Short communication

Effect of salt concentration on poly (vinyl chloride)/poly (acrylonitrile) based hybrid polymer electrolytes

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Abstract

Hybrid, solid polymer electrolyte films consisting of poly (vinyl chloride) (PVC), poly (acrylonitrile) (PAN) and, propylene carbonate (PC) with different concentrations of $LiClO_4$ are prepared by means of a using solvent-casting technique. The structure and complex formation are studied by X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy. The temperature dependence of the ionic conductivities of the polymer films is explained in terms of a free volume model. The conductivities of $PVC–PAN–LiClO_4–PC$ complexes are determined at different salt concentrations. The highest ionic conductivity ($8.35 \times 10^{-5}\,S\,cm^{-1}$) is obtained for 8 wt.% $LiClO_4$ in the polymer complex at 304 K. The thermal stability of the electrolyte is examined by thermogravimetric/differential thermal analysis (TG/DTA).
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1. Introduction

The pioneering work of Wright and co-workers [1,2] motivated research on solid polymer electrolytes three decades ago and later Armand et al. [3] realized that these materials have potential applications in batteries and other ionic devices. Solid polymer electrolytes are advantageous in terms of shape, geometry, mechanical strength and a capability for strong electrode–electrolyte contact. The disadvantage that precludes their usage in high-energy power sources and other devices is a relatively low ionic conductivity at ambient temperature compared with 'wet' or 'gel' analogues. The disadvantage with linear poly (ethylene oxide) (PEO)-based electrolytes is their partially crystalline nature. This results in low ionic conductivity due to the slow kinetics of crystallization of the polymer, because the conduction in polymer electrolytes is due to amorphous phases containing electrolyte salts.

In last few years, many approaches have been adopted to reduce the crystallinity of PEO-based electrolytes and to increase the segmental mobility of the host polymer, namely, through co-polymerization, grafting, network formation, modification of macromolecules by pendant PEO systems [4], and plasticization of matrix polymers.

Poly (vinyl chloride) (PVC) can act as a mechanical stiffener in the electrolyte due to its immiscibility with the plasticizer. A PVC-based polymer electrolyte system plasticized with ethylene carbonate and propylene carbonate has been reported [5] to be applicable to lithium metal and lithium-ion secondary batteries [5].

The use of poly (acrylonitrile) (PAN) as a host polymer was first reported by Reich and Michaeli [6] and then by many others [7–14]. Slane and Salomon [15] studied a composite polymer electrolyte that consisted of zeolite powders dispersed in PAN-based gels with $LiAsF_6$.

In the present work, hybrid solid polymer electrolyte films that consist of PVC, PAN, $LiClO_4$ and propylene carbonate (PC) are examined to overcome the problem inherent to gel electrolytes. The conductivities of the hybrid polymer complexes with different salt concentrations and temperatures are investigated and reported.

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Table 1
Ionic conductivity values of PVC–PAN–LiClO$_4$–PC systems with different salt concentrations

Film	Composition (wt.%)	Ionic conductivity $\times 10^{-3}$ S cm^{-1}				
		302 K	381 K	333 K	353 K	373 K
A1	5.6–22.4–10–62	0.065	0.120	0.186	0.269	0.329
A2	6–24–8–62	0.084	0.159	0.265	0.391	0.523
A3	6.4–25.6–6–62	0.046	0.080	0.099	0.119	0.147
A4	6.8–27.2–4–62	0.007	0.018	0.028	0.043	0.071

2. Experimental

The electrolytes were prepared from PVC (Aldrich, average molecular weight 1.5×10^5) and PAN (Aldrich, average molecular weight 94000) which were dried at 100 °C under vacuum for 10 h; LiClO$_4$ (Aldrich) was dried at 70 °C under vacuum for 24 h; PC (propylene carbonate) (Aldrich) was used without further purification. Appropriate quantities of PVC, PAN and LiClO$_4$ (Table 1) were dissolved by addition, in sequence, to DMF (Di-methyl formamide). After the incorporation of the required amount of plasticizer (PC), the solution was stirred for about 48 h at room temperature and then at 60 °C for 4 h before the electrolyte films were cast on finely-polished Teflon supports or Teflon-covered glass plates. The films were dried in a vacuum oven at 333 K under a pressure of 10^{-3} Torr for 24 h. The resulting films were visually examined for their dryness and free-standing nature. Chemical storage, film casting and cell assemblies were performed under a vacuum.

