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Li-ion conduction in PVAc based polymer blend electrolytes for lithium battery applications

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ABSTRACT

The present work describes the Li-ion conduction in Poly(vinyl acetate) (PVAc) based polymer blend electrolytes have been synthesized by solvent casting technique for lithium battery applications. Characterization by XRD, SEM, AFM, FTIR, TG/DTA and photoluminescence was performed for synthesized polymer electrolytes. The thermal behaviour of the samples was ascertained from differential scanning calorimeter (DSC) and TG/DTA. The temperature dependence of conductivity of the polymer electrolytes was measured and the maximum ionic conductivity of 0.5269×10^{-4} Scm^{-1} at 303 K for PVAc:PVdF-co-HFP ((25/75) wt%):$LiClO_4$ (8 wt%) complex. Surface morphology was examined from various surface scanning techniques such as scanning electron microscope (SEM) and atomic force microscope (AFM). Photoluminescence measurements demonstrated that the PVAc based polymer blend electrolyte shows minimum intensity and the results are detailed in this paper.

1. Introduction

Recently, solid polymer electrolytes are of interest for use in solid state lithium-based batteries because they provide advantages over conventional lithium ion batteries, including higher safety and added design flexibility for cells of unique shape and size [1–4]. Currently the solid polymer electrolytes are receiving a great deal of attention because of their proposed large scale use in secondary lithium ion batteries and electro-chromic smart windows [5,6]. The advantages of using solid polymer electrolytes (SPEs) are good compatibility with lithium metal, low self-discharge, easy processing, good electrical conductivity etc. Armand et al. [7] reported that the crystalline complexes formed from alkali-metal salts with polyethylene oxide (PEO) were capable of demonstrating significant ionic conductivity and highlighted their possible application as battery electrolytes. Solution type electrolytes consisting of polymers such as poly (ethylene oxide) PEO and poly(propylene oxide) PPO or their blend complexed with suitable salts ($LiClO_4$, $LiCF_3SO_3$, etc.) were prepared and reported [8]. It is noted that the salt content is effectively affecting the ionic conductivity. It has been well accepted that the efficient ionic transport mechanism should be associated with a high degree of dissolution of the ionic salt in the polymer–salt complexes. It is noted that the dramatic enhancement of the ionic conductivity reflects dynamic connectivity effects in a phase separated electrolyte passing through a smeared percolation threshold. Bushkova et al. [9] believed that when a critical cluster concentration has been achieved, all separate single clusters come into contact with each other thus forming an infinite cluster, promoting fast cationic transport process in the entire electrolyte. Recently, poly(vinylidene fluoride-co-hexafluoro propylene) (PVdF-co-HFP) has been considered to be one of the most promising candidates for lithium battery applications [10–12]. We have already optimized the blend of PVAc and PVdF-co-HFP with constant salt ratio [13].

In the present study, the influences of the salt concentration in the polymer blend complexes are investigated. The complexation and phase structure of the polymer complexes are studied by Fourier transform infrared (FTIR) and X-ray diffraction (XRD) analyses. Thermal behaviour of the films has been analysed with the help of differential scanning calorimeter (DSC). The ionic conductivities of PVAc:PVdF-co-HFP ((25/75) wt%):$LiClO_4$ (X wt%) (where X = 4, 6, 8, 10 and 12) complexes are studied by means of ac impedance technique. The surface morphology of the film having maximum ionic

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conductivity is analysed with the help of SEM and AFM. The orders of local viscosity are identified with the help of Photoluminescence studies.

