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Original article

Lithium ion conduction and ion-polymer interaction in poly(vinyl pyrrolidone) based electrolytes blended with different plasticizers

K. Kesavan, Chithra M. Mathew, S. Rajendran *

School of Physics, Alagappa University, Karaikudi, Tamilnadu 630003, India

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Poly(ethylene oxide), poly(vinyl pyrrolidone) (PEO/PVP), lithium perchlorate salt ($LiClO_4$) and different plasticizer based, gel polymer electrolytes were prepared by the solvent casting technique. XRD results show that the crystallinity decreases with the addition of different plasticizers. Consequently, there is an enhancement in the amorphousity of the samples responsible for the process of ion transport. FTIR spectroscopy is used to characterize the structure of the polymer and confirms the complexation of plasticizer with host polymer matrix. The ionic conductivity has been calculated using the bulk impedance obtained through impedance spectroscopy. Among the various plasticizers, the ethylene carbonate (EC) based complex exhibits a maximum ionic conductivity value of the order of 2.7279×10^{-4} S cm^{-1}. Thermal stability of the prepared electrolyte films shows that they can be used in batteries at elevated temperatures. PEO (72%)/PVP (8%)/$LiClO_4$ (8%)/EC (12%) has the maximum ionic conductivity value which is supported by the lowest optical band gap and lowest intensity in photoluminescence spectroscopy near 400–450 nm. Two and three dimensional topographic images of the sample having a maximum ionic conductivity show the presence of micropores.

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1. Introduction

Polymer blending is one of the most important contemporary ways for the development of new polymeric materials and a useful technique for designing materials with a wide variety of properties [1]. The significant advantages of polymer blends are that the properties of the final product can be tailored to the requirements of the applications. The manifestation of superior properties depends upon the miscibility of the blend. Blending can, however, have profound and sometimes unexpected effects on thermal stability, which cannot simply be predicted on the basis of the behavior of the components and their relative proportions [2]. A common approach is to add low molecular weight plasticizers to the polymer electrolyte system [3]. There has been significant work carried out on the pristine and plasticized PEO–lithium salt systems [4–7]. The plasticizers impart salt-solvating power and high ion mobility to the polymer electrolytes.

Poly(ethylene oxide) is the most interesting of the base materials because of its high chemical and thermal stability. PEO is a semi-crystalline polymer, possessing both amorphous and crystalline phases at room temperature. It can solvate a wide variety of salts even at very high salt concentrations [8]. On the other hand, poly(vinyl pyrrolidone) (PVP) is a second polymer, which deserves special attention among the conjugated polymers because of its good environmental stability, easy processability, moderate electrical conductivity and rich physics in charge transport mechanism. The presence of the carbonyl group ($C{=}O$) in PVP, leads to the formation of a variety of complexes with various inorganic salts that exhibit high T_g with good environmental, thermal and mechanical stability. Furthermore, PVP is highly soluble in polar solvents, such as alcohol, and the local modification of the chemical structure induces drastic changes in electronic properties [9].

This paper reports on the gel polymer electrolytes based on the PEO/PVP/$LiClO_4$ complex by the addition of different plasticizers using a well known solvent casting technique. The structural and complex formation features of the prepared electrolyte samples have been confirmed by XRD and FTIR analyses, respectively. The ionic conductivity of the prepared gel polymer electrolytes has also been studied.

2. Experimental

Poly(ethylene oxide) (PEO), $\sim M_w = 8 \times 10^3$, Sigma–Aldrich and poly (vinyl pyrrolidone) (PVP), $\sim M_w = 36 \times 10^4$, Sigma–Aldrich

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* Corresponding author.
E-mail address: sraj54@yahoo.com (S. Rajendran).

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were used without further purification. The salt $LiClO_4$ was purchased from Sigma–Aldrich Chemicals Limited, USA. The obtained PEO, PVP and $LiClO_4$ were dried at 55 °C for 4 h to remove moisture. The plasticizers and the solvent, methanol, used in this study were purchased from Sigma–Aldrich and E-Merck, respectively, and were used as received. The gel polymer electrolytes of constant proportions of PEO (72 wt%)/PVP (8 wt%)/$LiClO_4$ (8 wt%)/X (12 wt%), where X = EC, PC, GBL, DMC and DEC, were prepared using a solvent casting technique. The structural analysis of the prepared electrolyte was analyzed by X'pert PRO PANalytical X-ray diffractometer. Complex formation between the salt and polymer complex was obtained by using SPECTRA RXI, Perkin Elmer spectrophotometer in the range of 400–4000 cm^{-1}. The gel polymer electrolytes of constant ratios of PEO:PVP:$LiClO_4$:X, where X = EC, PC, GBL, DMC and DEC, were prepared with a view to identify the suitable plasticizer for high ionic conductivity.

Conductivity studies were carried out with the help of stainless steel blocking electrodes using a computer controlled microauto lab type III Potentiostat/Galvanostat in the frequency range of 100 Hz–300 kHz over the temperature range 303–353 K. Thermal stability of the polymer electrolyte was carried out by thermogravimetric analysis (TG/DTA) using PYRIS DIAMOND from r.t. to 700 °C. Roughness parameter was observed by AFM with the help of AFM (A100SGS). The photoluminescence studies were performed by Carry Eclipse Fluorescence Spectrophotometer. The optical band gap energies were calculated by UV–vis analysis using Shimadzu UV-1601.

