

Investigation of PEO-imidazole ionic liquid oligomer electrolytes for dye-sensitized solar cells

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Abstract

Ionic liquid oligomers prepared by incorporating imidazolium ionic liquid with PEO oligomers were investigated as electrolytes for dye-sensitized solar cells (DSSCs). The influences of PEO molecular weight and imidazolium group of the ionic liquid oligomers on the ionic conductivity, apparent diffusion coefficient of the redox species in the electrolytes and the performance of solar cells were examined. The structural effects of the ionic liquid oligomers on the kinetic behaviors of dye regeneration and triiodide reduction reactions taken place at nanocrystalline TiO₂ electrode and Pt counter-electrode, respectively, were further studied by cyclic-voltammetry and electrochemical impedance spectroscopy measurements. The increase of the PEO molecular weight of the ionic liquid oligomers results in the faster dye regeneration rate and lower charge transfer resistance of triiodide reduction leading to the improvement of cell performance effectively.

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Keywords: Ionic liquid; Oligomer electrolyte; Dye-sensitized solar cells; Ionic conductivity; Conversion efficiency

1. Introduction

There have been considerable efforts devoted to develop the dye-sensitized solar cells (DSSCs) as the high-efficiency and low-cost solar cells for photovoltaic applications [1–3]. Due to employing organic solvent-based volatile liquid electrolyte in these cells, the evaporation and leakage of organic solvent lead to a decay in the cell performance during the long-term operation, that may cause a limitation in the practical use. In order to improve the long-term stability, many attempts have been made to substitute the volatile liquid electrolyte with organic and inorganic solid-state charge transport materials [4–7] and polymer materials [8–11]. Furthermore, an alternative to the solid materials for improving the long-term durability of DSSCs is the use of quasi-solid-state materials, which can be prepared by solidifying the liquid electrolyte with incorporation of polymer [12–17] or nanoparticle [18–21].

Utilization of the quasi-solid-state electrolyte is promising for developing high-efficiency DSSCs.

Ionic liquids known as ambient temperature molten salts exhibit a series of properties distinct from the conventional aqueous or organic solvents. The unique properties of the ionic liquids in the stability for chemical and thermal, non-volatility, highly ionic conductivity, larger electrochemical window and good solvent behaviors have attracted considerable interests for the applications as reaction solvents in synthesis, catalysis and as ionic conductive matrix in electrochemical devices etc. Due to the most stable and the high ionic conductive characteristics, ionic liquids based on imidazolium salts have been studied extensively as non-volatile electrolyte in DSSCs [22–27]. Various imidazolium salts with different alkyl substituents and anions were employed in the DSSCs and the influence of chemical structure on the physical-chemical properties such as the viscosity, ionic conductivity etc. and cell performance were revealed [24,28–30]. Recently, the ionic liquid polymers based on imidazolium salts have been developed as high ionic conductive solid materials for the

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solid-state device applications [31]. The ionic liquid type polymer may have the desirable properties similar to that of ionic liquids for employing in fabrication of solid-state DSSCs or quasi-solid-state DSSCs by solidification of ionic liquid electrolyte enabling achievement of high efficiency and without evaporation and leakage of the electrolyte during long-term operation.

For this purpose, ionic liquid polymer was prepared by combination of the imidazole ionic liquid and poly(ethylene oxide) (PEO) [32]. This ionic liquid polymer exhibits the ionic conductivity about 10^{-4} S/cm at 25 °C. Additionally, its characteristics of high solubility with the inorganic salts due to the large polarity at the ether oxygen of PEO and good miscibility with the organic salts by virtue of the imidazole group are of great advantage for optimizing the inorganic and organic composition of the electrolytes. In this work, ionic liquid oligomers with different molecular weights of PEO oligomer were firstly studied. The ionic liquid oligomer as an intermediate state transiting from ionic liquid to the ionic liquid polymer possess simultaneously the unique properties of ionic liquid and the characters of polymer as increasing the molecular weight of the PEO. Studies of the influence of the PEO chain length of the ionic liquid oligomer on the physical-chemical properties and the performance of the solar cells such as the ionic conductivity, apparent diffusion coefficient of the redox species contained in the electrolyte, interfacial electron transfer behaviors and the photovoltaic performance will provide the useful information in developing the ionic liquid polymer with suitable structure for employing in the solid-state DSSCs.

