Journal of Photochemistry and Photobiology A: Chemistry 212 (2010) 147–152

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

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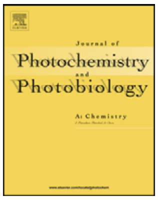

Electrochemical characterization and photovoltaic performance of the binary ionic liquid electrolyte of 1-methyl-3-propylimidazolium iodide and 1-ethyl-3-methylimidazolium tetrafluoroborate for dye-sensitized solar cells

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A R T I C L E I N F O

Article history:
Received 20 January 2010
Received in revised form 18 March 2010
Accepted 13 April 2010
Available online 21 April 2010

Keywords:
Ionic liquid electrolyte
Dye-sensitized solar cell
Diffusion coefficient
Charge-transfer resistance
Photovoltaic performance

A B S T R A C T

Determination of triiodide diffusion coefficient, charge-transfer resistance and photovoltaic performance of the binary ionic liquid electrolyte of 1-methyl-3-propylimidazolium iodide (MPII) and 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIMBF_4$) for dye-sensitized solar cells (DSSCs) were performed at varying volume ratios of MPII/$EMIMBF_4$. Compared to pure MPII ionic liquid, the addition of $EMIMBF_4$ not only increased triiodide diffusion coefficient, but also decreased charge-transfer resistance at Pt/electrolyte interface, leading to the notably improved photovoltaic performance of DSSC. The highest photoelectric conversion efficiency of 4.99% was obtained under light intensity of 100 mW/cm^2 for the DSSC with the binary MPII/$EMIMBF_4$ ionic liquid electrolyte when the volume ratio of MPII/$EMIMBF_4$ was 50/50, which was much higher than that of pure MPII ionic liquid electrolyte (2.6%).

1. Introduction

Dye-sensitized solar cells (DSSCs) based on nanocrystalline TiO_2 semiconductors have attracted much attention because of their low-cost production and high photovoltaic performance [1,2]. Although an impressive 11% light-to-electricity conversion efficiency has been achieved for DSSCs with organic solvent-based electrolytes [3], the presence of volatile liquid electrolyte in such devices results in some practical limitations for sealing and long-term operation of the devices. A good alternative to organic solvents, e.g. for electrochemical devices, are ionic liquids [4,5], due to their attractive chemical and thermal stability, non-volatility, and high ionic conductivity at room temperature [6]. Among the ionic liquid electrolytes used in DSSCs, most attention has been paid to the ionic liquids with 1,3-dialkylimidazolium cations [7], especially to 1-methyl-3-propylimidazolium iodide (MPII), an iodide source in the electrolyte. However, the energy conversion efficiency of DSSCs using ionic liquid solvents could not reach that of DSSCs with volatile liquid solvent due to the high viscosity of MPII (880 mPa at 21 °C) [8,9]. It has been reported that mixing some imidazolium melts containing nonelectroactive anions with MPII could decrease the viscosity of the electrolyte and improved the power conversion efficiencies of DSSCs [10–12]. The conversion efficiency of DSSC based on amphiphilic ruthenium sensitizer Z907 [11] was improved from 6% to 7% by the addition of 1-methyl-3-ethylimidazolium dicyanamides (EMIDCN) into MPII electrolyte. A stable DSSC also using sensitizer Z907 with a high conversion efficiency of 6.4% has been reported under simulated full sunlight (Air Mass 1.5, 100 mW/cm^2) using a binary ionic liquid electrolyte of MPII and 1-ethyl-3-methylimidazolium thiocyanate (EMINCS) [12].

In this study, imidazolium melts 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIMBF_4$) was used to improve conversion efficiency of DSSC due to its low viscosity (37 mPa at 25 °C [13]), high ionic conductivity [14], high electrochemical stability [15], and environment friendly. Although Zistler et al. [16] have recently reported the temperature dependent impedance analysis of binary ionic liquid electrolytes including $EMIMBF_4$/MPII, the study about the effect of the binary ionic electrolytes $EMIMBF_4$/MPII on the performance of solar cells has not reported yet. In this paper, the electrolytes with various volume ratios of MPII/$EMIMBF_4$ were analyzed via polarization measurements and electrochemical impedance spectroscopy (EIS). The effect of volume ratio of MPII/$EMIMBF_4$ on the photovoltaic performance of DSSC was studied. The highest conversion efficiency of 4.99% was achieved when

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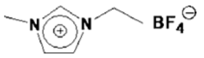
doi:10.1016/j.jphotochem.2010.04.009



Scheme 1. Molecular structure of $EMIMBF_4$ ionic liquid.

the volume ratio of MPII/$EMIMBF_4$ was 50/50, which was much higher than that of pure MPII ionic liquid electrolyte.

