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Structure, morphology and ionic conductivity of solid polymer electrolyte

Arup Dey [a], S. Karan [a], Ashis Dey [b], S.K. De [a,*]

[a] Department of Materials Science, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India
[b] Department of Chemistry, Sarsuna College, Sarsuna Upanagari, Kolkata 700061, India

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Abstract: Polyethylene oxide (PEO) complexed with potassium iodide (KI) is synthesized to investigate the ionic conductivity of alkaline based polymer electrolytes. The structural and morphological characterizations of the nanocomposite polymer electrolytes are performed by X-ray diffractometry (XRD), atomic force microscopy (AFM), differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR) measurements. The ionic conductivity increases with the increase of KI concentration up to about 20 wt.%. The effect of nanosized ceria ($CeO_2 \sim 10$ nm) fillers on ionic conductivity in PEO–KI polymer electrolyte is also carried out, keeping PEO to KI wt.% ratio 80:20 and 85:15. The result reveals that the addition of ceria nanoparticles enhances the conductivity by two orders of magnitude. The presence of ceria at the highest concentration induces the same molecular environment within PEO chain as that of undoped PEO. Temperature dependence of ionic conductivity follows Arrhenius mechanism.

1. Introduction

In recent years, more and more attentions have been paid to the polymeric materials due to their potential applications in solid-state batteries, fuel cell, smart windows, sensors and electrochemical devices [1–4]. Polyethylene oxide (PEO)-based polymer electrolyte is the most attractive host because of its easy fabrication of thin film, sub-ambient glass transition temperature, higher order of mechanical stability and comparatively high mobility of charge carriers. PEO also has the ability to dissolve high concentrations of a wide variety of metal salts to form polymer electrolytes. The ionic conductivity of pure PEO is in the order of 10^{-7} S cm^{-1} at ambient temperature [5,6]. It has been established that ion transport occurs through amorphous region assisted by the segmental motion of the polymer chain. High concentration of crystalline phase in pure PEO impedes the ionic conductivity and makes it unsuitable for practical applications. The materials based on alkali metal salts complexed with PEO, known as solid polymer electrolytes, play a critical role to improve the order of conductivity [7]. Increasing salt concentration, high levels ionic conductivity can be achieved but the major disadvantage of these polymer electrolytes is poor mechanical strength and potential stability. Most of the earlier studies were concentrated on Li and Na salts to investigate ionic conductivity. The potassium (K) ion has larger ionic radius (1.33 Å) than Li and Na. Higher ionic radius reduces the lattice energy of K salts. The degree of salt solvation of K salt is higher due to lower lattice energy. Moreover the softness of K metal widens technological applications. Considering these facts, KI is chosen as salt in the present study.

Many efforts are devoted to overcome these drawbacks and to develop the polymer electrolytes with high ionic conductivity. Recently, it is reported that the addition of various nanosized ceramic fillers such as SiO_2, Al_2O_3, TiO_2 in polymer matrix enhance ionic conductivity and improve mechanical properties at ambient temperature [8–13]. Most of the investigations on nanofiller added polymer electrolytes have revealed that Lewis acid–base interaction between the nanoparticles and the polymer electrolyte reduces the crystallization and enhances dissociation of the supporting salt so that more free ions are available for conduction. Being a strong Lewis acid, ceria can interact with PEO-based polymer electrolytes. In the present paper, we have reported the effect of CeO_2 nanoparticle on structural modification, morphology, thermal properties and ionic conductivity of PEO–KI polymer electrolyte.

2. Experimental

Ammonium Ceric nitrate $(NH_4)_2[Ce(NO_3)_6]$ (Qualigens, Mumbai, India) and citric acid monohydrate, as par analytical grade, were used to prepare ceria (CeO_2) nanoparticles by autoignition process and the details were given elsewhere [14].

