High performance dye-sensitized solar cells using ionic liquids as their electrolytes

Ryuji Kawano [a], Hiroshi Matsui [b,1], Chizuru Matsuyama [a], Akihiro Sato [a],
Md. Abu Bin Hasan Susan [a], Nobuo Tanabe [b,1], Masayoshi Watanabe [a,*]

[a] *Department of Chemistry and Biotechnology, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan*
[b] *Material Technology Laboratory, Fujikura Ltd., 1-5-1 Kiba, Koto-ku, Tokyo 135-8521, Japan*

Abstract

Room temperature ionic liquids have been used as electrolytes to investigate the performance and the characteristics in dye-sensitized solar cells (DSSCs). The ionic liquids used are 1-ethyl-3-methylimidazolium bis(trifluoromethane sulfonyl)imide (EMImTFSI), 1-ethyl-3-methylimidazolium tetrafluoroborate (EMImBF$_4$), 1-butyl-3-methylimidazolium hexafluorophosphate (BMImPF$_6$), 1-ethyl-3-methylimidazolium dicyanamide (EMImDCA), and 1-butylpyridinium bis(trifluoromethane sulfonyl)imide (BPTFSI), in which 1-ethyl-3-methylimidazolium iodide (EMImI) and I$_2$ are dissolved as a redox couple. The structure and the property greatly influence the DSSC performances. Especially, the photocurrents are affected by the ionic conductivity (viscosity) and charge transport by the exchange reaction between the iodide/tri-iodide redox couple. EMImDCA is specific in terms of enhancement of the open-circuit voltages. The photo-energy conversion efficiency of DSSCs with EMImDCA under 100 mW cm^{-2} can be optimized up to 5.5%, when [I$^-$] + [I$_3$$^-$] = 2 M and [I$^-$]:[I$_2$] = 10:1 with the addition of 4-*t*-butylpyridine and LiI.
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1. Introduction

Ionic liquids are room temperature molten salts that entirely consist of cations and anions. The ionic liquids have afforded and are expected to afford potentials for the use in diverse fields, such as non-volatile green solvents for syntheses [1] environmentally benign separation processes [2] and new electrolytes in electrochemical systems [3,4] based on their unique physico-chemical properties. There have been several attempts to use ionic liquids for electrochemical devices by utilizing their characteristics, such as non-volatility, non-flammability, high ionic conductivity, and gel-forming property with polymers [5]. The use of ionic liquids for dye-sensitized solar cells (DSSCs) [6–10] is one of the fascinating applications of ionic liquids, because DSSCs present an important alternative to current solar technology. The solar cell is constituted by nano-crystalline TiO$_2$, a molecular dye and an electrolyte containing a redox couple. The function of such devices is based on the injection of an electron from a photo-excited state of the sensitizer dye into conduction band of the nano-crystalline semiconductor. These cells usually employ a liquid electrolyte to reduce the dye cation, generated by the injection of the photo-excited electron [11,12]. Typically, an iodide/tri-iodide (I$^-$/I$_3$$^-$) redox couple dissolved in organic solvents has been used. However, use of the volatile solvents causes deterioration of the cell by evaporation of the solvent over the prolonged use. Ionic liquids with their characteristic properties seem to be the most appropriate solvents to solve such problems, whereas large viscosity of the ionic liquids is a serious problem for the development of such devices using these promising solvents. The viscosity of typical ionic liquids is about 100 times larger than that of acetonitrile, and also 30 times larger than that of water at room temperature [13,14]. Photocurrents in such systems are affected by the series resistances of the electrolytes, which are usually in proportion to the viscosity. Grätzel and coworkers reported [6] the use of ionic liquids, consisting of 1-hexyl-3-methylimidazoliun iodide (HMImI) and I$_2$, as an electrolyte of DSSCs and revealed the high short-circuit currents (J_{sc}), in spite of the extremely high viscosity. It was implicated that the Grotthuss-like mechanism

contributed to the electron transport between the I^- and I_3^- redox couple in such high viscosity media [15]. Recently, we succeeded in separating the contributions of physical diffusion (D_{phys}) and exchange-reaction-based diffusion (D_{ex}) of an I^-/I_3^- redox couple to the electron transport processes in EMImTFSI by using an ultra-microelectrode technique [16]. It has been found that the D_{ex} dominates over the whole charge transport processes at high I^-/I_3^- redox couple concentrations. This seems to be a reason for the fast charge transport in the ionic liquids, in spite of the high viscosity.