2. Experimental

1-oligo(ethyleneoxide)-3-methylimidazolium chloride (PEO(*X*)MImCl) with different molecular weights (*X*) of PEO were synthesized according to the literature methods [33,34]. Poly-ethylene glycol methyl ether (PEO(*X*), *X* = 150, 350, 550, 750) were purchased from Aldrich Chemical Co. Ltd. Synthesis of PEO(*X*)MImCl were performed by reference to the experimental procedure of PEO(750)MImCl which is described representatively as follows: PEO(750)-Cl was first prepared by reaction of PEO (750) with thionyl chloride in the presence of pyridine. The product was purified by washing with pure water. The formation of PEO(750)-Cl was confirmed by IR spectrum which showed a new absorption at 663 cm^{-1} corresponding to the stretching of C–Cl and the disappearance of the strong absorption for the stretching of –OH at $3400\text{--}3550\text{ cm}^{-1}$. Then, PEO(750)-Cl was dissolved in *N,N*-Dimethylformamide (DMF), and mixed with an excess of *N*-methylimidazole. The mixture was stirred at 80 °C for 2 days under N_2 atmosphere. The obtained product was purified with dehydrated diethylether and dried in vacuum at 60 °C for 2 days. The molecular structure of PEO(750)-MImCl was confirmed by $^1\text{H-NMR}$ spectroscopy in terms of the peaks for the imidazolium proton at 7.44, 7.75 and

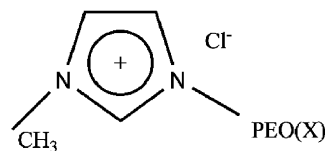
10.24 ppm. Scheme 1 shows the molecular structure of PEO(*X*)MImCl.

DSSCs were fabricated with a dye-sensitized nanocrystalline TiO_2 film as photoelectrode, a Pt foil as counter electrode and the electrolytes composed of 1.0 M LiI, 0.5 M I_2 and the ionic liquid oligomers PEO(*X*)MImCl (*X* = 150, 350, 550, 750). The nanocrystalline TiO_2 film was prepared by depositing TiO_2 colloidal paste on transparent conductive glass sheet (FTO, fluorine-doped SnO_2 , $20\ \Omega/\text{sq}$) and then sintering at 450 °C for 30 min in air. Film thickness is 10 μm and the porosity is 50%. Dye sensitization was performed by immersing the nanocrystalline TiO_2 film in 5×10^{-4} M cis-bis (thiocyanato)-*N,N'*-bis (2,2'-bipyridyl-4,4'-dicarboxylate) ruthenium (II) ethanol solution for overnight [35]. DSSCs were fabricated by injecting the ionic liquid oligomer electrolyte into the gap between the dye-sensitized nanocrystalline TiO_2 electrode and the Pt counter electrode and clamping with a holder. Cell performance measurements were performed after placing the cell at the room temperature about 1 h.

The ionic conductivity measurements were carried out by using DDSJ-308A conductivity meter. The apparent diffusion coefficients of redox species in the ionic liquid oligomer electrolyte were determined from the steady-state voltammetry obtained on PAR potentiostat (model 273) in an electrochemical cell composed of a 10 μm radius Pt ultramicroelectrode as working electrode, two Pt wires as counter electrode and reference electrode, respectively, at a scanning rate of 10 mV/s.

Cyclic-voltammetry measurements were carried out on a PAR potentiostat (model 273) at a scanning rate of 100 mV/s. A dye-coated FTO conductive glass using as the working electrode was prepared by immersing the conductive glass substrate, which was subject to prior warm at 100 °C (30 min), in 5×10^{-4} M cis-bis (thiocyanato)-*N,N'*-bis (2,2'-bipyridyl-4,4'-dicarboxylate) ruthenium (II) ethanol solution for 12 h. The adsorption of dye onto the conductive glass substrate was confirmed by UV–vis absorption spectrum of dye-coated FTO conductive glass which showed the typical absorption peak of ruthenium dye molecules at the wavelength of 540 nm. A three-electrode electrochemical cell consisted of a dye-coated FTO conductive glass sheet as the working electrode and two platinized FTO conductive glass sheets as the counter and reference electrodes were used in the measurements.