2. Experimental

2.1. Materials

The dye cis-$(SCN)_2$bis(2,2′-bipyridyl-4,4′-dicarboxylate) ruthenium (N3) was purchased from Solaronix SA. Titanium(IV) isopropoxide, 4-tert-butylpyridine (TBP) and 1-methyl-3-propylimidazolium iodide (MPII) were purchased from Aldrich. All the materials were reagent grade and used as received. The synthesis of ionic liquid, 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIMBF_4$) was carried out according to methods reported by Matsumoto et al. [17], and its molecular structure is shown in Scheme 1.

2.2. Sample preparation

Symmetric Pt electrochemical thin-layer cells were prepared for polarization curve and impedance spectroscopy measurements [18,19]. The cell consisted of two identical platinized, TCO-coated glass substrates (FTO, 20 Ω/square) sealed with a surlyn film (30 μm, DuPont). The cell was filled with the ionic liquid electrolyte at varying volume ratio of MPII/$EMIMBF_4$. All the measurements were performed at room temperature.

The TiO_2 (anatase) colloidal paste was prepared by hydrolysis of titanium tetraisopropoxide according to the previously reported process [20]. The TiO_2 paste was deposited using a simple doctor blade technique on completely cleaned FTO glass (4 mm thick, 75% transmittance in the visible, 20 Ω/square). The thickness and the size of the porous TiO_2 layer were controlled by an adhesive tape. Afterward, the film was heated at 450 °C for 60 min. The thickness of the resulting porous TiO_2 film was about 8 μm. Coloration of TiO_2 was carried out by soaking the film in dry ethanol containing 2.5×10^{-4} M N3 ruthenium complex for 20 h at room temperature. In order to avoid rehydration of the TiO_2 surface or capillary condensation of water vapor from ambient air inside the nanopores of the film, the dye adsorption was done immediately while the electrode was still hot, *i.e.*, its temperature was *ca.* 80 °C. A sandwich cell was prepared with a second conducting glass coated with Pt film, which was deposited from paste containing hexachloroplatinic acid, ethylcellulose and terpineol by screen printing process. The two electrodes were separated by a 30 μm surlyn spacer and sealed up by heating at 150 °C. The redox electrolyte was introduced into the space of inter-electrodes through the two holes predrilled on the back of the counter electrode. The two holes were sealed up using a surlyn film, on which a glass slide was pressed under heat. The redox electrolyte composed of 0.15 M I_2, 0.5 M 4-tert-butylpyridine and 0.1 M guanidinium thiocyanate in a mixture of MPII and $EMIMBF_4$ (the volume ratio of MPII/$EMIMBF_4$ ranging from 100% to 20%). The active area of DSSC was 0.194 cm^2.

2.3. Measurement

Viscosity measurements were conducted using a 4ARES-9a rheometer (Rheometric Scientific, USA) at room temperature. The viscosities given were averaged over the values obtained at shear rates from 10 to 1000 s^{-1}. Polarization curves and impedance spectroscopy measurements were performed using an IM6/IM6e (Zahner, Germany) electrochemical analyzer in a two-electrode configuration. A 10 mV AC perturbation was applied and the frequency range was 0.01–100 kHz. The scan rate was 10 mV/s. Photocurrent–voltage curves were recorded using a source meter (Keithley-2400, Keithley Co. Ltd., USA) under an illumination of 100 mW/cm^2 (1.5G Air Mass Filter, 1sun) from a 300 W Oriel solar simulator 91,160 at room temperature. The output beam size of the solar simulator was 2 × 2 in. The size of the cells was about 1 cm^2. A mask of 0.194 cm^2 was clipped on the TiO_2 side to define the active area of the cell.