The properties of ionic liquids can be tuned by controlling the structures of cations and anions. However, the structural effect of ionic liquids on the performances of DSSCs has not been revealed at all. In this study, EMITFSI containing an I^-/I_3^- redox couple was used as an electrolyte of DSSCs and the effects of the redox couple concentration, I^-/I_3^- ratios, photointensity, and additives (4-*t*-butylpyridine and LiI) on performances of the DSSCs were explored. Furthermore, a wide variety of ionic liquids containing the redox couple were adopted as the DSSCs electrolytes to know the structural effect on the performances. It was revealed that EMImDCA [12] containing suitable amounts of the redox couple and the additives was preferable to the DSSCs electrolytes in terms of the photo-energy conversion efficiency (5.5%).

2. Experimental

2.1. Materials

2.1.1. Photoelectrodes

TiO$_2$ nano-particles used were Solaronix T. P25 (Japan Aerosil) was also used when noted. *Cis*-di(thiocyanato)-*N*, *N*-bis(2,2′-bipyridil-4,4′-dicarboxylic acid)ruthenium(II) complex (N3 dye) was purchased from Kojima Chemical Reagents Inc. and Solaronix. Fluorine-doped SnO$_2$-layered (FTO) glass plates ($10\,\Omega\,cm^{-2}$) were purchased from Central glass and Asahi glass. The TiO$_2$ nano-particles were coated over the FTO plates and sintered at $450\,°C$ for 0.5 h to obtain nano-porous TiO$_2$ electrodes. The TiO$_2$ electrodes were immersed in an acetonitrile: *t*-butanol (1:1) mixed solution of N3 dye ($3 \times 10^{-4}\,M$) for 8 h and dried in air to obtain photoelectrodes.

2.1.2. Ionic liquids

Ethyl bromide (Wako Pure Chemical), butyl bromide (Wako), lithium bis(trifluoromethane sulfonyl)imide (LiTFSI, Morita Chemical), sodium dicyanamide (NaN(CN)$_2$, Wako), sodium tetrafluoroborate (NaBF$_4$, Junsei Chemical), sodium hexafluorophosphate (NaPF$_6$, Kanto Chemical), 1-methylimidazole (Wako) and pyridine (Wako) were used as received.

The ionic liquids used in this study are EMImTFSI, EMImBF$_4$, BMImPF$_6$, EMImDCA, and BPTFSI. Quart-

ernized bromide salts of 1-methylimidazole and pyridine with ethyl bromide or butyl bromide were synthesized and recrystallized, followed by ion exchange reactions, according to methods described in the literature [13,17,18]. After the ion exchange reactions, the ionic liquids were purified by either of the following two methods. For the hydrophobic and water-immiscible ionic liquids (EMImTFSI, BPTFSI and BMImPF$_6$) they were repeatedly washed with water in order to extract ionic impurities (LiBr, NaBr) after the ion exchange. The hydrophilic and water-miscible ionic liquids (EMImBF$_4$ and EMImDCA) were extracted by dichloromethane and were passed through silica gel columns to exclude the ionic impurities. A small amount of the obtained ionic liquids were dropped in a silver nitrate aqueous solution in order to confirm removal of the halide salts, except for EMImDCA (DCA anion makes a silver complex to be precipitated out). All the ionic liquids were colorless and transparent and were dehydrated under high vacuum. The ionic liquids were characterized by ^{1}H NMR, ^{13}C NMR, fast atom bombardment mass spectra and differential scanning calorimetry (DSC). These were stored in an argon atmosphere glove box (VAC, [O$_2$] < 1 ppm, [H$_2$O] < 1 ppm).

EMImI and I$_2$ (Wako) were used as a redox couple and were dissolved in the ionic liquids at different concentrations in the glove box. It was assumed that I$^-$ and I$_2$ immediately formed I$_3^-$ in the ionic liquids.

2.2. Fabrication of photo-electrochemical cells

The dye-immobilized photoanodes and Pt sputtered (thickness of Pt: 100 nm) FTO glasses are physically sandwiched together using cell holders, into which electrolyte solutions were infiltrated to fabricate photo-electrochemical cells.

