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Dye Sensitized Solar Cell Using Polymer Electrolytes Based on Poly(ethylene oxide) with an Ionic Liquid

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Summary: Polymer electrolytes were prepared by doping PEO:KI/I_2 with an ionic liquid (IL) 1-ethyl 3-methylimidazolium thiocyanate (EMImSCN). FTIR confirmed composite nature while X-ray diffraction (XRD) measurement affirmed the reduction in crystallinity, when IL was added. The ionic conductivity was improved by the addition of IL. The photoelectrochemical effect of the IL–doping in the terms of the current density J_{sc} and efficiency of a dye sensitized solar cells (DSSC) has also been discussed.

Keywords: conducting polymers; dye sensitized solar cell; FTIR; ionic liquid

Introduction

During the last few decades, polymer electrolytes are of great interest because we use it in every aspect of our daily lives as well as in electrochemical devices like electrochromic display devices and photoelectrochemical solar cell.[1–2] Among the polymer systems studied, the PEO-based polymer electrolytes have special interest due to their useful properties like availability of polar groups, easy complexation, low T_g etc. Apart from these advantages, the low conductivity and high crystallinity are the disadvantage of this material. The basic requirement of all such applications is high value of ionic conductivity. In polymer electrolytes, ionic liquids have been found to play the role of both as a cooperative electrolyte as well as non-volatile plasticizer.[3–5] The low viscosity and high electrical conductivity of these IL makes them suitable candidate for many devices like fuel cells, Li-batteries, dye sensitized solar cell, etc.[6,7] Dye-sensitized solar cell (DSSC) came in consideration after the pioneering work of Grätzel et al.[8,9] There are too many reports on DSSC based on liquid electrolytes, gel electrolytes and solid electrolytes[10–12] available in literature. The DSSC using PEO/titania and PEO-oligomer containing different dopants have been reported in literature and attained high conversion efficiency[13–18] while the detailed study on PEO with an ionic liquid is scanty. The ionic liquid EMImSCN is now well known for its low viscosity (22 mPas) and high ionic conductivity (18 mS cm^{-1}) at room temperature.[19] The temperature dependence plot of this IL shows VTF type behaviour and the DSSC based on this ionic liquid have already shown good performance.[20,21] Although the ionic liquids show high conductivity due to mobility of both cations and anions yet they can not be used in various applications due to their liquid nature at room temperature. One possible approach is to use these IL in a suitable polymer matrix and obtain the resulting electrolyte in the film form. Keeping this thing in view, we have prepared the PEO-polymer electrolyte films containing the IL and studied its electrical, structural and photoelectrochemical properties.

Experimental Part

Ionic liquid (EMImSCN) (Fluka), poly(ethylene oxide) (PEO, $Mw = 1 \times 10^6$)

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(Aldrich), potassium iodide (KI) (Aldrich), iodine (I_2, 99.99%) (Aldrich) were the starting materials used in the present study. Polymer electrolyte membranes containing PEO:KI/I_2 and IL 1-ethyl 3-methylimidazolium thiocyanate (EMImSCN) were prepared by the solution cast method.[22] PEO, KI (20wt %),[23] I_2 (10 wt% of KI salt) were dissolved in acetonitrile and then IL was added in stoichiometric ratio along with continuous stirring (24 hours) to obtain a homogeneous viscous solution which was then poured in polypropylene dishes. The solvent was allowed to evaporate slowly resulting in the formation of polymer electrolyte in the form of free standing films which were finally dried under a vacuum chamber. The opaque and thin nanostructured TiO_2 films were prepared using the doctor–blade technique on conductive glass substrates. Nanocrystalline TiO_2 paste (Ti-Nanooxide D, Solaronix) was cast onto the glass and then sintered at 450 °C for 30 min. The TiO_2 nanoparticles was sensitized overnight with Ru(dcbpy)$_2$ (NCS)$_2$ (dcbpy = 2,2′-bipyridyl-4,4′-dicarboxylato) dye solution (1×10^{-4} mol dm^{-3}) (535-bis TBA, Solaronix). On the other hand H_2PtCl_6 solution was coated (0.05 mol dm^{-3} in isopropyl alcohol) onto the conductive glass and then sintered at 400 °C. Finally, sticky polymer electrolyte film containing ionic liquid were sandwiched between the photoelectrode and platinized SnO_2 counter electrode by firmly pressing. Composite nature of the ionic liquid-incorporated polymer electrolyte films were confirmed by FTIR (Thermo Electron Corp./ Nicolet 380) in the range of 4000–500 cm^{-1}. The X-ray diffraction spectra of these films were carried out using X-ray diffractometer (Rigaku D/max-2500) in the range of $2\theta = 17$–$27°$ with scan rate of 1°/min. Ionic conductivity of the modified polymer electrolyte films was determined using complex impedance spectroscopy (Solartron SI 1287) at room environmental condition. Photocurrent and voltage of DSSC were measured with Keithley 2400 source meter under one sun light intensity (100 mW/cm^2) simulated by a solar simulator (Oriel, 91193 model equipped with 1000 W Xenon lamp) with an AM1.5 G filter. The light intensity was adjusted with a crystalline Si solar cell with KG5 filter for approximating one sun light intensity, where the reference cell was calibrated from NREL.

