



Balance between the physical diffusion and the exchange reaction on binary ionic liquid electrolyte for dye-sensitized solar cells

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ABSTRACT

A comprehensive characterizations of viscosities, conductivities, triiodide diffusion coefficients, charge-transfer resistances and photovoltaic performance of a potential dye-sensitized solar cell (DSC) electrolyte systems based on binary ionic liquid (IL) mixtures, namely, 1-ethyl-3-methylimidazolium dicyanamide (EMIDCA)/1-methyl-3-propylimidazolium iodide (PMII) with a fixed iodine concentration at varying EMIDCA volume fraction are investigated in the present study. Viscosity and conductivity values are accurately correlated with regard to temperature and EMIDCA volume fraction. The triiodide diffusion coefficients, the predominant electrolyte parameter for limitation of DSC efficiency, are determined by symmetrical cell methods. The physical diffusion and exchange reactions between the iodide and triiodide dominate the apparent triiodide diffusion coefficients at different range of EMIDCA volume fraction. A balance between the viscosity-dependent physical diffusion and the exchange reactions can get at an optimal volume percents of EMIDCA. Impedance spectroscopy and photovoltaic results both support the existence of an optimized binary IL electrolyte composition. Hence, for optimizing an IL-based electrolyte in regards to triiodide transport, a low viscosity is not the exclusive crucial factor since exchange reactions transport effects also play an important role to resolve the diffusion limitation of DSC efficiency.

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1. Introduction

Dye-sensitized solar cells (DSCs) are currently attracting worldwide scientific and technological interest because of their high energy conversion efficiency [1–3] and simple fabrication process. They have been widely regarded as a promising alternative to conventional silicon-based photovoltaic devices for sustainable energy supply at low cost and high environmental friendliness. In these devices, photo-to-electricity conversion is achieved by the ultrafast electron injection from a photo-excited dye into the conduction band of TiO₂ and subsequently dye regeneration and hole transportation to the counter electrode. By using a highly volatile electrolyte, an efficiency record of ~11% has been achieved among all types of organic photovoltaic cells [4–8].

However, use of the volatile organic solvents causes deterioration of DSCs by evaporation of the solvent, and thus seriously limits large-scale implementation of the technology due to poor long-term stability and the necessity of a com-

plex sealing process [9,10]. Therefore, it is pertinent to employ nonvolatile solvent-free ionic liquids (ILs) or all-solid-state hole-transporting materials (HTMs) in DSCs. ILs are used as promising alternatives for volatile organic solvents due to their unique properties, such as negligible vapor pressure, excellent electrochemical and thermal stability, and high ionic conductivity [11–15].

On the other hand, the high viscosity of 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 [16,17]. Photocurrents in such systems are commonly affected by the series resistances of the electrolytes, which are usually in proportion to the viscosity.

To mitigate the diffusion limitations, electrolytes based on binary ionic liquids with a high mole fraction of PMII (1-methyl-3-propylimidazolium iodide) together with other low-viscous ionic liquids [14,18–21] were reported as attractive solutions of the dilemma between viscosity and photocurrent. A high concentration of the redox couple is usually needed to achieve a domination of the exchange reaction-based fast charge transport process between iodide and triiodide in viscous electrolytes [11,22]. On the other hand, the absorption of visible light by triiodide competes with the

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absorption of the dye and high concentration of triiodide promotes the back electron transfer from conduction band of photoanodes to triiodide anions [22].

It was generally proposed that the triiodide transport in ionic liquid electrolyte was created by a combination of an ordinary physical diffusion process and a Grotthuss-type charge-exchange mechanism [9,11,23–25]. Diffusion-controlled currents reflect the contribution from physical diffusion of triiodide and iodide and electron exchange between them, as described for the coupling of physical diffusion mass transport and electron exchange by the Dahms–Ruff equation [11,26–28].

$$D_{\text{app}} = D_{\text{phys}} + D_{\text{ex}} = D_{\text{phys}} + \frac{k_{\text{ex}}\delta^2 c}{6} \quad (1)$$

where D_{app} , D_{phys} and D_{ex} are apparent diffusion coefficient, physical diffusion coefficient and electron exchange diffusion coefficient, respectively, k_{ex} is the rate constant of electron exchange, c and δ are the concentration and average center-to-center distances between redox species, respectively.