2.3. Photocurrent measurements

Photo-electrochemical measurements were performed using an AM 1.5 solar simulator (YSS-150, EIKO Instruments) furnished with a xenon lamp (1 kW, UXL-10S, Ushio), and the photointensity was $100\,mW\,cm^{-2}$. The measurements were made on open cells (sealless cells), and the electrode size was $0.45\,cm^2$, unless otherwise noted. The light intensity was tuned using a ND filter (metallic grids). The measurements were carried out three times and the mean was used as the results.

2.4. Standard organic electrolyte cells

We used a standard organic electrolyte cell in order to compare the DSSC results with those using the ionic liquid electrolytes. 1,2-Dimethyl-3-propylimidazolium iodide (DMPImI, 0.3 M), LiI (0.1 M), I$_2$ (0.05 M) and 4-*t*-butylpyridine (*t*-BPy, 0.5 M) were dissolved in methoxyacetonitrile to obtain an organic electrolyte solution for the standard cell. Performance of DSSCs ($0.45\,cm^2$) using

the standard organic electrolyte with N3 dye under the photointensity of AM 1.5 (100 mW cm^{-2}) was as follows: short-circuit current (J_{sc}) 14.5 mA cm^{-2}; open-circuit voltage (V_{oc}) 745 mV; fill factor (FF) 0.62; conversion efficiency (η) 6.7%.

3. Results and discussions

3.1. I^-/I_3^- redox couple concentration and their ratios in EMImTFSI

As reported earlier [16], fast charge transport of an I^-/I_3^- redox couple in EMImTFSI was revealed to be caused by the contribution of the exchange reaction between I^- and I_3^-, and the contribution to the total charge transport process dominates when concentration of the redox couple is high, and [I^-] and [I_2] are close together. In this study, the ionic liquid electrolytes with varying [I^-]/[I_2] ratios were employed in DSSCs. The electrolyte used was EMImTFSI in which EMImI and I_2 were dissolved. The molar ratios of [I^-]:[I_2] were varied from 2:1 to 10:1 and a series of samples were prepared maintaining the total concentration of I^- and I_3^- in the range of 0.01–2 M for each molar ratio.

The dependence of short-circuit photocurrent density (J_{sc}) on [I^-] + [I_3^-] with different [I^-]:[I_2] ratios is shown in Fig. 1. The J_{sc} increases and tends to level off with an increase in the concentration. When the molar ratio ([I^-]:[I_2]) is 2:1, the J_{sc} significantly decreases at the concentration higher than 1.0 M, while for the other compositions a slight decrease was observed at 2.0 M. The exchange-reaction-based fast charge transport process between I^- and I_3^-, observed for the electrolytes with comparable [I^-] and [I_2] [16], resulted in a second order increase in the redox current with the redox couple concentration. However, the non-linear increase is not seen in
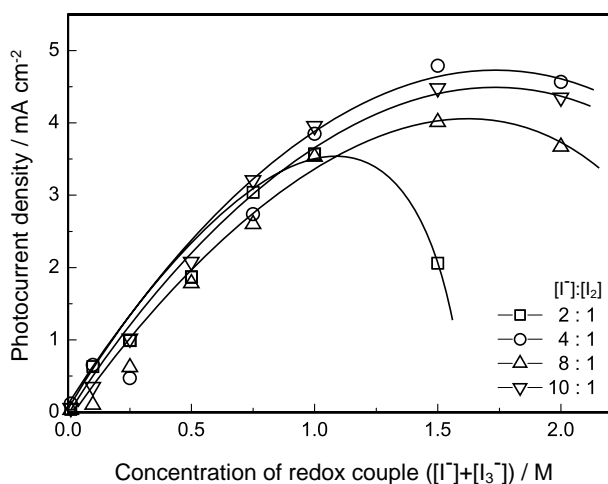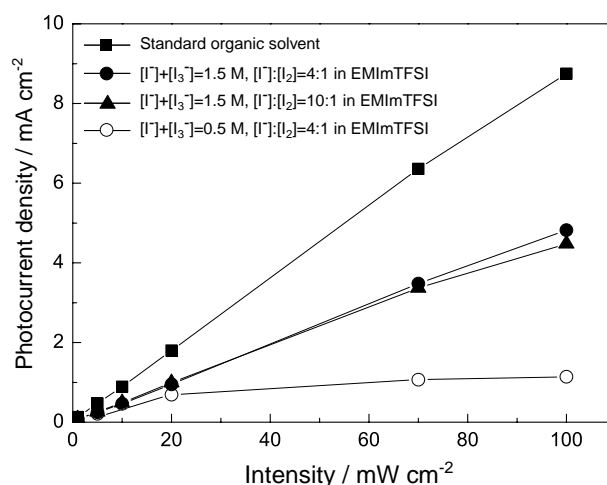
Fig. 2. Dependence of short-circuit photocurrent on photointensity (TiO$_2$: P25; cell area: 1.0 cm^{-2}).