Results and Discussion

FTIR

The typical FTIR spectra of PEO: KI/I_2+80 wt% IL is given in Figure 1 along with those of pure IL and PEO: KI/I_2. A close look and comparison of the FTIR spectra of PEO:KI/I_2 (curve a), PEO:KI/I_2 + 80 wt% IL (curve b) and ionic liquid (curve c) leads to the conclusion that PEO:KI/I_2 + 80 wt% IL is essentially a "composite." It can be seen that all the peaks of PEO:KI/I_2 (curve a) are retained in the spectra of the composite (curve b) as well. Similarly, it is also obvious that the dispersoid IL (EMImSCN)-related peaks (curve c) also manifest themselves in the FTIR spectra of the composite (curve b). In brief, thus, we can state that both the host polymeric matrix and the dispersoid IL retain their identity. Hence, our film of PEO: KI/I_2 + 80 wt% IL is essentially an IL dispersed polymeric composite film.

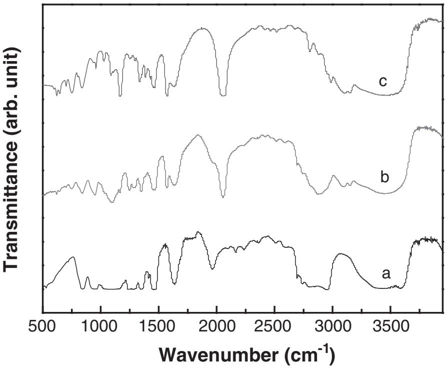

Figure 1.
FTIR spectra of (a) PEO:KI/I_2 (b) PEO:KI/I_2+80 wt% IL and (c) pure ionic liquid.

XRD

Figure 2 shows the selected region XRD patterns of PEO:KI/I_2 and PEO:KI/I_2 polymer electrolytes films with different IL concentration. It was obvious that the XRD-pattern of the PEO:KI/I_2 (curve a) showed two well known semicrystalline peaks at 19.1° and 23.4°. With the addition of the 40 wt% IL concentration (curve b), the intensity of the crystalline peaks has decreased. Further enhancement in IL concentration i.e. 80 wt% resulted in the reduction in the intensity and a noticeable broadening of the area under the peaks. This is a clear indication of the reduction in the crystalline phase in the polymer electrolyte at room temperature. We have also noticed the shift in peak positions of the PEO:KI/I_2 with IL polymer electrolyte films. This may be attributed to possible interaction between ether oxygen of PEO with cations (potassium/imidazolium) or cation (potassium) and anion (thiocyanate).

Ionic Conductivity

The calculated values of ionic conductivity are listed in Table 1. It is well known that the factors controlling the values of conductivity are: the number of charge carriers (n) and the mobility (μ) since $\sigma = nq\mu$. Therefore, a change in the conductivity implies either a change in n or μ or both. In PEO:KI polymer-salt complex system it has been found that conductivity increased with increasing salt concentration due to enhanced concentration of free ions from salt.[23–24] It can be seen that the addition of ionic liquid decreases crystallinity and hence increases ionic conductivity (Table 1). Similar behaviour has also been observed by Z. Changneng et al.[25] using MP II (1-methyl 3-propylimidazolium iodide) ionic liquid. The maximum conductivity in our system was 7.62×10^{-4} Scm^{-1} at 80 wt% IL concentration. After that it was harder to get stable film. This conductivity enhancement can be understood by the fact that the ionic liquid is a kind of electrolyte. As a result ionic liquid could provide additional charge carriers while its low viscosity help in reduction of crystallinity.[22] It is well known for PEO-polymer electrolyte, amorphous region is high conducting region and ions will prefer to dissolve in this region. Hence doping of IL provided charge carriers/amorphous region which would certainly assist the conductivity enhancement.

Table 1.
Ionic conductivity of PEO:KI/I_2+IL polymer electrolyte system at room temperature.