3. Results and discussion

Generally, a DSSC comprises a dye-sensitized nanocrystalline porous TiO_2 film immobilized on a transparent conducting oxide TCO-coated glass substrate, an electrolyte containing an I^-/I_3^- redox couple, and a platinized TCO-coated glass substrate as counter electrode. When the sensitizer dye molecules absorb solar energy, electrons are injected rapidly from the excited state of the dye into the conduction band of TiO_2. The injected electrons diffuse into the conduction band of TiO_2 and reach the outer circuit through the back contact. The oxidized dye molecules are reduced by I^- ions in the electrolyte via the reaction $3I^- \rightarrow I_3^- + 2e$, where

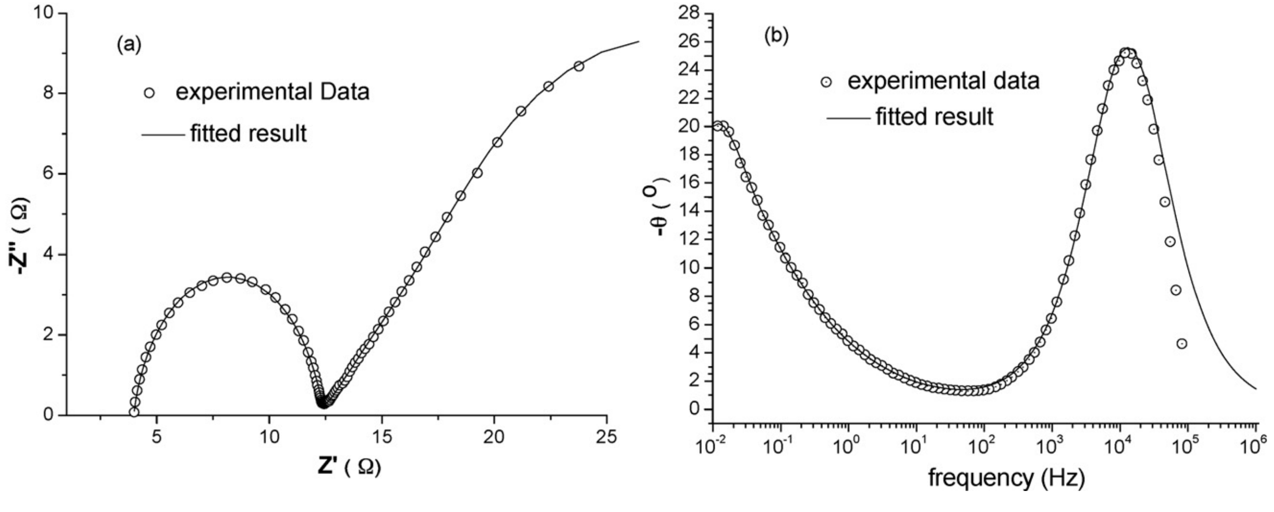


Fig. 1. (a) Typical Nyquist plot and (b) Bode plot of the impedance spectrum of the binary ionic liquid electrolyte (MPII/$EMIMBF_4$ volume ratio 20/80) measured at a thin layer cell.

I^- ion is oxidized into I_3^- ion by losing two electrons. At Pt counter electrode, the reverse reaction $I_3^- + 2e \rightarrow 3I^-$ takes place, where I_3^- ion is reduced to I^- ion by gaining two electrons from counter electrode. In the iodide-based electrolyte, I^- ions diffuse from counter electrode to dye, and I_3^- ions diffuse from dye to counter electrode. Among the above reactions, both the charge-transfer process at the Pt/electrolyte interface and the diffusion process of ions in the electrolyte are important for the efficiency of the DSSC.

3.1. *Influence of the MPII concentration on the charge-transfer resistance at Pt/electrolyte interface*

A typical impedance spectrum of the binary ionic liquid electrolyte ($MPII/EMIMBF_4 = 20/80$, in volume) measured at a Pt-Pt thin layer cell was shown in Fig. 1(a) and (b) in a Bode and a Nyquist plot, respectively. In Fig. 1(a), the first part of the impedance spectrum was attributed to the kinetics at the Pt electrode [16], the second was related to diffusion processes of I_3^- ions. The diffusion impedance is related to only I_3^- species since there are excess I^- ions in the electrolyte. The equivalent circuit shown in Fig. 2 was used for the fitting of the impedance spectrum. R_s is the ohmic serial resistance (including resistances of the electrolyte, TCO-coated glass and the cables), R_{ct} is the charge-transfer resistance at the counter electrode/electrolyte interface, C_{dl} is the capacitance of electrical double layer, Z_W is the Warburg impedance, which is attributed to diffusion process of I_3^- ions in the electrolyte. The impedance W_s is given by [21,22]:

$$Z = R_D \frac{\tanh(\sqrt{i\omega\tau_D})}{\sqrt{i\omega\tau_D}} \tag{1}$$

where R_D is Warburg parameter, τ_D is associated to the diffusion coefficient and δ is the Nernst-distance to the electrode. For the thin layer cell, diffusion coefficient of I_3^- ions ($D_{I_3^-}$) in the electrolyte can be calculated from the electrode distance $\delta = l/2$ and the parameter τ_D obtained by fitting the impedance spectrum according to the following equation:

$$D_{I_3^-} = \frac{\delta^2}{\tau_D} = \frac{(l/2)^2}{\tau_D} \tag{2}$$

The curve fitting was realized using Z-view software (Scribner Associate, Inc.). To compensate for the roughness of the electrode surface, constant phase element (CPE) was used in the model in place of a capacitor keeping the exponent CPE-P quite close to the perfect capacitor value, CPE-P ≈ 1. The fitting results were in a good agreement with measured impedance values. The values of the fitted parameters were listed in Table 1. As shown in Table 1, the R_{ct} value decreased with the decrease of MPII content, which meant the kinetic behavior of the I^-/I_3^- redox couple depending on I^- concentration in ionic liquid electrolyte was different from that in aqueous as well as organic solvent solutions where the influence of the iodide concentration was inverse [23] for aqueous and negligible for organic solvent solutions [19]. A minimum of 2.1 Ω for R_{ct} was achieved when the volume ratio of $MPII/EMIMBF_4$ was 20/80. For the electrolyte of DSSC, a strong influence of viscosity on R_{ct} has been reported [24]. Therefore, the influence of MPII content on the R_{ct} value was mainly attributed to the increase in viscosity, but not to the concentration of I^-. This illustrates that a low viscosity of the ionic liquid electrolyte is a key property not only for the diffusion of ions in the electrolyte, but also the kinetics of I^- regeneration at the counter electrode of the DSSC. The decreased R_{ct} would facilitate the I^- regeneration at the counter electrode, leading to an improved photovoltaic performance of DSSC. In addition, both the values of R_D and τ_D decreased with the decrease of MPII content, which indicated an improved diffusion property of ions with decreasing MPII content. Although R_D and τ_D were correlated to the diffusion coefficients of ions, it could only be used for qualitative analysis due to its small effect on the impedance spectra for the electrolytes with a high viscosity. So the exact diffusion coefficients should be determined from diffusion-limited currents, which were studied in the following section.

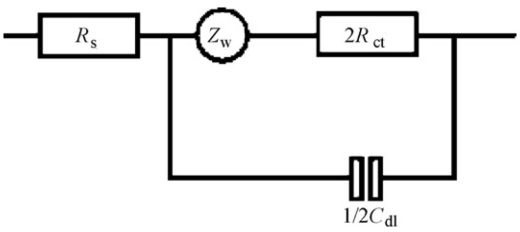


Fig. 2. Equivalent circuit used for the analysis of the impedance spectrum including serial resistance R_s, charge-transfer resistance R_{ct}, double layer capacity C_{dl}, and Warburg impedance Z_w.

Table 1
Fitted parameters of the binary ionic liquid electrolytes with various volume ratios of $MPII/EMIMBF_4$.

Volume ratio of $MPII/EMIMBF_4$	R_{ct}/Ω	R_D/Ω	τ_D/s	$D_{I_3^-}$ (10^{-7} cm^2/s)
100/0	4.2	26.1	64	0.35
80/20	3.6	25.2	45.1	0.50
65/35	3.3	22	37.5	0.60
50/50	2.8	14.1	33	0.68
35/65	2.4	13.2	31	0.73
20/80	2.1	11.2	29.1	0.77

3.2. *Influence of the MPII concentration on the diffuse coefficients of ions*

Fig. 3 shows a typical polarization curve for the binary ionic liquid electrolyte ($MPII/EMIMBF_4 = 20/80$, in volume). It was found that the current density was achieving its limiting value j_{lim} when the applied voltage V was increased. Due to the large excess of I^- relative to I_3^- and the diffusion coefficients of both species are in nearly the same order of magnitude, I_3^- ions are the diffusion-limiting species. Diffusion coefficient of I_3^- ions ($D_{I_3^-}$) in the electrolytes could be determined from the limiting current density (j_{lim}) by the following equation [25]:

$$D_{I_3^-} = \frac{j_{lim} L}{2nFC_{I_3^-}} \tag{3}$$

where n is the number of electrons transferred in each reaction (here $n = 2$); F is Faraday's constant; L is the distance between the