the J_{sc} of the DSSCs (Fig. 1). This may be attributed to the absorption of visible light by I_3^-, which competes with the absorption by the dye, and to the back electron transfer from conduction band of a photoanode to I_3^-, when the concentration of I_3^- becomes high.

Ionic liquids have high viscosities compared with those of common organic solvents. Especially, HMImI, an ionic liquid having iodide counter anion, is highly viscous (η=1800 mPa s), nevertheless, it has been used as a DSSCs electrolyte [6]. The viscosities at 25 °C of the electrolytes used in this study; the ionic liquids in which the I^-/I_3^- redox couple was dissolved, were about 10^2 mPa s, which is lower than that of HMImI but much higher than those of common organic solvents. The dependence of short-circuit photocurrent on photointensity is shown in Fig. 2. The photointensity was changed from 1 to 100 mW cm^{-2}. The photocurrent for the DSSCs with the electrolytes containing a high concentration of the redox couple ([I^-] + [I_3^-]=1.5 M) is proportional to the photointensity up to 100 mW cm^{-2}. These results are similar to those of a DSSCs with the standard organic electrolyte. It is interesting to note that the photocurrent of DSSCs with the ionic liquid electrolytes is ca. a half of that with the standard electrolyte solution, although the viscosity of the former is more than 10 times larger than that of the latter. Fast charge transport in the electrolytes is accomplished even under the strong photointensity, when concentrations of the redox couple are high. In contrast, when concentration of the redox couple ([I^-] + [I_3^-]) is 0.5 M, the photocurrent saturates at 20 mW cm^{-2}. The flux of transporting electron to a photoanode and to a counter cathode under a photo-steady-state is proportional to the redox couple concentration and their diffusivity that is generally in proportion to the inverse of the electrolyte viscosities. Furthermore, in the ionic liquid with high I^-/I_3^- redox couple concentrations, the exchange-reaction-based diffusion dominates over

Fig. 1. Short-circuit photocurrent as a function of concentration of iodide/tri-iodide redox couple in EMImTFSI (TiO$_2$: P25; cell area: 1.0 cm^{-2}; light intensity: 100 mW cm^{-2}).

the whole charge transport processes. Thus, a high concentration of the redox couple as an electron carrier is necessary in the DSSCs with electrolytes having high viscosities such as the ionic liquid electrolytes used in this study. The high redox couple concentration keeps the electron flux toward the electrodes high, especially under strong photointensity.

3.2. Effects of additives (4-t-butylpyridine and lithium iodide) in EMImTFSI

Photo-voltaic performances of the ionic liquid cells using EMImTFSI were lower than those using the standard organic electrolyte. Especially, the V_{oc} was ca. 540 mV, which was lower than that of the standard electrolyte cell by 200 mV. It is known that the addition of t-BPy in organic solvents increases the V_{oc} [19]. This is explained to date by inhibition of the back electron transfer from conduction band of TiO_2 to the dye-cation and/or I_3^-, and by rise of the Fermi energy level, due to absorption of t-BPy onto the TiO_2 surface. The V_{oc} changes upon the addition of t-BPy with varying concentrations in the ionic liquid electrolyte are summarized in Fig. 3 (top), where 1.5 M EMImI and 0.15 M I_2 in EMImTFSI are used as the electrolytes. The point of commencement of dark current, shown in Fig. 3 (bottom), shifts to a higher voltage with increasing t-BPy concentration. In order to know the mechanisms, the additional effect of t-BPy on the equilibrium potentials of the I^-/I_3^- redox couple was electrochemically studied, however, the potential change could not be observed. The shift of V_{oc} with the addition of t-BPy may, thus, be attributed to inhibition of the back electron transfer and rise of the Fermi energy level, as is explained in the organic electrolyte cells.