Composition	Conductivity (σ) (S cm^{-1})
PEO:KI/I_2 (80:20)	8.80×10^{-6}
PEO:KI/I_2+20 wt% IL	1.39×10^{-5}
PEO:KI/I_2+40 wt% IL	1.90×10^{-5}
PEO:KI/I_2+60 wt% IL	5.99×10^{-4}
PEO:KI/I_2+80 wt% IL	7.62×10^{-4}

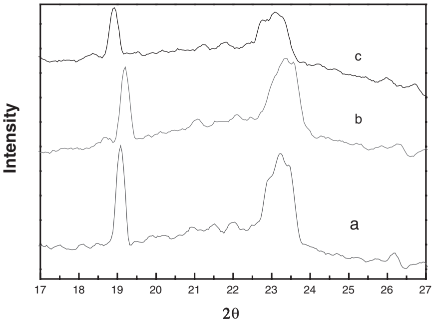

Figure 2.
XRD patterns for (a) PEO:KI/I_2 (b) PEO:KI/I_2+40 wt% IL and (c) PEO:KI/I_2+80 wt% IL polymer electrolyte films.

DSSC Performance

In order to examine the photoelectrochemical performance, the photocurrent density-voltage characteristics of DSSC have been measured at 100 mW cm^{-2} (Figure 3). The values of the short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF) and conversion efficiency (η) obtained from this curve are summarized in Table 2. It was clear that the J_{sc} of the solar cells increased with the increasing amount of ionic liquid in the electrolyte, which is good agreement with the changes of the ionic conductivity. The increase of J_{sc} was

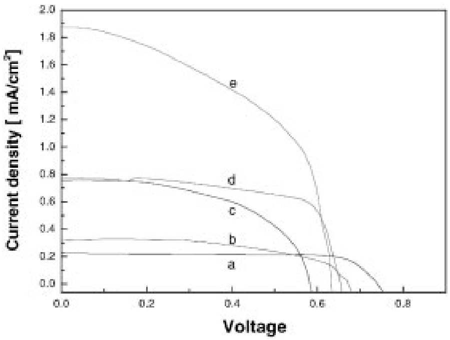

Figure 3.
Current-voltage characteristics of DSSC using polymer electrolyte system (PEO:KI/I_2)+ x wt% IL with (a) x = 0; (b) x = 20; (c) x = 40; (d) x = 60 and (e) x = 80 arradiated at 100 mW cm^{-2}.

attributed to the improved transportation of I^-/I_3^- anions because of the increased ionic conductivity of PEO electrolyte and a more amorphous cooperative medium provided by IL which would certainly improve the interfacial contact between electrode/ electrolyte and better mobility. Though there is an appreciable rise in ionic conductivity with increase in IL concentration from 40 to 60 wt%, the J_{sc} value did not show similar jump. It may be noted that no direct (one to one) relation has been observed so far with the conductivity and J_{sc} value. In our case J_{sc} values were found to rise by 1%. However, we could not get much high efficiency because efficiency is also related to V_{oc} which is basically the energy difference between the energy level of the semiconductor electrode and the redox potential of the redox couple. Since we had already fixed KI/I_2[23] concentration which would affect the redox potential (I^-/I_3^-) concentration[16] and hence overall efficiency. Further, the optimizations of the electrolyte composition with redox couple for efficient solar cell are still under process in our laboratory.

Table 2.
The Short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF) and conversion efficiency (η) of DSSC assembled with PEO:KI/I_2+IL polymer electrolyte at 100 mW cm^{-2} irradiation.

Composition	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	η (%)
PEO:KI/I_2 (80:20)	0.22	0.74	77.4	0.1
PEO:KI/I_2+20 wt% IL	0.32	0.67	56.0	0.1
PEO:KI/I_2+40 wt% IL	0.76	0.58	54.8	0.2
PEO:KI/I_2+60 wt% IL	0.78	0.65	68.3	0.3
PEO:KI/I_2+80 wt% IL	1.88	0.63	50.7	0.6

Conclusions

PEO-based polymer electrolytes with an ionic liquid were prepared by solution cast method. FTIR and XRD showed the composite nature and reduction in crystallinity, respectively. The ionic conductivity and photovoltaic performances of the solar cell were found to be significantly improved by adding ionic liquid. The maximum conductivity of PEO:KI/I_2+80 wt% IL was 7.62×10^{-4} S/cm. The solar cell using this optimum conductivity showed conversion efficiency of 0.6% at 100 mW cm^{-2} irradiation.

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