The crystalline structure of the resultant electrolyte film was investigated by means of an X-ray diffractometer [Bruker (08 Advances)]. The fundamental vibrations of the polymer complexes were studied by Fourier transform infrared (FTIR) analysis in the range 4000–400 cm^{-1} using a Jasco FTIR 460 plus spectrophotometer.

The bulk electrical conductivity of the electrolyte was determined by sandwiching the electrolyte between stainless-steel electrodes. The measurements were performed under vacuum and were made with a Keithley LCZ meter model 3330. The conductivity values were evaluated from complex impedance isotherms in the temperature range 302–373 K.

The film with highest conductivity was subjected to thermogravimetric/differential thermal analysis (TG/DTA) using a Perkin-Elmer (Pyris Diamond, USA) instrument with a heating range from 32 to 450 °C at the rate of 10 °C per min.

3. Results and discussion

3.1. X-ray diffraction (XRD) studies

In order to investigate the influence of the concentration of lithium salt, XRD studies were performed for PVC, PAN, LiClO$_4$ and complexes Fig. 1 (a)–(g). It is evident that the intensity of the peak decreases with increase in salt concentration. The results can be interpreted in terms of the criterion of Hodge et al. [16] that has established a correlation between the height of the peak and the degree of crystallinity. Most of the peaks
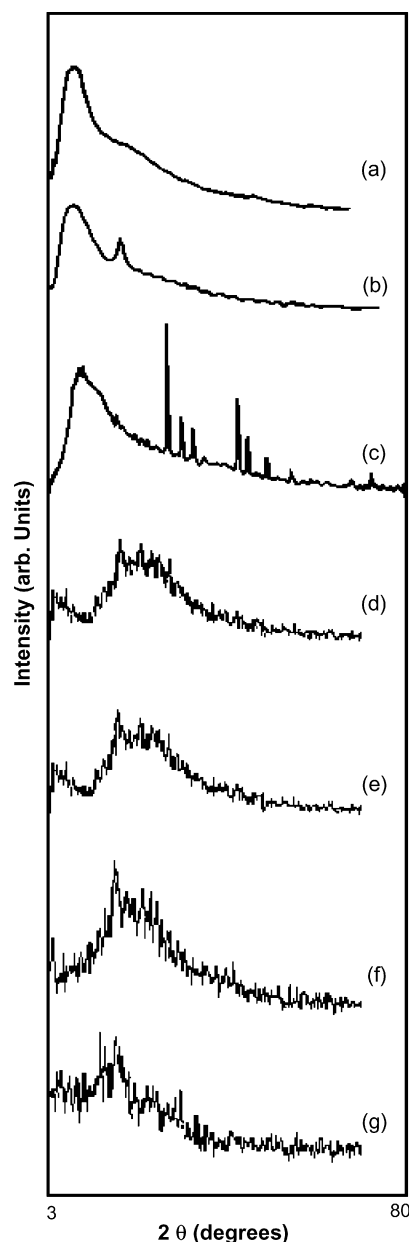

Fig. 1. X-ray diffraction patterns of (a) pure PVC, (b) pure PAN, (c) LiClO$_4$, (d) PC, (e) PVC(5.6)–PAN(22.4)–LiClO$_4$(10)–PC(62), (f) PVC(6)–PAN(24)–LiClO$_4$(8)–PC(62), (g)PVC(6.4)–PAN(25.6)–LiClO$_4$(6)–PC(62), and (h) PVC(6.8)–PAN(27.2)–LiClO$_4$(4)–PC(62).

pertaining to LiClO$_4$ disappear in the complexes and this indicates the complete dissolution of the salt in the polymer matrix. Hence, the XRD studies confirm the fact that there exist a definite complexation between the polymers, salt and plasticizer.