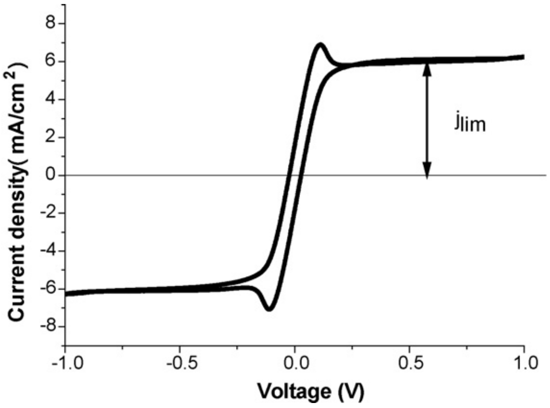


Fig. 3. Typical polarization curve of the binary ionic liquid electrolyte ($MPII/EMIMBF_4 = 20/80$, in volume) at a thin layer cell.

Table 2
Limiting current density (j_{lim}), diffusion coefficient ($D_{\mathrm{I_3}^-}$) and viscosity of the binary ionic liquid electrolyte with various volume ratios of MPII/EMIMBF$_4$.

Volume ratio of MPII/EMIMBF$_4$	j_{lim} (mA/cm^2)	$D_{\mathrm{I_3}^-}$ (10^{-7} cm^2/s)	Viscosity (mPa)
100/0	1.66	0.86	884
80/20	2.12	1.1	455
65/35	3.89	2.01	288
50/50	4.54	2.35	157
35/65	5.26	2.72	124
20/80	6.08	3.17	77

two electrodes (here $L = 30\,\mu$m) and $C_{\mathrm{I_3}^-}$ is the molar concentration of $\mathrm{I_3}^-$ (here $C_{\mathrm{I_3}^-} = 0.15$ M). The j_{lim} and the corresponding $D_{\mathrm{I_3}^-}$ values for the binary ionic liquid electrolytes with various volume ratios of MPII/EMIMBF$_4$ were summarized in Table 2. It was found that the diffusion coefficient of triiodide showed a strong increase with decreasing MPII content. For the electrolyte with MPII/EMIMBF$_4$ volume ratio of 20/80, the diffusion coefficient of triiodide was 3.17×10^{-7} cm^2/s, which was three times more than pure MPII electrolyte (0.86×10^{-7}cm^2/s). According to Einstein–Stokes rule [26], the product of viscosity and diffusion coefficient (the Walden product) was approximately constant [26,27], therefore the Einstein–Stokes ratio $D\eta/T$ should also be constant for a constant temperature. However, as shown in Fig. 4, the values of the Einstein–Stokes ratios of the $\mathrm{I_3}^-$ diffusion coefficients of the electrolytes with varying MPII concentration did not stay constant with increasing MPII concentration and increasing viscosity, but the values grow with the increase of MPII concentration. The deviation was explained by that the triiodide transport was not only created by an ordinary diffusion process, but also by a Grotthus-type charge-exchange mechanism [28]. So the Einstein–Stokes ratio increased with increasing iodide concentration. Diffusion of triiodide in the electrolyte often became a limiting process in an ionic liquid electrolyte based DSSC, especially when the iodine concentration and consequently the triiodide concentration in the electrolyte were low [29]. Improved diffusion coefficient of triiodide not only could facilitate I$^-$ regeneration and hence the dye molecule regeneration, but also would suppress the recombination between $\mathrm{I_3}^-$ ions and injected electrons in TiO$_2$ conduction band, both of which would enhance the photovoltaic performance of DSSC.

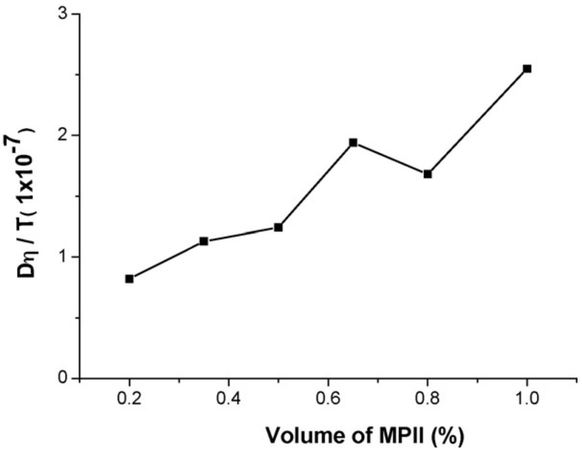


Fig. 4. Einstein–Stokes ratio calculated with diffusion coefficient determined with polarization measurement at a thin layer cell.