However, the low-viscous imidazolium based ionic liquid with anions, such as thiocyanate, dicyanoamide, tricyanomethide, tetracyanoborate, triflate, etc. [14,18–21] are nonelectroactive. Note that mixing iodide melts with such nonelectroactive ionic liquids to lower the electrolyte viscosity may not only increase the physical diffusion coefficient (D_{phys}) but also decrease the electron exchange diffusion coefficient (D_{ex}). Actually, a high diffusion flux of iodide is desirable for the fast dye regeneration, which can avoid the charge recombination between oxidized sensitizers and injected electrons in TiO_2 films.

In order to distinguish the above-mentioned triiodide transport mechanism, the viscosities, conductivities, triiodide diffusion coefficients, and photovoltaic performance of a potential DSC electrolyte systems based on binary IL mixtures, namely, 1-ethyl-3-methylimidazolium dicyanamide [EMIDCA]/1-methyl-3-propylimidazolium iodide [PMII] with a fixed iodine concentration at varying EMIDCA volume fraction were investigated in details in the present study.

2. Experimental

2.1. Materials

All chemicals and solvents used were of puriss quality. *N*-Methylbenzimidazole (NMBI) and guanidinium thiocyanate (GNCS) were purchased from Aldrich. PMII and EMIDCA were purchased from Merck AG (Germany). TiO_2 pastes and N719 dye ($[(\text{C}_4\text{H}_9)_4\text{N}]_2[\text{Ru}(\text{II})\text{L}_2(\text{NCS})_2]$, where $L=2,2'$ -bipyridyl-4,4'-dicarboxylic acid, ruthenium TBA535), were purchased from Solaronix (Switzerland). Conducting glass plates (FTO glass, fluorine doped tin oxide over-layer, sheet resistance $15 \Omega \text{ cm}^{-2}$, purchased from Nippon Sheet Glass Co., Japan) were used as substrates for screen printing TiO_2 porous films.

2.2. Thermogravimetric analysis

Thermogravimetric (TG) analysis was carried out with a TGA 2050 analyzer (TA Instruments, USA) at a heating rate of $10^\circ\text{C min}^{-1}$ in a flow of nitrogen.

2.3. Viscosity measurements

Viscosity measurements were conducted using a modular compact rheometer from Anton Paar (Physica MCR 300, Graz, Austria). Temperature control (better than 0.02 K) was maintained by a TC 20 temperature control unit. The viscosities given were averaged over the values obtained at shear rates ranging

from 10 to 500 s^{-1} . The estimated uncertainties are in the range of 3%–5%.

2.4. Conductivity measurements

A conductivity meter (S30K, Mettler-Toledo Instruments, Switzerland) was used to measure conductivities over a board temperature range from 293 to 343 K.

2.5. Diffusion measurements

The diffusion coefficient of I_3^- was measured by the method described in the previous literature [29]. Symmetrical cells, sandwiched with two identical sputtered Pt electrodes fabricated on F:SnO₂ conducting glass substrates, were used for the measurement. The cell gap was controlled to be 25 μm . Electrolytes were filled in the cell and sealed. Cyclic voltammetry measurements were performed on a computer-controlled CHI650C electrochemical analyzer (CH Instrument Corp., USA). The voltage was swept from -0.6 to $+0.6 \text{ V}$. When the voltage increased from 0 to 0.6 V, the current went up and reached a constant value corresponding to the limiting current. The apparent diffusion coefficient was calculated by using the following formula [9,29]

$$D_{\text{app}} = \frac{I_{\text{lim}} d}{2nFC} \quad (2)$$

where D_{app} is apparent diffusion constant, I_{lim} is limiting currents, d is cell gap, n is the number of electrons involved in the electrochemical reduction of triiodide at the electrode (2), F is Faraday constant, and C is initial concentration of triiodide anions.