3. Results and discussion

3.1. XRD analysis

Fig. 1 represents the X-ray diffraction patterns of pure $LiClO_4$, PEO, PVP and the prepared complexes respectively. The XRD pattern of pure $LiClO_4$ salt shows well defined sharp peaks at 20.9, 22.92, 26.56, 32.75 and 35.4° corresponding to the lattice planes (1 0 1), (1 1 0), (2 0 0), (2 0 1) and (2 1 0) which indicate its crystalline nature. However, these peaks disappear in the polymer blend films. The characteristic peaks at $2\theta = 19.2$ and 23.5° corresponding to the reflection of (1 2 0) and (0 1 0) plane, respectively, confirm the semicrystalline nature of PEO. No such well defined, sharp peaks attributable to PVP could be observed. Instead a broad peak was observed around at 22.7°, which suggests the amorphous nature of PVP.

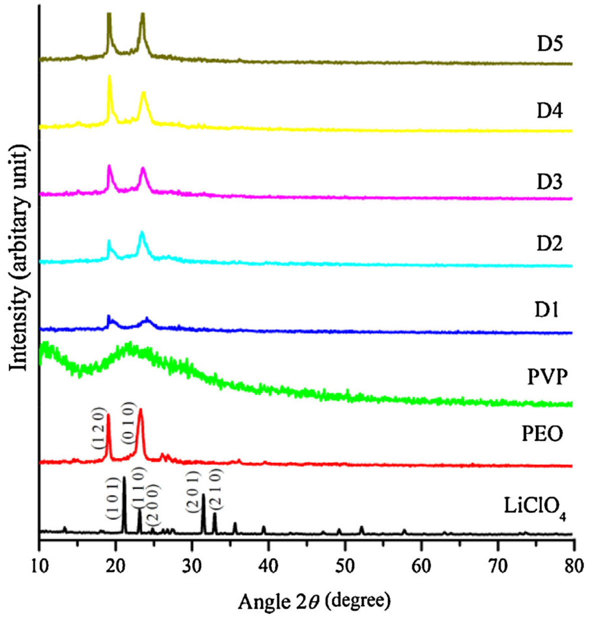

Fig. 1. XRD patterns of the pure and prepared complexes.

From Fig. 1, it is observed that with the addition of lithium salt and different plasticizers to the polymer blend, the intensity of these peaks decreases gradually and becomes relatively broader suggesting a decrease in the degree of crystallinity of the complex. The percentage of degree of crystallinity (χ) for the prepared sample has been calculated from the relation [10].

$$\chi = \frac{S}{S_o} \times 100$$

where S is the sum of the areas of all the crystalline peaks and S_o the total area under the diffractogram. For the prepared samples D1, D2, D3, D4 and D5, the degree of crystallinity is found to be 16%, 22%, 24%, 27%, and 29%, respectively. This shows that the degree of crystallinity of the prepared samples increases with different plasticizers, with the EC based electrolyte having reduced crystallinity showing higher ionic conductivity. This is due to the existence of large free volume and flexibility of total chain segmental motion in the polymer electrolyte [11] and hence the higher conductivity. These observations apparently revealed that the polymer undergoes significant structural reorganization upon adding different plasticizers. The plasticizers may have induced significant disorder into the original polymers and this is attributed to the interactions between the polymer and the solvents, which resulted in polymer electrolytes with much lower crystallinity. Hence, the absence of peaks pertaining to lithium perchlorate salt in the complexes indicates the complete dissolution of the salt in polymer matrix.

3.2. FTIR studies

FTIR transmittance spectra of pure and prepared complexes are presented in Fig. 2.

The vibrational bands at 1343, 1282 and 1236 cm^{-1} are assigned to CH_2 bending, CH_2 asymmetric stretching and CH_2 symmetric twisting respectively of pure PEO [12]. The bands corresponding to the wave numbers 1343 and 1236 cm^{-1} are shifted to (1350, 1348, 1347, 1346 and 1350 cm^{-1}) and (1242, 1244, 1244, 1248 and 1243 cm^{-1}) respectively, whereas the vibrational peak at 1282 cm^{-1} is present in the complexes D1 and D3 without any change, and shifted in the complexes D2, D4 and D5 to the wave numbers 1283, 1283 and 1284 cm^{-1} respectively.

The absorption band of PEO at 1799 cm^{-1} represents the ether oxygen group which is shifted to the wave numbers 1794, 1794, 1794, 1792 and 1794 cm^{-1} respectively. The characteristic band at 1100 cm^{-1} is assigned to C–O–C (symmetric and asymmetric stretching) of PEO which is shifted in all the complexes [12]. Apart from this, the mode responsible for the band at 845 cm^{-1} is primarily due to the CH_2 rocking motion with a little contribution from C–O stretching motion of PEO, while band at 947 cm^{-1} originates primarily from the C–O stretching motion with some CH_2 asymmetric rocking motion [13].

On the other hand for pure PVP, a vibrational band at 2900 cm^{-1} is attributed to aliphatic C–H stretching which is shifted to 2887, 2886, 2884, 2892 and 2899 cm^{-1}, respectively [14]. The C=O stretching and CH_2 wagging mode of vibration of pure PVP observed at 1651 and 1451 cm^{-1} are shifted in the complexes with the wave numbers (1652, 1655, 1655, 1653 and 1655 cm^{-1}) and (1462, 1462, 1462, 1459 and 1461 cm^{-1}), respectively. The C–N stretching mode of pure PVP at 1232 cm^{-1} is shifted to 1230, 1229, 1231, 1233 and 1230 cm^{-1}, respectively [15]. The C–C bending

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