The addition of t-BPy in the ionic liquid causes a considerable increase in the V_{oc}, whereas the photocurrents decrease with increasing its concentration (Fig. 3) and the photo-energy conversion efficiency is finally lowered at
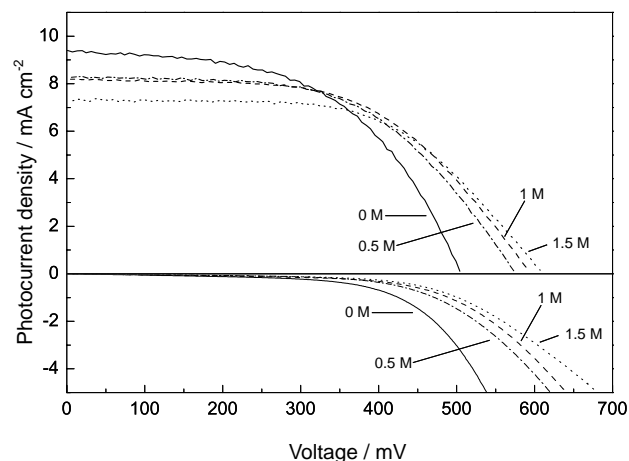
Fig. 3. Photocurrent density as a function of cell voltage (top), and dark-current density as a function of cell voltage (bottom), for DSSCs with electrolytes containing different amounts of t-BPy in EMImTFSI.

1.5 M. As a result, an appropriate amount of the addition is considered to be 0.5–1.0 M in this system.

It is reported that the adsorption of Li^+ onto the TiO_2 surface enhances diffusion coefficient of electron in TiO_2, leading to enhancement of the photogeneration of electrons [20,21]. We, thereby, examined cell performances with the ionic liquid electrolytes upon the addition of LiI and t-BPy. Concentration of t-BPy was fixed at 0.5 M. Fig. 4 shows the dependence of J_{sc} and V_{oc} on the addition of LiI. The J_{sc} and V_{oc} increase with the addition of LiI. However, the J_{sc} saturates with the further increase in concentration of LiI, and the V_{oc} and FF change to a smaller extent. Therefore, the concentration of LiI should be kept between 0.1 and 0.2 M, in terms of the cell performances. The V_{oc}, however, cannot be increased to the value, as observed for the standard electrolyte cell, even with the addition of t-BPy and LiI. It is of our great interest to know how V_{oc} changes depending on structure of ionic liquids used in DSSCs, as discussed in Section 3.3.
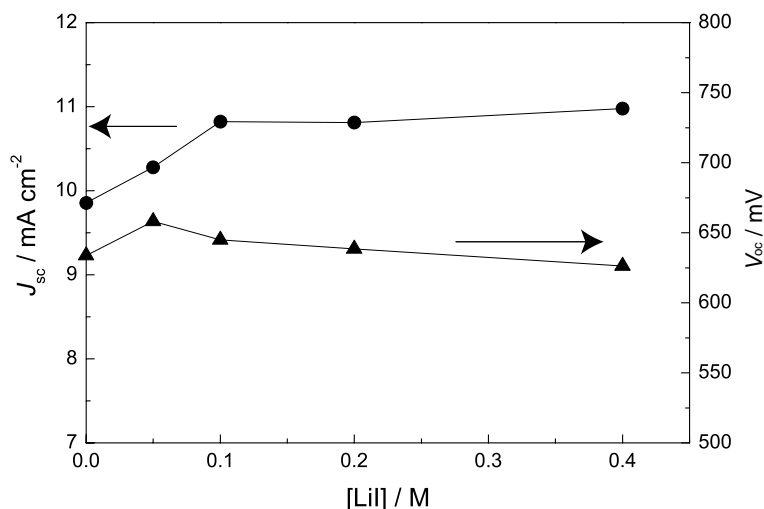
Fig. 4. Short-circuit photocurrents (J_{sc}) and open-circuit voltages (V_{oc}) as a function of concentration of LiI.

Table 1
Physical properties of ionic liquids at 20 °C

Ionic liquids		T_m (°C)	Viscosity (mPa s)	σ ($\times 10^{-3}$ S cm^{-1})
EMImTFSI	Hydrophobic	−15 [13]	39 [13]	7.7 [13]
EMImBF$_4$	Hydrophilic	11 [13]	43 [13]	12.4 [13]
BMImPF$_6$	Hydrophobic	−61 (T_g) [22]	352 [22]	1.1 [22]
BPTFSI[a]	Hydrophobic	25 [13]	72 [13]	1.8 [13]
EMImDCA	Hydrophilic	−21 [17]	21 [17]	17.6

[a] Calculated values at 20 °C.