Charge-transfer resistances were monitored by the method described in previous literature [30–33]. Charge-transfer resistances between Pt electrodes and ionic liquid electrolytes were estimated by using a Cole–Cole plot. Impedance spectra were recorded over frequency ranges from 0.01 to 100 kHz by using a CHI650C electrochemical analyzer (CH Instrument Corp., USA) with amplitude of the alternative signal being 10 mV.

2.6. Fabrication of photovoltaic devices

TiO_2 electrodes were obtained by spreading TiO_2 paste on F:SnO₂ conducting glass electrode using screen printing technique. The film was then annealed at 500°C for 30 min. The sintered TiO_2 film was treated with 40 mM TiCl_4 solution, then rinsed with water and ethanol and sintered again at 500°C for 30 min. The thickness of the TiO_2 film, characterized by a step profiler (XP-1, MTS, USA), was about 11 μm . The active area of the DSC was 0.16 cm^2 . The resulting TiO_2 film was then sensitized by immersing it in a 0.5 mM anhydrous ethanolic solution of N719 dye at room temperature for 16 h. To minimize the hydration of TiO_2 from moisture in the ambient air, the films were immersed in the dye solution while they were at a temperature of around 100 – 120°C after the annealing step. Afterward, the dye-sensitized TiO_2 electrode was rinsed with anhydrous ethanol and dried in moisture free air. Platinized counter electrode was prepared by sputtering with 20 s to get a satisfied catalytic activity, and sealed with the TiO_2 electrodes by a 25 μm thick Surlyn hot-melt ring (Dyesol Ltd.). The internal space was filled with electrolyte through a filling hole pre-made by a bench drill on the counter electrode glass substrate. Finally, the electrolyte introduction hole was sealed with a Surlyn sheet under a thin glass cover by heating to produce the device.

As shown in Table 1, all the electrolytes used in this study contained 0.2 M I_2 , 0.5 M NMBI, 0.1 M GNCS in combined binary IL mixtures, namely, EMIDCA/PMII with various EMIDCA volume fraction from 0 to 80%.

Table 1
Composition of various electrolytes used in the study.

Electrolyte	Composition
E1	0.2 M I ₂ , 0.5 M NMBI, 0.1 M GNCS in EMIDCA (0 vol%)/PMII
E2	0.2 M I ₂ , 0.5 M NMBI, 0.1 M GNCS in EMIDCA (20 vol%)/PMII
E3	0.2 M I ₂ , 0.5 M NMBI, 0.1 M GNCS in EMIDCA (40 vol%)/PMII
E4	0.2 M I ₂ , 0.5 M NMBI, 0.1 M GNCS in EMIDCA (60 vol%)/PMII
E5	0.2 M I ₂ , 0.5 M NMBI, 0.1 M GNCS in EMIDCA (80 vol%)/PMII

2.7. Photovoltaic measurements

The photocurrent–photovoltage (J – V) characteristics of DSCs were obtained under an illumination of AM 1.5 (100 mW cm⁻²), realized by a solar simulator (91192, Oriel, USA, calibrated with standard crystalline silicon solar cell). J – V curves were measured by applying an external bias voltage to the cell and measuring the generated photocurrent with a digital source meter (Keithley 2400, Keithley Instruments, USA).

3. Results and discussions

3.1. Water trace measurements

It has been reported that moisture may detach dye molecules from the TiO₂ surface into the electrolyte solution, based on the observation that water enhances the trapping of the charge carriers at the defects in the nanocrystalline TiO₂ film [34,35]. Regarding the long-term stability, it has been mentioned that water should be reduced to some extent within a DSC device. Considering the hydrophilic nature of the employed ionic liquids (PMII and EMIDCA), water trace was first characterized by thermogravimetric (TG) analysis with a heating rate of 10 °C min⁻¹ in a flow of nitrogen.