Electrochemical impedance spectroscopy (EIS) was measured in a symmetric thin-layer cell consisting of two identical platinized FTO conductive glass electrodes and a Surlyn film with the thickness of $\sim 40\ \mu\text{m}$ as the spacer [35].



Scheme 1. Molecular structures of PEO(*X*)MimCl.

The active area of the electrode was 0.25 cm^2 . The measurements were performed by using Solartron 1255B frequency response analyzer and Solartron SI 1287 electrochemical interface system at the zero bias under the frequency range over 0.05 Hz – 1 MHz .

The photovoltaic performance of the DSSCs was measured under the irradiation of 100 mW/cm^2 detected by an optical power meter (Model 350) and a detector (Model 262) from a 500 W xenon lamp with a 0.5 cm glass filter and a 10 cm water filter. The active area was 0.2 cm^2 .

3. Results and discussion

The ionic conductivities of the ionic liquid oligomers PEO(X)MImCl with different molecular weights of PEO i.e. different chain lengths of PEO was studied. The ionic conductivity of PEO(X)MImCl (at $30\text{ }^\circ\text{C}$) listed in Table 1 improves with the PEO molecular weight increasing from 150 to 750. An increase of the degree of freedom for longer PEO chain segment leads to promoting the ionic dissociation and improving the ionic conductivity. Further increasing the PEO molecular weight by higher than 750, considerable drop in the ionic conductivity of the ionic liquid oligomer is observed due to the state transforming from the liquid into solid.

The dependence of ionic conductivity on the temperature was further examined in the different ionic liquid oligomer electrolytes composed of 1.0 M LiI , 0.5 M I_2 and ionic liquid oligomers PEO(X)MImCl ($X = 150, 350, 550, 750$). The results were better fitted with the Vogel–Tammann–Fulcher (VTF) equation:

$$\sigma(T) = AT^{-1/2} \exp[-B/T - T_0] \quad (1)$$

where T_0 is the thermodynamic Kauzmann temperature, T is the absolute temperature, A and B are the constants [20]. The fitting results are given in Fig. 1. The improvement of the ionic conductivity of the ionic liquid oligomer electrolytes follows the order: PEO(750)MImCl > PEO(550)MImCl > PEO(350)MImCl > PEO(150)MImCl. This is in agreement with the data shown in Table 1.

The steady-state voltammograms for the redox reaction of triiodide/iodide in the ionic liquid oligomer electrolytes are depicted representatively in Fig. 2. From the cathodic steady-state currents (I_{ss}) shown in the voltammograms, the apparent diffusion coefficients (D_{app}) of the triiodide can be determined by using the Eq. (2) [36]:

$$I_{ss} = 4nCaFD_{app} \quad (2)$$

where n is the electron transfer number of the redox reaction, C is the bulk concentration of electroactive species, a is the radius of the Pt ultramicroelectrode and F is the Faraday constant. The calculated apparent diffusion coefficients of triiodide $D_{app}(I_3^-)$ for different ionic liquid oligomer electrolytes are compared in Table 1. It is observed that the calculated apparent diffusion

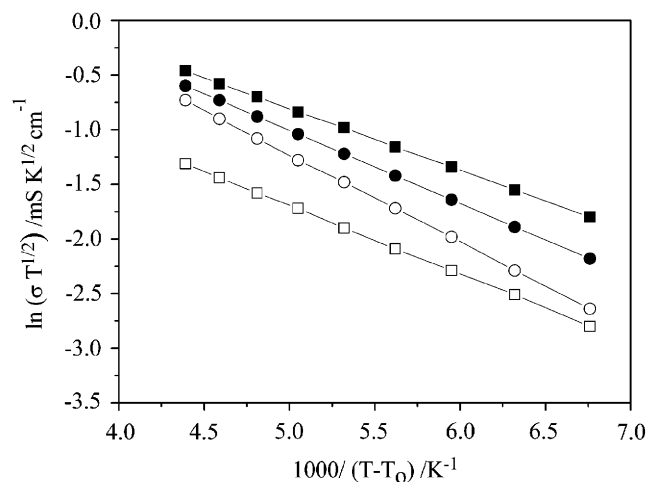


Fig. 1. Ionic conductivity-temperature plots of the ionic liquid oligomer electrolytes containing 1.0 M LiI , 0.5 M I_2 and the ionic liquid oligomers: PEO(750)MImCl (filled square); PEO(550)MImCl (filled circle); PEO(350)MImCl (open circle); PEO(150)MImCl (open square) fitting to the VTF equation, $T_0 = 150\text{ K}$.