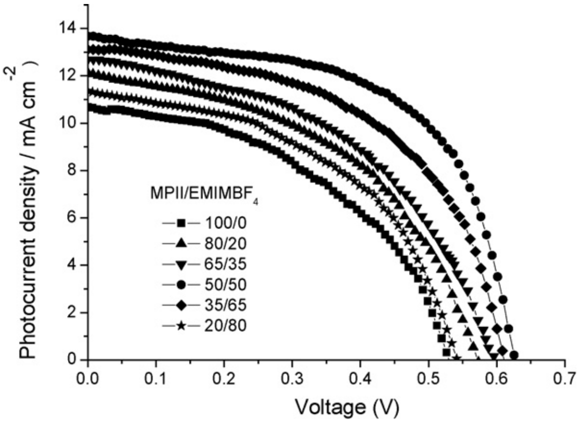


Fig. 5. Photocurrent–voltage curves of DSSCs as a function of MPII/EMIMBF$_4$ volume ratio.

3.3. Influence of the MPII concentration on the photovoltaic performance of DSSC

Fig. 5 depicts the photocurrent–voltage characteristics curves of DSSCs based on the electrolytes with various volume ratios of MPII/EMIMBF$_4$. The corresponding photovoltaic characteristic parameters of DSSCs were summarized in Table 3. The photoelectric conversion efficiency η was enhanced upon the addition of EMIMBF$_4$ and the maximum of 4.99% was achieved when the volume ratio of MPII/EMIMBF$_4$ was 50/50, where both J_{sc} and V_{oc} reached their maximum values of 0.625 V and 13.673 mA/cm^2, respectively. The increased photocurrent with decreasing MPII content was attributed to the improved diffusion coefficient of $\mathrm{I_3}^-$ and the reduced charge-transfer resistance, as discussed in the previous sections. It has been reported that the relation between open circuit (V_{oc}) of DSSC and concentrations of $\mathrm{I_3}^-$ and oxidized dyes (D$^+$) could be expressed as [30,31]:

$$V_{\mathrm{oc}} = \frac{RT}{nF} \ln\left(\frac{AI}{n_0 k_1 C_{I_3^-} + n_0 k_2 C_{\mathrm{D}^+}}\right) \tag{4}$$

where k_1, k_2, and I are kinetic constants for the recombination of the injected electrons with $\mathrm{I_3}^-$, with oxidized dyes (D$^+$), and incident photon flux, respectively. And n_0 is the concentration of accessible electronic states in the conduction band. It was apparent that the open-circuit voltage V_{oc} was reciprocally proportional to k_1, k_2, $C_{\mathrm{I_3}^-}$ and C_{D^+}. Under illumination, $\mathrm{I_3}^-$ ions produced *in situ* by dye regeneration diffuse to the counter electrode. The improved diffusion coefficient of $\mathrm{I_3}^-$ resulted in the decreased local $\mathrm{I_3}^-$ concentration around TiO$_2$ nanoparticles and, thus, would slow down the possible charge recombination between the injected electrons and $\mathrm{I_3}^-$ at TiO$_2$/electrolyte interface. According to the equation (4), the V_{oc} value increased when the recombination kinetic constant of k_1 decreased. In summary, when the volume ratio of MPII/EMIMBF$_4$ was above 50/50, the photocurrent J_{sc}, the open-circuit voltage V_{oc} and hence the conversion efficiency η of DSSC increased with decreasing MPII content.

Table 3
Photovoltaic parameters of DSSCs based on the binary liquid electrolyte with different volume ratios of MPII/EMIMBF$_4$.