The TG and its corresponding derivate curves of ionic liquid PMII, EMIDCA and a mixture of EMIDCA (40 vol%)/PMII are shown in Fig. 1. Obvious weight loss step were not found in the temperature range from 300 to 470 K in either of the TG curves, suggesting the trace of physisorbed water molecules in ionic liquid was rare (less than 0.5%). Smooth lines in the derivate TG curves at the same temperature range were in good accordance with the above-mentioned conclusion. Therefore, influences of the water trace within the ionic liquid electrolytes were not considered as a dominating factor in the present research.

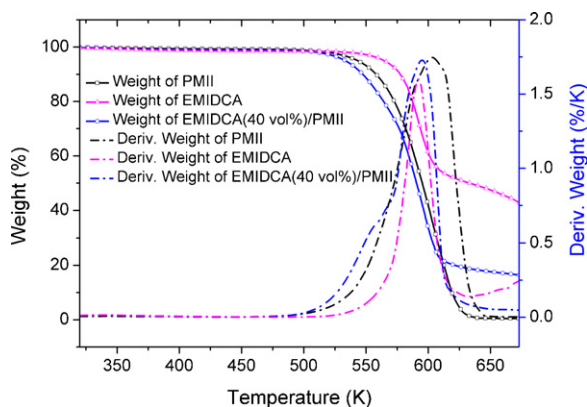


Fig. 1. Thermogravimetric curves of ionic liquid PMII, EMIDCA and a mixture of EMIDCA (40 vol%)/PMII.

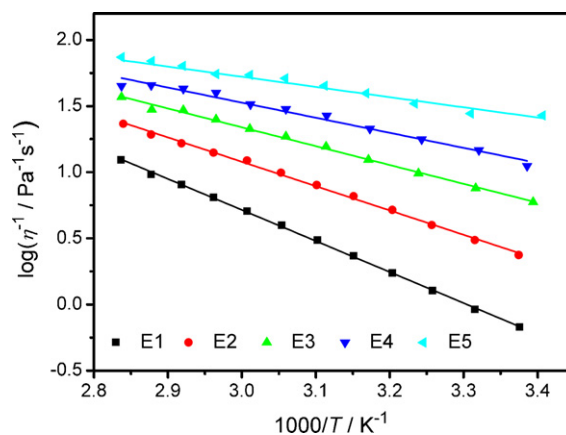


Fig. 2. Arrhenius plots of viscosity versus temperature with various EMIDCA/PMII binary IL electrolytes (E1, E2, E3, E4, E5: EMIDCA 0%, 20%, 40%, 60%, 80%, respectively).

3.2. Viscosity and conductivity measurements

A simultaneous determination of viscosities and conductivities is essential for a complete understanding of the fluidity dependence on the triiodide diffusion coefficient. Viscosities were determined in the temperature range from 293 to 353 K. The measured viscosities of the blends EMIDCA/PMII system with various EMIDCA volume fractions are shown in Fig. 2. As is apparent from Fig. 2, binary ionic liquid (EMIDCA/PMII) blends showed much decreased viscosity compared with the blank PMII solvent. At 293 K, the viscosity of EMIDCA is 33.7 cP, which is 30 times lower than 1090 cP for blank PMII. The viscous behavior of ionic liquids can be understood by the interplay of Columbic and van der Waals interactions as well as hydrogen bond formation [36]. The viscosity of the binary ILs decreased with increasing the EMIDCA volume fraction. The temperature dependence of the recorded viscosities was analyzed by fitting the measurement data according to the Arrhenius equation,

$$\eta_0(T) = A \exp \left[\frac{-E_a}{RT} \right] \quad (3)$$

where η_0 is viscosity, E_a is activation energy, A is pre-exponential factor and R is the gas constant, and T is the absolute measurement temperature.

Similar to the viscosity of the blends EMIDCA/PMII system, the influence of the EMIDCA volume fraction on the ionic conductivity was examined as well as its temperature dependence. Here, conductivities were measured in the temperature range from 293 to 343 K. The determined conductivities at each PMII volume fraction and the temperature dependence are indicated in Fig. 3. At 293 K, the conductivity of EMIDCA is 25.4 mS cm⁻¹, exceeding that of PMII (1.14 mS cm⁻¹) by a factor of more than 20. The temperature dependence can also be well fitted by the Arrhenius equation. The enhanced conductivity of the binary ILs is expected to benefit the charge transport in the electrolyte.