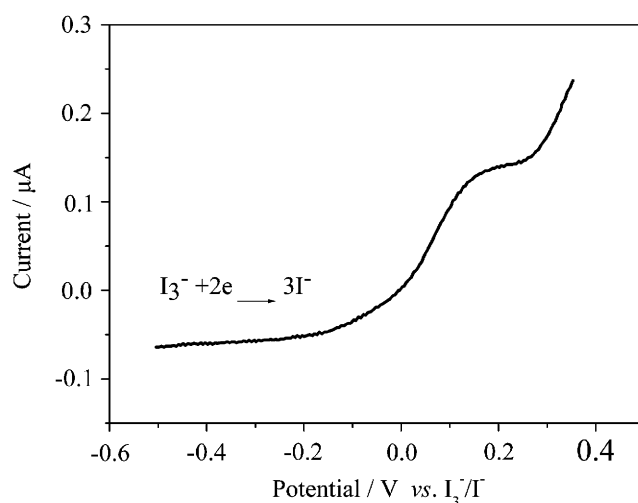


Fig. 2. Steady-state voltammogram for the Pt ultramicroelectrode in the PEO(750)MImCl electrolyte containing 1.0 M LiI and 0.5 M I_2 . Scanning rate: 10 mV/s .

Table 1

Ionic conductivities and apparent diffusion coefficients of I_3^-

Ionic liquid oligomer	PEO(150)MimCl	PEO(350)MimCl	PEO(550)MimCl	PEO(750)MimCl
$\sigma \times 10^{-4}\text{ S/cm}$	4.29	5.82	6.12	6.56
$D(I_3^-) \times 10^{-7}\text{ cm}^2/\text{s}^a$	1.48	1.45	1.47	1.45

^aMeasured in the ionic liquid oligomer electrolytes containing 1.0 M LiI , 0.5 M I_2 .

coefficients of triiodide at different ionic liquid oligomer electrolytes are about the same in spite of the fact that the viscosity of the electrolyte becomes higher as increasing the PEO molecular weight of the ionic liquid oligomers. This result reveals the different mechanisms of ionic transport involved in the ionic liquid oligomer electrolytes as compared to the organic solvent electrolytes. A Grotthuss-type electron exchange reaction between triiodide and iodide seems to make significant contribution to the D_{app} (I_3^-) [12]. The photovoltaic performance of the solar cells with different ionic liquid oligomer electrolytes is listed in Table 2. It is found that the short-circuit photocurrent density (J_{sc}) improves with increasing the PEO molecular weight of the ionic liquid oligomer in the electrolyte. The open-circuit photovoltage (V_{oc}) and the fill factor (FF) keep nearly constant. The high conversion efficiency (η) of the solar cell is obtained in the PEO(750)MImCl electrolyte containing 1.0 M LiI, 0.5 M I_2 due to the larger J_{sc} . The improvement of J_{sc} with increasing the PEO molecular weight of the ionic liquid oligomer can be related to the increased ionic conductivity of the electrolyte, while both V_{oc} and FF are independent on the PEO molecular weight of the ionic liquid oligomer.

For further analyzing the effect of PEO molecular weight of ionic liquid oligomer on the cell performance, the dye regeneration reaction ($3I^- + 2Dye^+ \rightarrow I_3^- + 2Dye$) and the triiodide reduction ($I_3^- + 2e \rightarrow 3I^-$) taken place at nanocrystalline TiO_2 electrode and Pt counter electrode, respectively, were studied in terms of cyclic-voltammetry and EIS measurements. Fig. 3 illustrates the cyclic-voltammograms obtained in different ionic liquid oligomer electrolytes under the scanning range of 0 to +1.5 V (vs. I^-/I_3^-). The voltammograms show the anodic peaks, which cannot be observed for the blank FTO electrode assigning to anodic oxidization of iodide by oxidized dye. The anodic peak potential shifts negatively and the anodic peak current density gradually increases when the PEO molecular weight of ionic liquid oligomer in the electrolyte changes from 150 to 750. The cathodic peak cannot be presented in this scanning range implying the irreversible behavior of this electrochemical reaction at dye-coated FTO electrode. The negative shifts of anodic peak potential and the increases of anodic peak current density shown in the voltammograms indicate the faster dye regeneration rate in the electrolyte with increased PEO molecular weight of ionic liquid oligomer. This may lead to the improvement of J_{sc} .