2. Experimental

Poly(vinyl acetate) (PVAc) ($M_w = 14 \times 10^4$) and poly(vinylidene fluoride-co-hexaflouropropylene) (PVdF-co-HFP) ($M_w = 40 \times 10^4$) and $LiClO_4$ were procured from Aldrich chemicals limited, USA. The polymer electrolyte films consisting of fixed ratio of PVAc and PVdF-co-HFP with various concentrations of $LiClO_4$ were prepared by means of solvent casting technique. The polymer salt complex was stirred well around 24 h with the help of magnetic stirrer and degassed to remove air bubbles. The obtained slurry was cast on a glass plate and the solvent THF was allowed to evaporate slowly in air at room temperature for 48 h. The films were further dried for 5 h in vacuum at 60 °C to remove any trace of solvent, which provided mechanically stable, free standing and flexible films. Finally the prepared films were stored in highly evacuated desicator. The nature of the materials and the dissolution of the salt could be determined by XRD diffractrometer. Laboratory X-ray diffraction pattern (XRD) of nature of the materials and the dissolution of the salt were acquired at room temperature with X'pert PRO PANalytical diffractometer using Cu Kα radiation as source and operated at 40 KV. The sample was scanned in the 2θ ranging from 10 to 80° for 2 s in the step scan mode. FTIR spectroscopy studies were carried out for confirming the complex formation using SPECTRA RXI, Perkin-Elmer spectro-photometer in the range 400–4000 cm^{-1}. The bulk electrical conductivity of the electrolyte was measured by sandwiching the electrolyte between stainless-steel electrodes. Conductivity measurements were performed under vacuum to avoid contamination of the film with moisture, and by means of ac impedance analysis to avoid electrode effects. The measurements were made with a computer controlled micro auto lab III Potentiostat/Galvanostat in the frequency range 1 Hz–300 KHz and in the temperature range of 303–363 K. TG/DTA thermal analysis of the film having maximum ionic conductivity was studied using PYRIS DIAMOND under air atmosphere with the scan rate of 10 °C min^{-1}. The decomposition and the melting point of the prepared samples were measured using differential scanning calorimeter (DSC) [model of Mettler Toledo DSC 822e] and the samples were heated from −100 °C to 350 °C at a heating rate of 10 °C min^{-1}. The electrolyte film having maximum ionic conductivity was subjected to atomic force microscopy [model Veeco-diCP-II]. The pore size and the root mean square (rms) roughness of the film were measured from the topography image. Secondary electron images of the sample were examined by using JEOL, JSM-840A scanning electron microscope. The photoluminescence studies were performed by Carry Eclipse Fluorescence spectrophotometer.

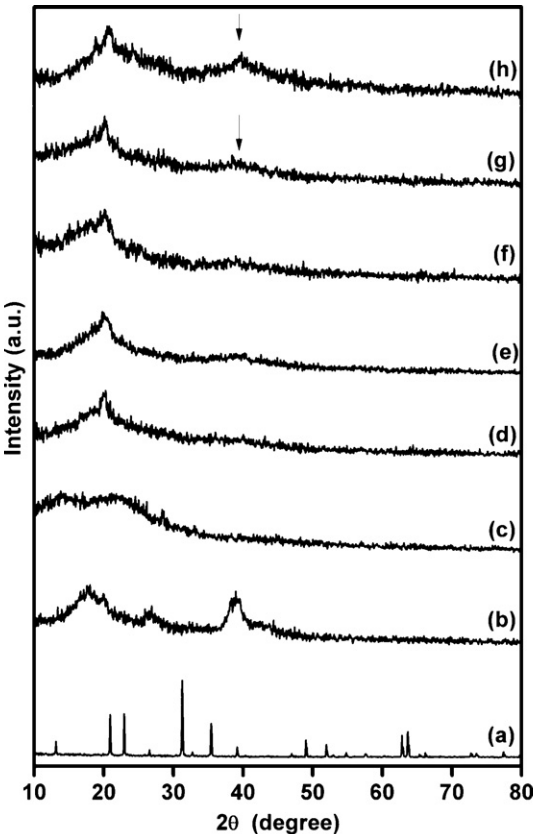

Fig. 1. XRD patterns of (a) $LiClO_4$, (b) PVdF-co-HFP, (c) PVAc, (d) PVAc: PVdF-co-HFP ((25/75) wt%):$LiClO_4$(4 wt%), (e) PVAc:PVdF-co-HFP ((25/75) wt%):$LiClO_4$(6 wt %), (f) PVAc:PVdF-co-HFP ((25/75) wt%):$LiClO_4$(8 wt %), (g) PVAc:PVdF-co HFP ((25/75) wt %):$LiClO_4$(10 wt%), (h) PVAc:PVdF-co-HFP ((25/75) wt%):$LiClO_4$(12 wt%).