Pure polyethylene oxide (molecular weight, $MW = 10^6$) film and different concentrations of PEO and potassium iodide (KI) complexed films were prepared in the wt.% ratios (95:5), (90:10), (85:15), (80:20) and (75:25) by solution-casting technique using methanol as solvent. The solution was thoroughly mixed and

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[*] Corresponding author. Tel.: +91 3324733073; fax: +91 3324732805.
E-mail address: msskd@iacs.res.in (S.K. De).

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stirred using a magnetic stirrer at room temperature until the bubbles disappeared. The resulting homogeneous solution was poured into polypropylene petri dish and allowed to evaporate slowly in air at room temperature. The films were then vacuum dried at 50 °C for 48 h to remove all traces of the solvent. The thin films obtained were then preserved in a vacuum desiccator. The solubility of PEO depends on the dielectric constant of solvent. Generally acetonitrile is used as a solvent for higher dielectric constant, $\epsilon = 36$. The value of ϵ for methanol is 32.5, which is very close to that of acetonitrile [15]. Good quality films of PEO–KI complex were obtained using methanol as solvent in the present synthesis.

The effect of CeO_2 nanoparticles in PEO–KI system were also investigated keeping PEO to KI wt.% ratio 80:20 and 85:15 in order to study the influence of KI amount on ionic conductivity in the nanocomposite. Methanolic solution of PEO and KI with the required wt.% ratio was first thoroughly mixed and stirred using a magnetic stirrer at room temperature. When the bubbles were disappeared and the polymeric solution became viscous, CeO_2 was added in estimated amount (3, 5, 8, 10, 15, 20 and 25 wt.%) and mixed with continuous stirring. The resulting homogeneous solution was poured into polypropylene petri dish and vacuum dried at 50 °C for 48 h to remove all traces of solvent. The thin films were preserved in a vacuum desiccator.

X-ray powder diffraction patterns of the pure CeO_2, pure PEO, PEO–KI and the PEO–KI–CeO_2 composite polymer in the form of films were recorded by high resolution X'Pert PRO Panalytical X-ray diffractometer in the range 15–60° using Cu Kα radiation. Atomic force microscopic (AFM) studies were performed using an Autoprobe CP Base Unit, Model no. AP0100. Differential scanning calorimeter (DSC) was carried out on PerkinElmer Diamond DSC at a heating rate of 20 °C/min from -60 °C to 80 °C heating scan under a constant flow (100 ml/min.) of nitrogen gas to avoid any contact of atmospheric moisture. Pure indium was used for temperature and enthalpy calibration of the instrument. The Fourier Transform Infrared (FTIR) spectra were obtained by a computer interfaced Shimadzu FTIR-8300 spectrometer in the frequency range of 1500–800 cm^{-1}. In this experiment the gelatinous polymer solution was cast on a KBr palette and dried in vacuum. The ionic conductivity of the composite electrolyte films was measured using stainless steel electrodes and Agilent 4192A Impedance Analyzer. The sample was sandwiched between two polished stainless steel blocking electrodes. The bulk resistance was determined from the cross point at high frequency of frequency dependent impedance with the real axis. The ionic conductivity was calculated from the geometrical factors and bulk resistance. Temperature was monitored by Eurotherm temperature controller Model no. 2404 using a thermocouple sensor. The ion transference number in the polymer electrolyte was measured by a configuration of stainless steel/polymer electrolyte/stainless steel under a fixed dc voltage of 0.8 V. The resulting current was monitored as a function of time. After polarizing the electrolyte, the transport number, t_{ion}, was calculated from the initial current, I_0, and the saturation current, I_S using the equation,

$$t_{\text{ion}} = \frac{I_0 - I_S}{I_0} \tag{1}$$

The current as function of time was measured by Keithley Electrometer, Model no. 6517A.