Table 2

Photovoltaic performance of DSSCs with different ionic oligomer electrolytes

Ionic liquid oligomer electrolyte ^a	V_{oc}/V	$J_{sc}/mA/cm^2$	FF	$\eta/\%$
PEO(150)MimCl	0.63	4.65	0.70	2.1
PEO(350)MimCl	0.68	5.75	0.73	2.9
PEO(550)MimCl	0.65	6.05	0.75	2.9
PEO(750)MimCl	0.64	6.80	0.73	3.1

^aContaining 1.0 M LiI, 0.5 M I_2 .

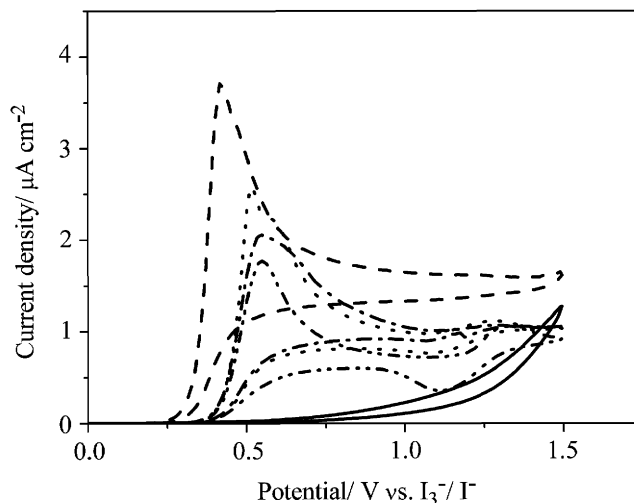


Fig. 3. Cycle voltammograms for the dye-coated FTO electrode in the electrolytes containing 1.0 M LiI, 0.5 M I_2 and the ionic liquid oligomers: PEO(750)MImCl (dashed line); PEO(550)MImCl (dotted line); PEO(350)-MImCl (dashed-dotted line); PEO(150)MImCl (dashed-dotted-dotted line); PEO(150)MImCl using the bare FTO electrode (solid line). Scanning rate: 100 mV/s.

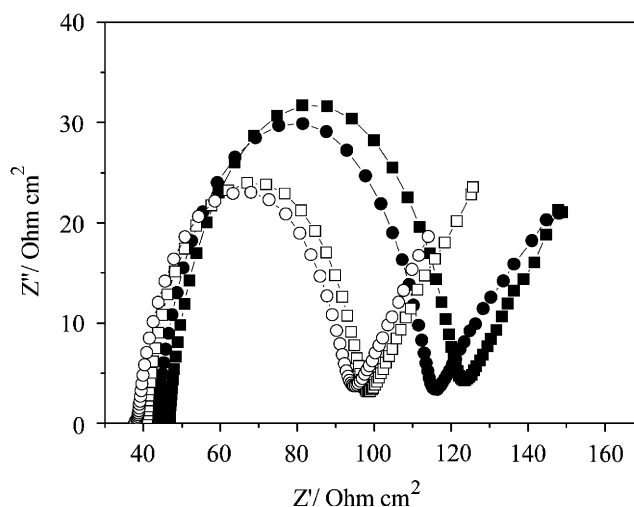


Fig. 4. Electrochemical impedance spectra for a thin-layer cell composed of two platinized FTO electrodes and the electrolytes containing 1.0 M LiI, 0.5 M I_2 and the ionic liquid oligomers: PEO(150)MImCl (filled square); PEO(350)MImCl (filled circle); PEO(550)MImCl (open square); PEO(750)MImCl (open circle) measured at the zero bias under the frequency range of 0.05 Hz–1 MHz.