3.3. Structural effects of ionic liquids

The DSSCs characteristics using EMImTFSI as the electrolyte has been described. We have chosen a wide variety of ionic liquids to know the structural effect of ionic liquids on the DSSC performances. Properties of the ionic liquids are shown in Table 1. EMImTFSI, BMImPF$_6$, and BPTFSA are hydrophobic and immiscible with water, while EMImBF$_4$ and EMImDCA are hydrophilic and miscible with water. The magnitude of viscosity follows the order: BMImPF$_6$ > BPTFSI > EMImBF$_4$, EMImTFSA > EMImDCA. The ionic conductivity (σ) is the highest for EMImDCA and the lowest for BMImPF$_6$. Fig. 5 shows I–V curves of the DSSCs using these ionic liquids ([I$^-$]:[I$_2$]=10:1, [I$^-$] + [I$_3{}^-$] = 1.0 M). Even at the same redox concentration and the same [I$^-$]:[I$_2$] ratio, the DSSC performances considerably differ depending on the structures of the ionic liquids. The J_{sc} for the cells with EMImBF$_4$ and EMImTFSI are relatively high, and the J_{sc} of BMImPF$_6$ is the lowest, possibly due to the high viscosity and low conductivity. Except for EMImDCA, the J_{sc} changes depending on the magnitude of conductivity of the ionic liquids, and the higher the conductivity, the higher the J_{sc}. However, the J_{sc} does not quantitatively depend on either of the conductivities and the viscosities. The most interesting finding in Fig. 5 seems to be the high V_{oc} of a cell using EMImDCA. The V_{oc} of the cell with EMImDCA
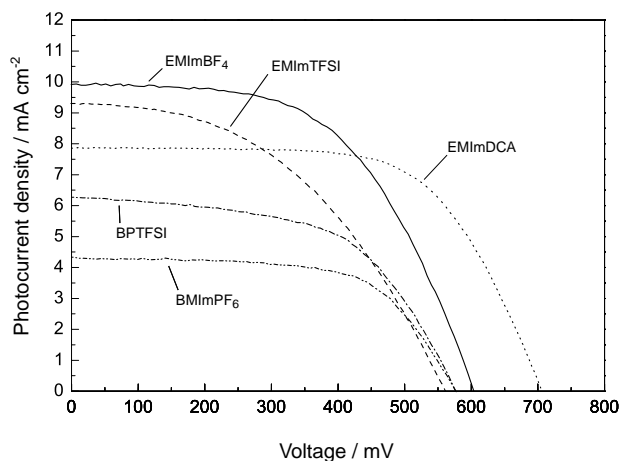

Fig. 5. Photocurrent density vs. voltage curves obtained for DSSCs with different ionic liquids. Each electrolyte contains iodide/tri-iodide redox couple ([I$^-$]:[I$_2$] = 10:1, and [I$^-$] + [I$_3{}^-$] = 1 M) in each ionic liquids.

Table 2
Photo-electrochemical properties of DSSCs using ionic liquids as electrolytes

Ionic liquids	J_{sc} (mA cm^{-2})	V_{oc} (mV)	FF	η (%)
EMImTFSI	9.4	550	0.45	2.4
EMImBF$_4$	9.9	602	0.55	3.3
BMImPF$_6$	4.3	576	0.62	1.6
BPTFSI	6.3	577	0.56	2.0
EMImDCA	7.8	703	0.66	3.8

The experimental conditions: [I$^-$]:[I$_2$] = 10:1; [I$^-$] + [I$_3{}^-$] = 1 M; AM 1.5 (100 mW cm^{-2}) illumination; cell active area = 0.45 cm^2.