3.2. FTIR studies

Infrared spectral (IR) analysis is a powerful tool for identifying the nature of bonding and different functional groups present in a sample by monitoring the vibrational energy levels of the molecules, which are essentially the fingerprint of different molecules [17,18]. The IR spectra of PVC, PAN, LiClO$_4$, PC and the complexes are shown in Fig. 2(a)–(h), respectively.
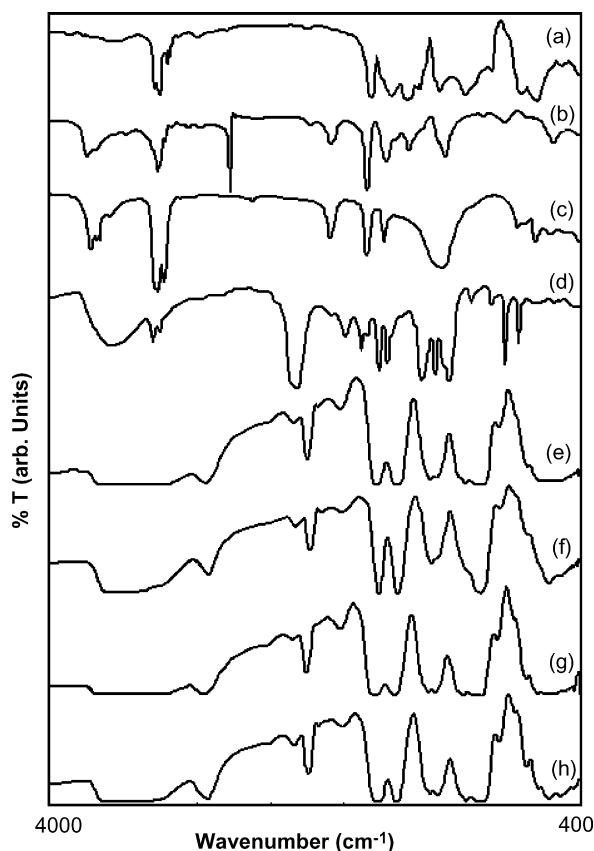
Fig. 2. FTIR spectra of (a) pure PVC, (b) pure PAN, (c) LiClO₄, (d) PC, (e) PVC(5.6)–PAN(22.4)–LiClO₄(10)–PC(62), (f) PVC (6)–PAN(24)–LiClO₄(8)–PC(62), (g) PVC(6.4)–PAN(25.6)–LiClO₄(6)–PC(62), and (h) PVC(6.8)–PAN(27.2)–LiClO₄(4)–PC(62).

Fig. 3. Impedance diagram for PVC–PAN–LiClO₄–PC (6–24–8–62 wt.%) at 302 K.

The C≡N stretching band in the IR spectrum is by far the most characteristic feature of nitriles; it appears at 2245 cm^{-1} for pure PAN. The nitrile band is displaced towards the higher frequency region around 2249 cm^{-1} due to the inductive effect created by the interaction of N atoms in −C≡N with Li$^+$ ions [19]. The vibrational peak at 1250 cm^{-1}, which is assigned to the C−N stretching of pure PAN, is shifted to 1252 cm^{-1} in all the complexes.

The CH₂ symmetrical bending vibration of pure PVC at 1428 cm^{-1} is shifted to a lower frequency of 1423 cm^{-1}, except for the film containing 8 wt.% LiClO₄ (film A2). The trans CH wagging of pure PVC at 966 cm^{-1} is shifted to 953 cm^{-1} in all the complexes. The absorption peak at 612 cm^{-1}, which is assigned to the γ (C−Cl) stretching of pure PVC [20–22], is shifted to 617 cm^{-1} in all the complexes.

The characteristic frequency at 1077 cm^{-1}, which is assigned to the carbonyl stretching in pure PC, is shifted in all the four complexes. The frequency reduces constantly, however, on the addition of salt (4–10 wt.%) from 1114 to 1069 cm^{-1}. This shows the dissociation of salt by the plasticizer [23].