Fig. 4 depicts the electrochemical impedance spectra measured in the different ionic liquid oligomer electrolytes. The semicircle presented at high frequency represents the charge-transfer process, which is usually described by the charge transfer resistance R_{ct} . The response at low frequency is related to the diffusion process of triiodide. According to the equivalent circuit [37,38], R_{ct} is taken as the diameter of the semicircle and the ohmic serial resistance R_s composed of the resistance of the substrate and the electrolyte is determined by the high-frequency intercept at the axis of real part. The parameters R_{ct} and R_s

Table 3
Parameters of electrochemical impedance spectra

Ionic liquid oligomer electrolyte ^a	$R_s/\Omega/\text{cm}^2$	$R_{ct}/\Omega/\text{cm}^2$
PEO(150)MimCl	49.0	9.5
PEO(350)MimCl	45.5	8.7
PEO(550)MimCl	41.0	7.3
PEO(750)MimCl	37.5	5.5

^aContaining 1.0 M LiI, 0.5 M I₂.

obtained from the impedance spectra are listed in Table 3. It is observed that both R_s and R_{ct} decrease with increasing PEO molecular weight of the ionic liquid oligomer in the electrolyte. The decrease of charge transfer resistance R_{ct} of triiodide reduction according to the reaction $I_3^- + 2e^- \rightarrow 3I^-$ on the counter-electrode gives rise to improving the J_{sc} . The lower value of ohmic serial resistance R_s , which corresponds to the high ionic conductivity of the ionic liquid oligomer electrolyte may also cause the larger J_{sc} .

The faster rate of dye regeneration at the nanocrystalline TiO₂ electrode and the lower charge transfer resistance of triiodide reduction at the Pt counter-electrode observed in the electrolyte with increased PEO molecular weight of ionic liquid oligomer can be rationalized by the steric effect of the ionic liquid oligomer attaching on the electrode surface via the adsorption of imidazole cations. As increasing the PEO molecular weight, the molar concentration of the ionic liquid oligomer in the electrolyte decreases. In this case, attachment of less ionic liquid oligomer to the electrode surface may occur in the electrolyte with lower molar concentration of the ionic liquid oligomer leading to reduce the steric hindrance for the dye regeneration and triiodide reduction reactions at both electrodes.

In order to clarify the effect of imidazole group of the ionic liquid oligomer on the ionic conductivity, apparent diffusion coefficient of triiodide in the electrolyte and the photovoltaic performance of solar cells, a comparison is made between the ionic liquid oligomer PEO(750)MimCl and the oligomer PEO(750). The ionic conductivity of PEO(750) is 1.17×10^{-4} S/cm (at 30 °C), and the apparent diffusion coefficient of triiodide for the PEO(750) electrolyte with the same composition as the electrolyte of PEO(750)MimCl is 0.62×10^{-7} cm²/s. With respect to the data given in Table 1, the significant decreases in the values of both the ionic conductivity and apparent diffusion coefficient of triiodide are observed in the electrolyte of PEO(750). The increases in the ionic conductivity and the apparent diffusion coefficient of triiodide in the PEO(750)-MimCl electrolyte are ascribed to the high ion contents and the contribution of Grotthus-type electron exchange of I^-/I_3^- redox couple to the ion transport in ionic liquid oligomer electrolytes.

Fig. 5 shows the photocurrent density-voltage curves of DSSCs using the electrolytes of PEO(750)MimCl and PEO(750). The short-circuit photocurrent density (J_{sc}), open-circuit photovoltage (V_{oc}), fill factor (FF) and the

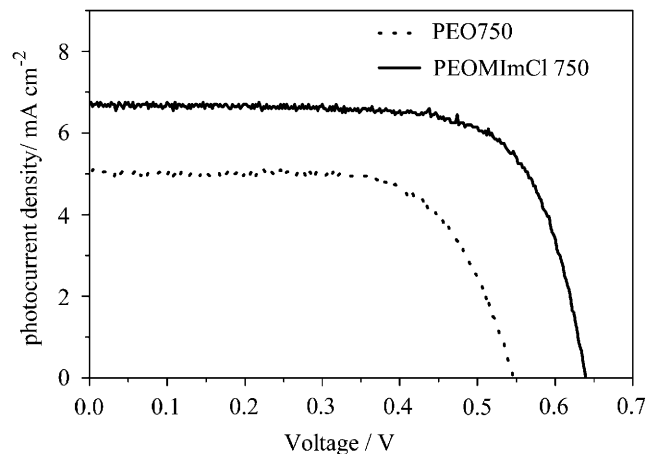


Fig. 5. Photocurrent–voltage characteristics of DSSCs with the electrolytes containing 1.0 M LiI, 0.5 M I₂ and PEO(750)MimCl (solid line); PEO(750) (dotted line) measured at 100 mW/cm² irradiation from 500 W Xenon lamp.