3. Results and discussion

3.1. XRD analysis

In order to investigate the influence of the concentration of Li salt, XRD studies were performed for PVAc, PVdF-co-HFP, $LiClO_4$ and complexes (Fig. 1(a)–(h). Fig. 1(a) shows intense peaks at angles $2\theta = 20.9$, 22.92, 26.56, 32.75 and 35.4° which confirm the crystalline nature of $LiClO_4$ salt. Presence of moderate intense peaks at $2\theta = 17.3$, 18.59 and 38.78° confirm the semicrystalline nature of PVdF-co-HFP polymer as shown in Fig. 1(b). Complete amorphous nature of PVAc polymer is confirmed by the two broad peaks at $2\theta = 14.5$ and 19° as shown in Fig. 1(c). From the Fig. 1(d)–(h) that there is a decrease in the relative intensity of the apparent peaks with increasing salt concentration up to 8 wt%. These results can be interpreted in terms of Hodge et al. [14] criterion which has established a correlation between the height of the peak and the degree of crystallinity. The disappearance of high intense peak confirms the maximum dissolution of the salt, which gives rise to the ionic conductivity of the polymer matrix. Salt concentration above 10 wt% reduces the ionic conductivity of the electrolyte film. This may be due to the formation of separate crystallization phase of excess salt in the complex, which confirms the presence of small hump in the complex of XRD pattern shown in Fig. 1(g) and (h).

3.2. FTIR analysis

Infrared spectral (IR) analysis is a powerful tool for identifying the nature of bonding and the presence of different functional groups in a sample by monitoring the vibrational energy levels, which are essentially the fingerprint of different molecules [15,16]. Fig. 2 shows the FTIR spectra of PVAc, PVdF-co-HFP and their blends with various salt concentrations. The vibrational bands observed at 2933, 2465 and 1373 cm^{-1} was ascribed to $-CH_3$ asymmetric, symmetric stretching and symmetric bending vibrations of pure PVAc respectively. In Fig. 2(a), the vibrational bands at 1734, 1033 and 1243 cm^{-1} is ascribed to C=O stretching, C–O stretching and C–O–C stretching vibrations of pure PVAc respectively. The vibrational peak at 946 cm^{-1} was assigned to CH bending vibration and the peak at 608 cm^{-1} was assumed to be linked with CH_3 (C–O) group. The C–H wagging modes of vibration were confirmed by the presence of band at 799 cm^{-1} [17]. In the complexes, the stretching frequency observed at 1734 cm^{-1} which corresponds to C=O of pure PVAc, was shifted to (1717–1730 cm^{-1}). The band at 502 cm^{-1} was assigned to bending vibration of $-CF_2$ and the peak in the complexes were shifted to (494–539 cm^{-1}). Crystalline phase of PVdF in PVdF-co-HFP polymer was identified by the vibrational bands at 985, 763 and 607 cm^{-1}. The vibrational band at 872 cm^{-1} corresponds to the amorphous phase of PVdF-co-HFP [18] and disappearance of this vibrational band in the polymer matrix indicates the complex formation. The strong absorption peaks appeared at 1173 and 1390 cm^{-1} were assigned to the symmetrical stretching of $-CF_2$ and $-CH_2$ groups respectively [19,20] and the peak corresponds to $-CF_2$ modes of vibrations was shifted to 1390–1401 cm^{-1} in the complexes. Apart from these, some unassigned peaks appeared at 1186, 883, 835 and 429 cm^{-1} and some peaks were disappeared.