3.3. Diffusion and EIS measurements

It was generally confirmed that the role of iodide in the electrolyte of DSCs is to regenerate dye cation after photo-injection by electron donation according to the reaction: $3I^- + 2Dye^+ \rightarrow 2Dye + I_3^-$, triiodide is then reduced back to iodide ($I_3^- + 2e^- \rightarrow 3I^-$) at the counter electrode. Therefore, physical diffusion of iodide and especially triiodide in the electrolyte is an important process that can influence the performance of DSCs. Generally, a successful redox shuttle must reduce the dye cation before the dye cation recombines with an electron in the photoanode,

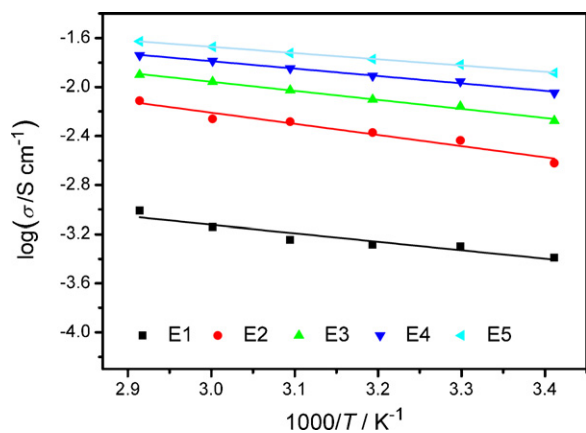


Fig. 3. Arrhenius plots of conductivity versus temperature with various EMIDCA/PMII binary IL electrolytes (E1, E2, E3, E4, E5: EMIDCA 0%, 20%, 40%, 60%, 80%, respectively).

without allowing the oxidized form of the shuttle to intercept an electron from the photoanode. The dual criteria of fast dye regeneration and slow interception place a very challenging constraint on identifying effective redox shuttles.

To determine the charge transport in the electrolyte, symmetrical cells, sandwiched with two identical sputtered Pt electrodes fabricated on F:SnO₂ conducting glass substrates, were used for the measurement. As shown in Eq. (2), charge transport (physical diffusion together with the exchange reactions) between two electrodes in a symmetric cell could be well described with a limiting current density (I_{lim}). Dependence of the I_{lim} and D_{app} values on the EMIDCA volume fraction is presented in Fig. 4. Within the range of EMIDCA volume fraction increased from 0 to 40%, I_{lim} increases from 3.75 to 11.29 mA cm⁻², D_{app} increases from 1.21 to 3.66×10^{-7} cm² s⁻¹ at meanwhile. The observed linear increase of D_{app} is primary due to a decrease in the viscosity of the binary IL electrolyte and enhanced conductivity, which were mentioned above. This indicates that the viscosity-dependent physical diffusion dominates over the exchange reactions when the EMIDCA volume fraction is less than 40%. However, when further increased the EMIDCA fraction to 80%, I_{lim} decreases to 7.99 mA cm⁻², D_{app} decreases to 2.59×10^{-7} cm² s⁻¹ at the same time. This change suggests that when the EMIDCA volume fraction is higher than 40%, the exchange reactions become the determinant factor over the physical diffusion. Therefore, it can be concluded from the observed change of the apparent diffusion coefficient that the binary ILs electrolyte with 40 vol% of EMIDCA can get a balance between the viscosity-dependent physical diffusion and the exchange reactions.