is more than 100 mV higher than those of the other ionic liquid cells. The V_{oc} indicates the potential gap between Fermi energy level of TiO$_2$ and equilibrium potential of the iodide/tri-iodide redox couple. EMImDCA may affect either or both of the potential(s), for which we are now conducting more detailed study. Table 2 summarizes the results of solar
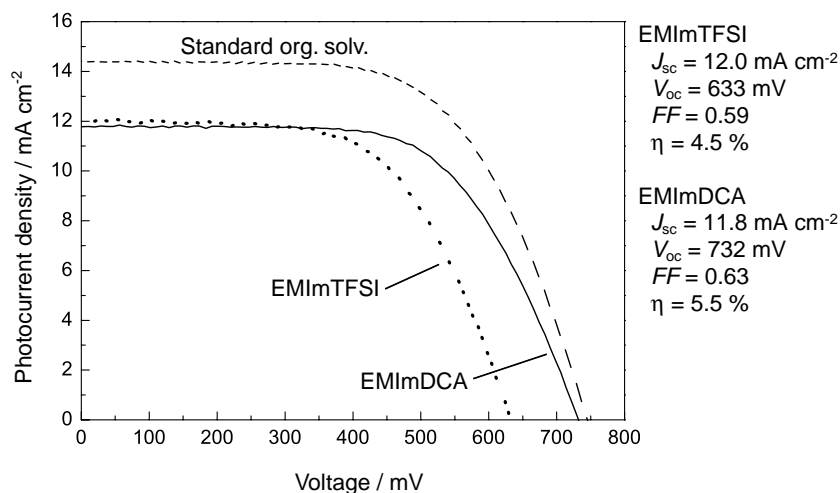

EMImTFSI
J_{sc} = 12.0 mA cm^{-2}
V_{oc} = 633 mV
FF = 0.59
η = 4.5 %

EMImDCA
J_{sc} = 11.8 mA cm^{-2}
V_{oc} = 732 mV
FF = 0.63
η = 5.5 %

Fig. 6. Photocurrent density vs. voltage curves of DSSCs with standard organic solvent, EMImDCA ([I$^-$]:[I$_2$] = 10:1, [I$^-$] + [I$_3{}^-$] = 2 M, t-BPy = 1 M and LiI = 0.5 M); EMImTFSI ([I$^-$]:[I$_2$] = 10:1, [I$^-$] + [I$_3{}^-$] = 1.5 M, t-BPy = 1 M and LiI = 0.1 M) under AM 1.5 (100 mW cm^{-2}) illumination.

cell performances. The cell with EMImDCA has a high fill factor as well as a high V_{oc}, as compared to the cells with the other ionic liquids. As a result, the photo-voltaic cell with EMImDCA exhibits the highest photo-energy conversion efficiency, η of 3.8% among the studied cells.

The performances of DSSCs with EMImTFSI and EMImDCA have been optimized by the addition of *t*-BPy and LiI. The results are shown in Fig. 6, together with the standard cell characteristics. Although, the DSSC performances with the ionic liquids are lower than those with the standard organic electrolyte, the photo-energy conversion efficiency of the cell with EMImDCA reaches 5.5%. As far as we know, this conversion efficiency is relatively high among the DSSCs using ionic liquids as their electrolytes. If we take the advantages of ionic liquids, such as non-volatility, non-flammability, and thermal and chemical stability, into consideration, the results obtained in this study is quite promising for the development of durable DSSCs using ionic liquids as their electrolytes.

4. Conclusions

Performances of DSSCs with ionic liquids as their electrolytes have been explored in detail. In spite of their high viscosities, the DSSCs with ionic liquid electrolytes exhibit relatively high performances. Especially, the J_{sc} reaches higher than 80% of the J_{sc} of the cell with the standard electrolyte solution, although, the viscosity of the ionic liquid electrolytes is more than 10 times higher than that of the standard electrolyte. The main reason for this phenomenon seems to be caused by the contribution of the exchange-reaction-based diffusion process between I^- and I_3^- dissolved in the ionic liquids as a redox couple. For this contribution, concentrations of the redox couple should be much higher than those in common organic electrolyte solutions. When the concentration is high, the photocurrents linearly increase up to $100\,mW\,cm^{-2}$. The V_{oc} of ionic liquid cells can be altered by changing structures of the ionic liquids. EMImDCA is quite effective in terms of enhancement of the V_{oc}. The addition of *t*-BPy and LiI in the ionic liquids can also improve the DSSCs performances, as seen in conventional organic solvent electrolytes. The photo-energy conversion efficiency of DSSCs with EMImDCA can be optimized up to 5.5%. Ionic liquids, having the ideal properties as DSSCs electrolytes, such as non-volatility, non-flammability, and thermal and chemical stability, will be able to be tuned to different structures suitable for the use in DSSCs.

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