conversion efficiency (η) of the cell with PEO(750) electrolyte are 5.1 mA/cm², 550 mV, 0.67 and 1.9%, respectively. The corresponding photovoltaic parameters of the cell with PEO(750)MimCl electrolyte are 6.8 mA/cm², 640 mV, 0.73% and 3.1%, respectively. Obviously, cell performance is improved considerably by using PEO(750)-MimCl electrolyte. The improvement of J_{sc} and FF may be attributed to the higher ionic conductivity and the larger apparent diffusion coefficient of triiodide in the PEO(750)-MimCl electrolyte. The larger V_{oc} is due to the suppression of the dark current which arises from the reduction of triiodide by the conduction band electrons at the nanocrystalline TiO₂/electrolyte interface [39]. An decrease of the dark current density in the cell with PEO(750)MimCl electrolyte as compared to that with PEO electrolyte at corresponding voltage is observed in the dark current–voltage characteristics of DSSCs illustrated in Fig. 6. The suppression of the dark current density in the cell with PEO(750)MimCl electrolyte can be attributed to the adsorption of imidazolium cations at nanocrystalline TiO₂ surface. Imidazolium cations adsorbed at TiO₂ surface play an important role in blocking the surface states, which act as the mediators of the charge transfer from the conduction band electrons of TiO₂ to triiodide. As a result, the rate constant of the reduction reaction of triiodide and the conduction band electrons decreases leading to suppression of the dark current density and increase of the V_{oc} . [40]. The performance of the cell with the PEO(750)MimCl electrolyte has been further improved by combination of the ionic liquids 1-hexyl-3-methylimidazolium iodide (HMImI). The conversion efficiency has attained to 6.8% which will be reported elsewhere.

4. Conclusion

Ionic liquid oligomers have been prepared by incorporating imidazolium ionic liquid with PEO oligomers. PEO

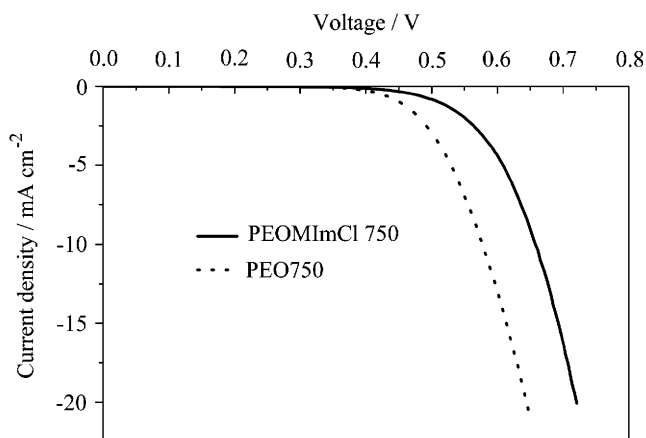


Fig. 6. Dark current–voltage characteristics of DSSCs with the electrolytes containing 1.0M LiI, 0.5M I₂ and PEO(750)MImCl (solid line); PEO(750) (dotted line).

molecular weight and imidazolium group of ionic liquid oligomers play an important role in determining the ionic conductivity, apparent diffusion coefficient of triiodide contained in the electrolytes, the interfacial electron transfer behaviors and the photovoltaic performance of DSSCs. The results indicate that the ionic conductivity increases with increasing PEO molecular weight. A significant contribution of Grotthuss-type electron exchange of I⁻/I₃⁻ redox species to the ionic transport in the ionic liquid oligomer electrolyte leads to the larger apparent diffusion coefficient of triiodide. The higher conversion efficiency in the solar cell using the ionic liquid oligomer PEO(750)MImCl electrolyte containing I⁻/I₃⁻ redox couple is attributed to the higher ionic conductivity, larger apparent diffusion coefficient of triiodide, faster dye regeneration rate and the lower charge transfer resistance of triiodide reduction. These results are particularly useful in the further studies of ionic liquid polymer for employing in fabrication of the quasi-solid-state DSSCs.

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