3. Results and discussion

X-ray diffraction patterns of pure PEO, PEO–KI (wt.% ratio 80:20), PEO–KI–CeO_2 nanocomposites and pure CeO_2 are shown in Fig. 1, respectively. In Fig. 1(a) characteristic crystalline peaks of PEO are observed at $2\theta = 19.13$ and 23.30° which are assigned to (1 2 0) and (1 1 2) planes, respectively. These peaks for PEO–KI as displayed in Fig. 1(b) become less intense compared to pure PEO. The intensity of the peak at smaller angle is higher than that of larger angle. This indicates the decrease in degree of crystallinity and complexation of PEO with KI salt. Interaction between the K^+ ions and ether oxygen of PEO chains disrupts the previous ordered arrangements of the PEO chains, resulting in the reduction of crystallinity. XRD patterns of composite polymer electrolytes are shown in Fig. 1(c and d), respectively. It is found that four additional peaks appear at $2\theta = 28.4$, 32.9, 47.3 and 56.1° in the CeO_2 added composite polymer electrolytes. These are attributed to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes of cubic calcium fluorite structure of CeO_2 (Fig. 1(e)), respectively. It is also observed that with the increase in the content of filler the intensity of peaks corresponding to CeO_2 increases. The crystallite size of the nanofillers is estimated by Scherrer formula [16]. The initial size of CeO_2 is found to be approximately 10 nm. The size of CeO_2 does not vary with increase of concentration.

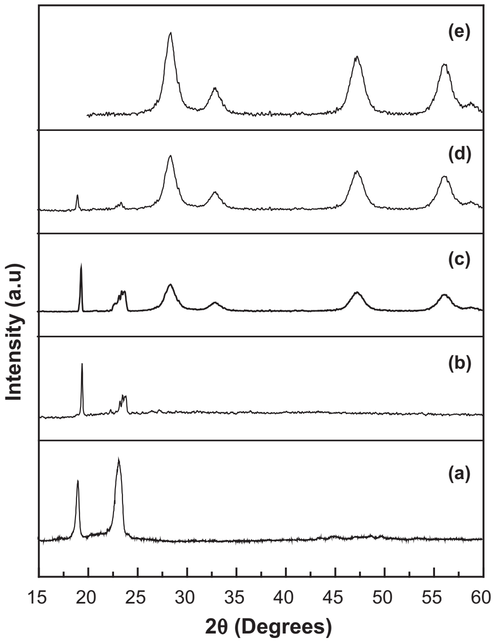

Fig. 1. X-ray diffraction patterns of (a) pure PEO; (b) PEO–KI (wt.% ratio 80:20) and (c) 8 wt.% CeO_2; (d) 25 wt.% CeO_2 of PEO–KI–CeO_2 composite polymer electrolytes and (e) pure CeO_2 nanoparticles.

Two-dimensional AFM topographic images of pure PEO, PEO–KI (wt.% ratio 80:20) and CeO_2 added composite polymer electrolytes are shown in Fig. 2(a–d), respectively. The image of pure PEO (Fig. 2(a) presents a crystallized network of regular spherulites developing spirals and branches of well-distributed surface contours. This is the evidence of semicrystalline nature of pure PEO. AFM micrographs indicating changes in the PEO surface morphology with the addition of KI salt as shown in Fig. 2(b). Interaction of KI salt with the PEO destroys the regular crystallized network and reduces the degree of crystallinity of the polymer complex remarkably. Introduction of the CeO_2 nanoparticles into the polymer matrix produces dramatic morphological changes to the host polymer electrolyte. When 20 wt.% of CeO_2 nanoparticles are added, the composite polymer electrolyte exhibits almost a flat surface (Fig. 2(c). In contrast, Fig. 2(d) shows the development of granular morphology when the value of CeO_2 content in the composite polymer electrolyte reaches 25 wt.%. This structural modification promotes different crystallization behavior in the polymer electrolyte system. AFM pictures suggest that the insertion of CeO_2 produces different morphologies of the composite polymer electrolytes. The favorable microstructure