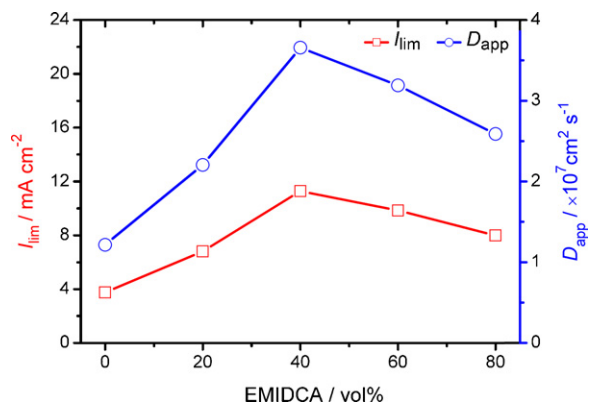


Fig. 4. Dependence of the limiting current density and the apparent diffusion coefficient on the EMIDCA volume fraction in the binary IL electrolyte.

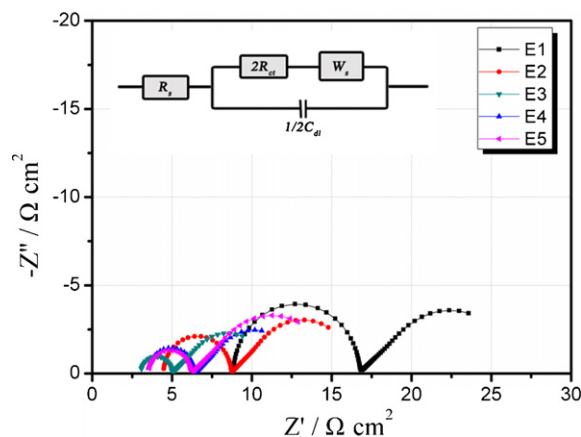


Fig. 5. Nyquist plots of symmetrical cells with various EMIDCA/PMII binary IL electrolytes. The Randles circuit is shown in the inset, including a component R_s = series resistance, R_{ct} = charge-transfer resistance, C_{dl} = double layer capacitance, and W_s = Warburg impedance. The cells were measured without applied voltage (0V).

It is generally concluded that the reduction of I_3^- at the counter electrode is a key process in DSC. Thus the charge-transfer resistance at the Pt-electrode/electrolyte interface is an important parameter for the efficiency of DSC [29,37–39]. Impedance spectroscopy at symmetrical cells was used to benchmark the quality of these electrolytes with regard to the kinetic of I^- regeneration at the platinum counter electrode of the DSC. The ZView software was used to fit the experimental data of DSCs with various EMIDCA volume fractions.

Fig. 5 shows the Nyquist plots obtained from symmetrical cells with various electrolyte compositions. By fitting of the experimental data, useful parameters to understand the underlying mechanisms for electron transport with different EMIDCA fraction were obtained, which was indicated in Table 2. It can be found notably that, the serial resistance (R_s) and the charge-transfer resistance at the counter electrode/electrolyte interface (R_{ct}), as well as the second semicircle, representing the Warburg diffusion resistance in the electrolyte, were greatly affected by the electrolyte compositions. Among all the electrolytes, E1, the blank PMII IL electrolyte, showed the highest resistance, which was mainly attributed to its highest viscosity. Blends of binary IL electrolyte showed somewhat reduced resistance as a result of the much decreased viscosities. Of particular note, electrolyte E3 (with 40 vol% EMIDCA) showed the lowest resistance, which was in good accordance with the above-mentioned apparent diffusion coefficient result.

3.4. J–V curves with variation of PMII volume fractions

The photovoltaic performance of devices with various PMII volume fractions, keeping all other additives constant, has been checked. Devices (A to E) were fabricated using electrolytes with different EMIDCA volume fractions (E1 to E5). Fig. 6 presents

Table 2

Fitted parameters (R_s , R_{ct} and R_e) of symmetrical cells with various EMIDCA/PMII binary IL electrolytes.