The absorption band at about 950 cm^{-1} is assigned to the totally symmetric vibration of perchlorate anions [24]. The frequency of this band is sensitive to ion association, since the polarizing effect of the counter ion in an ion pair or a multiple ion aggregate leads to an up-shift of the frequency as compared
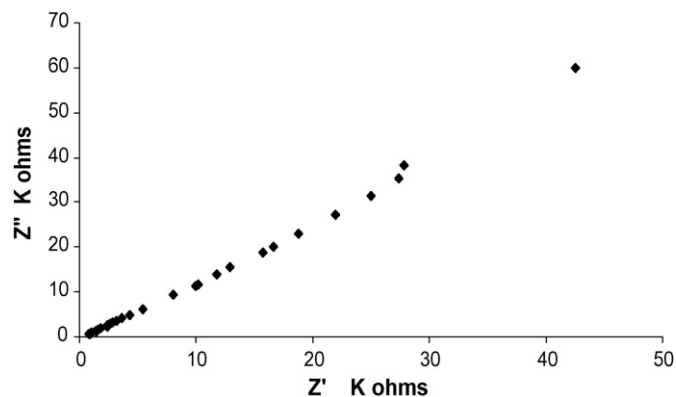
with the unperturbed anion. From the spectrum, it is found that the band maximum is at 952 cm^{-1} up to 8 wt.% LiClO₄ and is shifted to 957 cm^{-1} in the complex with 10 wt.% LiClO₄. This implies the aggregation of multiple ions when the salt concentration is increased above 8 wt.%, which could be the reason for the decrease in conductivity of the electrolyte film A1.

The vibrational peaks at: (i) 2913, 2849, 1333 and 966 cm^{-1} of PVC, (ii) 2812 and 1074 of PAN, (iii) 1832, 1366, 1097 and 712 cm^{-1} of LiClO₄, and (iv) 2989, 1633, 1340 and 849 cm^{-1} of PC are all absent in the complexes. In addition, there are the following additional new peaks for the complexes: 3629, 2028, 1380, 1358, 1191, 760, 455, 431 and 412 cm^{-1}. The above analysis establishes the formation of polymer salt complex [25–30].

3.3. Conductivity studies

The ionic conductivity of a polymer electrolyte depends on the concentration of carriers and on their mobility. The complex impedance plot for the PVC–PAN–LiClO₄–PC complex at room temperature is given in Fig. 3. In the impedance response curve, the absence of a high-frequency, semi-circular region validates that the current carriers are ions and therefore the total conductivity is mainly the result of ion conduction. The conductivity values of the complex with different wt.% of LiClO₄ are listed in Table 1. The data show that the conductivity increases with increase in temperature. This can be rationalized by the free-volume model [26].

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 [31]. 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 free volume increases. This leads to an increase in ion mobility and segmental mobility that will assist ion transport and virtually compensate for the retarding effect of ion clouds.

The dependence of salt concentration on the ionic conductivity, σ, is described by examining plots of log σ versus wt.% LiClO₄ for all samples (Fig. 4). As a general trend, at low salt concentration there is a build-up of charge carriers that results in an increase in ionic conductivity. The highest ionic conductivity
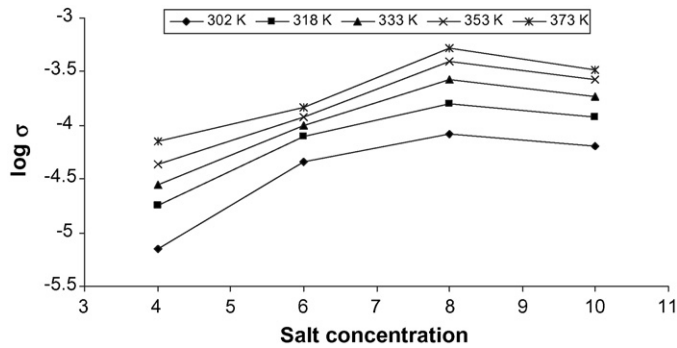
Fig. 4. Dependence of ionic conductivity on salt concentration for PVC–PAN–LiClO$_4$–PC polymer complexes at different temperature.

