polymer electrolyte system has been confirmed from FTIR studies.
- DTA/TGA studies to identify thermal stability. From the weight loss calculations, a possible and

TABLE II TGA results in PVC-Li_2SO_4-DBP-ZrO_2 polymer complexes PVC-Li_2SO_4-DBP (25-5-70 mol%)

		σ values ($\times 10^{-8}$ S cm^{-1})					
Sample	wt% of ZrO_2 to PVC-Li_2SO_4-DBP	304 K	328 K	338 K	348 K	358 K	373 K
S1	0	0.03	0.05	0.15	0.25	0.66	0.94
S2	5	6.32	8.46	11.24	13.26	19.25	21.48
S3	10	10.21	14.27	19.34	22.41	26.74	33.64
S4	15	2.55	4.27	5.24	7.26	9.43	13.75

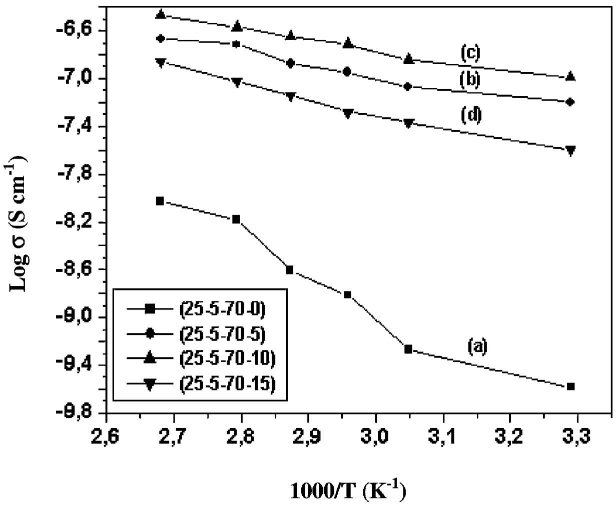

Figure 4 Arrhenius plot of log conductivity against reciprocal temperature for PVC-Li_2SO_4-DBP-ZrO_2 polymer complexes: polymer complexes with (a) 0, (b) 5, (c) 10 and (d) 15 weight ratio of ZrO_2 to PVC-Li_2SO_4-DBP.

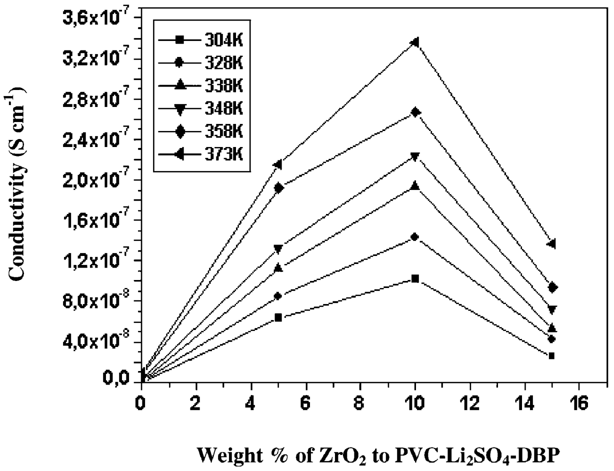

Figure 5 Variation of conductivity of PVC-Li_2SO_4-DBP system as a function of ZrO_2 concentration at different temperatures.

suitable combination of additives was identified so as to form a thermally stable polymer film.

- Conductivity increases and then dips with the addition of ZrO_2. The maximum value of conductivity obtained is 1.02×10^{-7} S cm^{-1} for samples with a 10 wt% ratio of ZrO_2 to the PVC-Li_2SO_4-DBP polymer electrolyte system.

Acknowledgment

The author is grateful to the Alexander von Humboldt Foundation for supporting this research.

References

1. M. MURATA, S. IZUCHI and Y. YOSHIHISA, *Electrochim. Acta.* **8/9** (2000) 1501.
2. M. WATANABE, T. ENDO, A. NISHIMOTO, K. MIURS and O. YANAGIDA, *J. Power Sources* **81/82** (1999) 789.
3. T. ITOH, M. IKEDA, N. HIRATA, Y. MORIYA, M. KUBO and O. YAMAMOTO, *ibid.* **81/82** (1999) 824.
4. M. ALAMGIR and K. ABRAHAM, *J. Electrochem. Soc.* **L 96** (1993) 140.
5. M. SUKESHINI, A. NISHIMOTO and M. WATANABE, *Solid State Ion.* **86** (1996) 385.
6. S. RAMESH and A. K. AROF, *ibid.* **136/137** (2000) 1197.
7. S. RAJENDRAN, T. UMA and T. MAHALINGAM, *Ionics* **5** (1999) 227.
8. D. L. VIEN, N. B. COLTHUP, W. G. FATELEY and J. G. GRASSELLI, "Infrared and Raman Characteristic Frequencies of Organic Molecules" (Academic Press, New York, 1991).
9. M. B. ARMAND, J. M. CHABAGNO and M. J. DUCLOT, in "Fast-ion Transport in Solids," edited by P. Vasgishta, J. N. Mundy and G. Shenoy (North-Holland, Amsterdam, 1979).
10. V. G. TAMMAN and H. HESSE, *Z. Anorg. Allg. Chem.* **19** (1926) 245.

Received 11 August
and accepted 30 October 2003