	EMIDCA (vol%)	R_s (Ω cm ²)	R_{ct} (Ω cm ²)	R_e (Ω cm ²)
E1	0	8.86	7.85	9.84
E2	20	4.47	4.21	7.75
E3	40	3.05	1.93	6.02
E4	60	3.51	2.88	6.45
E5	80	3.54	2.63	8.79

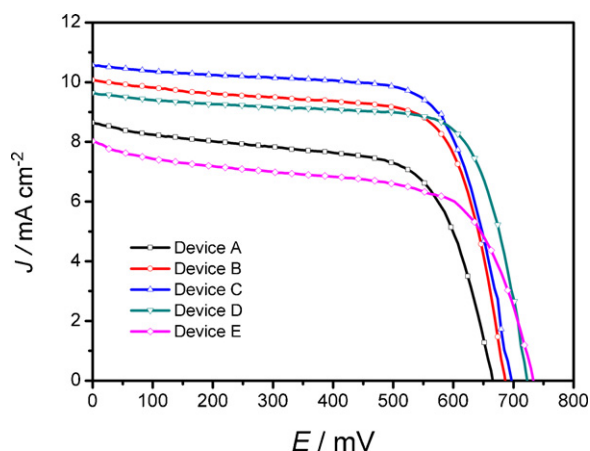


Fig. 6. J - V characteristics of devices A–E with various EMIDCA/PMII binary IL electrolytes measured under AM 1.5 illumination (100 mW cm^{-2}).

Table 3

Photovoltaic parameters (V_{oc} , J_{sc} , ff and η) of devices A–E with various EMIDCA/PMII binary IL electrolytes.

	Electrolyte	V_{oc} (mV)	J_{sc} (mA cm^{-2})	ff	$\eta/\%$
Device A	E1	666	8.64	0.68	3.89
Device B	E2	686	10.07	0.70	4.86
Device C	E3	697	10.57	0.71	5.20
Device D	E4	723	9.64	0.73	5.05
Device E	E5	734	8.02	0.70	4.13

the J - V curves of DSCs with binary IL electrolyte containing different fraction of EMIDCA under illumination of 100 mW cm^{-2} . Detail of the photovoltaic performance parameters (photocurrent density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (ff), and overall conversion efficiency (η)) are shown in Table 3. It was observed that V_{oc} and ff increased when the volume fraction of EMIDCA increased from 0 to 80%. The increased V_{oc} was mainly due to the decreased recombination between the injected electrons with triiodide in the binary IL electrolyte, which was brought by the lower iodide concentrations. On the other hand, the slightly increased fill factor was primarily attributed to the decreased resistance, which was associated with the lower viscosities of the binary IL electrolytes. Note that the change in J_{sc} was consistent with the variation of the limiting current density and the apparent diffusion coefficient. With an optimum EMIDCA volume fraction (40 vol%), photovoltaic parameters (J_{sc} , V_{oc} , and ff) of device C are 10.57 mA cm^{-2} , 697 mV and 0.71, respectively, yielding a maximum overall photo-to-energy conversion efficiency (η) of 5.20%, which is almost 30% higher than that of a blank PMII solvent based device A.

4. Conclusions

In summary, a potential DSC electrolyte systems based on binary IL mixtures, namely, EMIDCA/PMII with a fixed iodine concentration at varying EMIDCA volume fraction were investigated in terms of the viscosities, conductivities, triiodide diffusion coefficients, charge-transfer resistances and photovoltaic performance. Viscosities and conductivities of the binary IL electrolyte were accurately correlated with regard to temperature and EMIDCA volume fraction. The temperature dependence of the recorded viscosities and conductivities were well fitted to the Arrhenius equation. The physical diffusion and exchange reactions dominated the apparent triiodide diffusion coefficients at different EMIDCA volume fraction range. A balance between the viscosity-dependent physical diffusion and the exchange reactions can get

at a fixed EMIDCA volume percents (40 vol%). Device with the optimized binary IL electrolyte showed a J_{sc} of 10.57 mA cm^{-2} , a V_{oc} of 697 mV and a ff of 0.71, respectively, yielding a maximum overall photo-to-energy conversion efficiency (η) of 5.20%, which is almost 30% higher than that of device with blank PMII solvent. Hence, for optimizing an IL-based electrolyte in regards to the triiodide transport, a low electrolyte viscosity is not the exclusive crucial factor since exchange reactions transport effects also play an important role to resolve the diffusion limitation of DSC efficiency.

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