Fig. 6. TG/DTA curves of PVC (6)–PAN(24)–LiClO$_4$(8)–PC(62) complex.

of the polymer films is found at a salt concentration of 8 wt.% over the range of temperature investigated. At high salt concentrations, the build-up of charge carriers is offset by the retarding effect of ion clouds. Thus, the ionic conductivity decreases as this latter effect begins to dominate. The conductivity decreases when the ratio of LiClO$_4$ is 10 wt.%. This may be due to the restricted mobility of charge carriers in the more rigid matrix.

The Arrhenius plot of the ionic conductivity with a fixed amount of PVC/PAN blend and various concentrations of salt with plasticizer is given in Fig. 5. The temperature dependence of the ionic conductivity is not linear, which indicates that ion conduction follows the William–Landel–Ferry (WLF) mechanism [32]. That is, ion transport in a polymer electrolyte is correlated with polymer segmented motion [33].

3.4. TG/DTA analysis

The TG/DTA technique has been used widely to study all physical processes that involve weight changes and, as such, has been used to measure the diffusion characteristics and the moisture uptake. Also, it is used to investigate the thermal degradation phase transitions and crystallization of polymers. The TG/DTA curves of a PVC–PAN–LiClO$_4$–PC system with a maximum conductivity is shown in Fig. 6. Ramesh and Arof [34] reported that for pure PVC the weight loss begins at above 100 °C, and for a PVC complexed system with salt starts to lose mass at temperatures below 100 °C. In the present study, the TG curve
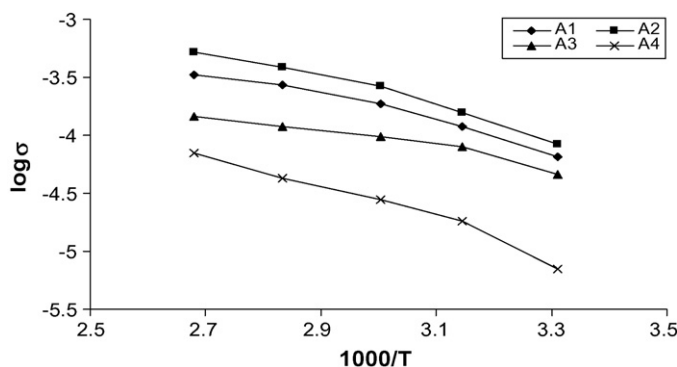
shows the first decomposition at 245 °C with a gradual weight loss of 16%. There follows a rapid weight loss up to 270 °C with a weight loss of 26%, beyond which the film decomposes. From the DTA curve, a sharp exothermic peak is observed at around 280 °C. This demonstrates the decomposition of the polymer film, which is in agreement with the TG curve. From the above discussion, it is concluded that the polymer electrolyte film is stable up to 250 °C.

4. Conclusions

From the above study, the following conclusions can be drawn.

(i) PVC–PAN–LiClO$_4$–PC blended polymer electrolytes have been prepared by a solvent casting technique.
(ii) Complex formation of PVC–PAN–LiClO$_4$–PC has been confirmed by FTIR and XRD studies.
(iii) a.c. impedance studies have been used to determine the ionic conductivity of the polymer electrolyte. An ionic conductivity of 8.35×10^{-5} S cm^{-1} was obtained for a polymer electrolyte containing 8 wt.% LiClO$_4$.
(iv) The film with maximum conductivity is characterized for TG/DTA and its thermal stability is ascertained.