Volume ratio of MPII	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)
100/0	10.691	0.528	0.46	2.60
80/20	12.133	0.572	0.47	3.29
65/35	12.692	0.597	0.47	3.56
50/50	13.673	0.625	0.58	4.99
35/65	13.114	0.610	0.53	4.23
20/80	11.376	0.542	0.48	2.97

However, when the volume ratio of MPII/EMIMBF$_4$ was below 50/50, J_{sc}, V_{oc} and hence η decreased with the decrease of MPII content. The deteriorated photovoltaic performance was probably attributed to the lack of I^- ions in the electrolyte. The role of the iodide in the electrolyte is to regenerate the positively charged photoexcited dye by electron donation according to the redox reaction: $3I^- + 2Dye^+ \rightarrow 2Dye + I_3^-$. The lack of I^- led to the incomplete dye regeneration and hence the decreased photocurrent J_{sc}, open-circuit voltage V_{oc}, and hence conversion efficiency η of DSSC. Recently, Grätzel's group have reported the similar result for 3-methoxyproprionitrile (MPN)-based electrolytes with different concentration of MPII [32]. It indicated that the dye regeneration process was incomplete when the MPII concentration was lower than 1.5 M in the electrolyte, which was proved by time-resolved laser experiments. In our study, the electrolytes with the MPII/EMIMBF$_4$ volumes ratio of 20/80 and 65/35 correspond to the MPII concentrations of 0.8 M and 1.39 M, respectively. In the same manner, the low I^- concentration (less than 1.5 M) in the electrolyte would lead to the incomplete dye regeneration thus the decreased photovoltaic performance. Compared to the reported DSSC using binary ionic liquid electrolyte, the DSSC using MPII/EMIMBF$_4$ electrolyte in this study was always very stable while MPII/EMIDCN ionic liquid electrolyte showed instability of the cells under visible light soaking [11]. It was worth mentioning that the conversion efficiency of DSSC increased noticeably from 2.60% to 4.99% upon the addition of EMIMBF$_4$ although it was still lower than that of ionic liquid EMINCS/MPII (6.4%) [12]. The relatively low conversion efficiency in our study was probably attributed to the N3 sensitizer used in the device. Because it has been reported that the conversion efficiency of 6.6% and 5% was obtained for the same binary ionic liquid electrolyte when the TiO$_2$ photoanode was sensitized with Z907 and N719 dye, respectively [11]. It can be concluded that Z907 sensitizer should show a higher photovoltaic performance than N719 and N3 sensitizer for DSSC using ionic liquid electrolyte. So the conversion efficiencies of DSSC with the binary MPII/EMIMBF$_4$ ionic liquid electrolyte in the study are expected to be notably improved if Z907 sensitizers are used in the devices. Further work is under progress.

4. Conclusions

The polarization and impedance spectroscopy measurements were performed for the binary ionic liquid electrolyte at varying volume ratio of MPII/EMIMBF$_4$. It was found that the diffusion coefficients of triiodide increased and the charge-transfer resistance at Pt/electrolyte interface decreased with the increase of MPII/EMIMBF$_4$ volume ratio. In comparison with the pure MPII, the diffusion coefficients of triiodide increased by three times and the charge-transfer resistance decreased by twice for the electrolyte when the volume ratio MPII/EMIMBF$_4$ equals 20/80. Both the photocurrent J_{sc} and the open-circuit voltage V_{oc} were enhanced as a function of MPII content when the volume ratio of MPII/EMIMBF$_4$ was above 50/50. The highest photoelectric conversion efficiency of 4.99% was obtained under an illumination of 100 mW/cm^2 for the DSSC based on the binary ionic liquid electrolyte MPII/EMIMBF$_4$ (volume ratio of 50/50), with an increase of 92% improvement in comparison with DSSC based on pure MPII ionic liquid electrolyte (2.6%). However, further decrease of MPII content caused a deteriorated photovoltaic performance of DSSC because a high volume ratio of MPII is required in the binary systems for the fast dye regeneration and to maintain photovoltaic performance even if the triiodide concentration is sufficient to avoid diffusion limitation of the photocurrent. The dye-sensitized solar cells with the electrolyte, which was composed of 0.15 M of I$_2$, 0.5 M of 4-tert-butylpyrdine in the binary ionic liquid electrolyte of MPII and EMIMBF$_4$ (volume ratio of 50/50), gave short circuit photocurrent density of 13.673 mA/cm^2, open-circuit voltage of 0.625 V, and fill factor of 0.58, corresponding to the highest photoelectric conversion efficiency of 4.99% under a 100 mW/cm^2 illumination.

Acknowledgements

The authors acknowledge financial support from National Nature Science Foundation of China (50802051), National High Technology Research and Development Program of China (863 Program, 2006AA03Z218), and Chinese Postdoctoral Science Foundation (20060400055).

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