References

[1] D.E. Fenton, J.M. Parker, P.V. Wright, Polymer 14 (1973) 589.
[2] P.V. Wright, Br. Polym. J. 7 (1975) 319.
[3] M.B. Armand, J.M. Chabagano, M. Duclot, in: P. Vashista, J.N. Mundy, G.K. Shenoy (Eds.), Fast Ion Transport in Solids, North-Holland, Amsterdam, 1979, p. 131.
[4] M. Armand, Adv. Mater. Res. 2 (1990) 278.
[5] M. Alamgir, K.M. Abraham, J. Electrochem. Soc. 140 (1993) L96.
[6] S. Reich, I. Michaeli, J. Polym. Sci. Phys. Ed. 13 (1975) 9.
[7] M. Watanabe, M. Kanaba, H. Matsuda, K. Mizoguchi, I. Shinohara, E. Tsuchida, K. Tsunemi, Makromol. Chem. Rapid Commun. 2 (1981) 741.
[8] M. Watanabe, M. Kanaba, K. Nagaoka, I. Shinohara, J. Appl. Electrochem. 27 (1982) 4191.
[9] M. Watanabe, M. Kanaba, K. Nagaoka, I. Shinohara, J. Polym. Sci., Polym. Phys. 21 (1983) 939.
[10] E. Tsuchida, N. Kobayashi, H. Ohno, K. Tsunemi, Solid State Ionics 11 (1983) 227.

Fig. 5. Arrhenius plot of PVC–PAN–LiClO$_4$–PC complexes for different concentrations.

[11] K. Tsunemi, H. Ohno, E. Tsuchida, Electrochim. Acta 28 (1983) 833.

[12] K.M. Abraham, M. Alamgir, J. Electrochem. Soc. 137 (1990) 1657.

[13] D. Peramunage, D.M. Pasqueriello, K.M. Abraham, J. Electrochem. Soc. 142 (1995) 1789.

[14] C.R. Yang, J.T. Perng, Y.Y. Wang, C.C. Wan, J. Power Sources 62 (1996) 89.

[15] S. Slane, M. Salomon, J. Power Sources 55 (1975) 7.

[16] R.M. Hodge, G.H. Edward, G.P. Simon, Polymer 37 (1996) 1371.

[17] T. Nagamoto, C. Ichikawa, O. Omoto, J. Electrochem. Soc. 134 (1987) 305.

[18] T. Nagamoto, H. Kakehata, C. Ichikawa, O. Omoto, Jpn. J. Appl. Phys. 24 (1985) 305.

[19] U.-S. Park, Y.-J. Hong, Seung M. Oh, Electrochem. Acta 41 (1996) 849.

[20] S. Krimm, V.L. Folt, J.J. Shipman, A.R. Berene, J. Polym. Sci. A1 (1963) 2621.

[21] S. Mizushima, T. Shimanouchi, K. Nakamura, M. Hayashi, S. Tsuchida, J. Chem. Phy. 26 (1957) 970.

[22] J.P. Sibila, C.J. Wincklhofer, Appl. Polym. Sci. 6 (1962) S56.

[23] Z. Wang, B. Huang, H. Huang, R. Xue, L. Chen, Fasong Wang, J. Electrochem. Soc. 14 (1996) 5.

[24] D. Ostrovshii, A. Brodin, M. Torell, G.B. Appetechi, B. Scrosati, J. Chem. Phy. 109 (1998) 7618.

[25] M.M.E. Jacob, S.R.S. Prabaharan, S. Radhakrishnan, Solid State Ionics 104 (1997) 267.

[26] T. Miyamoto, K. Shibayana, J. Appl. Phy. 44 (1973) 5372.

[27] H. Vogel, Phys. Z. 22 (1992) 645.

[28] V.G. Tamman, H. Hesse, Z. Anorg, Allg. Che. 19 (1926) 245.

[29] G.S. Fulcher, J. Am. Ceram. Soc. 8 (1925) 339.

[30] H.J. Rhoo, H.T. Kim, J.K. Park, T.S. Hwang, Electrochim. Acta. 42 (1997) 1571.

[31] M.A. Ratner, D.F. Shriver, Chem. Rev. 88 (1988) 109.

[32] M.L. Williams, R.F. Landell, J.D. Ferry, J. Am. Chem. Soc. 77 (1955) 3701.

[33] Y. Onamoto, T.F. Ych II., S. Lee, T.A. Skotheim, J. Polym. Sci. Part A. Polym. Chem. 31 (1993) 2573.

[34] S. Ramesh, A.K. Arof, J. Power sources 99 (2001) 41.