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# Characterisation of DSSC-electrolytes based on 1-ethyl-3-methylimidazolium dicyanamide: Measurement of triiodide diffusion coefficient, viscosity, and photovoltaic performance

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## Abstract

A comprehensive characterisation of an ionic liquid based electrolyte for dye-sensitised solar cells (DSSC) was performed by determination of triiodide diffusion coefficients, viscosities and photovoltaic performances. The electrolyte, consisting of 1-ethyl-3-methylimidazolium dicyanamide, 1-methyl-3-propylimidazolium iodide (MPII), and iodine, was examined at varying ionic liquid molar ratio and fixed iodine concentration, as well as at fixed ionic liquid molar ratio and varying iodine concentration. All measurements were conducted at controlled temperature over a broad temperature range to analyse the electrolyte properties in view of thermal stress of the DSSC during later practical application. The triiodide diffusion coefficient increases with decreasing MPII concentration or increasing temperature, caused by decreasing electrolyte viscosity. Additionally, strong non-Stokesian behaviour over the whole ionic liquid mixing range was found, decreasing at higher temperatures. Photovoltaic measurements showed that the DSSC efficiency is limited by triiodide diffusion at low temperatures and low iodine concentrations whereas at high temperatures it is limited by recombination processes, leading to a maximum for DSSC efficiency at a certain temperature. The exchange between diffusion limitation of DSSC efficiency and limitation by recombination and therefore the maximum for DSSC efficiency is shifted to lower temperatures by increasing iodine concentration.

*Keywords:* Ionic liquid electrolyte; Dye-sensitised solar cell; Diffusion coefficients; Photovoltaic performance

## 1. Introduction

The dye-sensitised solar cell (DSSC) has been proposed as a low-cost and high-efficiency alternative to conventional photovoltaic cells by O'Regan and Grätzel [1] in 1991. In DSSCs, electrons of a dye adsorbed on the surface of nanocrystalline $TiO_2$ are photo-excited by incident light and injected into the conducting band of $TiO_2$. The oxidized dye is regenerated by the reduced species of a redox-couple, typically $I^-/I_3^-$ that is dissolved in the electrolyte. The resulting $I_3^-$ diffuses to the Pt-counter electrode where it is reduced. At present, efficiencies of more than 10% can be obtained for DSSCs using electrolytes based on volatile organic solvents [2]. The usage of these volatile organic electrolytes seriously limits a large scale implementation of this technology due to the poor long-term stability of the cells and the necessity of a complex sealing process [3,4]. Therefore, ionic liquids (ILs) are used as possible alternatives for volatile organic solvents due to their unique properties, such as

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negligible vapour pressure, excellent electrochemical and thermal stability, and high ionic conductivity [5–7]. On the other hand, physical transport processes are slower in ILs as in conventional electrolytes due to the comparative high viscosity of ILs. Nevertheless ILs currently seem to be the most promising solvents for DSSCs [8].

The efficiency of a DSSC is limited by the following four major processes in the solar cell: light harvesting, recombination of the dye-cation or reduction of $I_3^-$ with previously injected electrons at the $TiO_2$ electrode, diffusion of $I_3^-$ to the counter electrode and its reduction at the counter electrode. Except for light harvesting, all limiting processes are influenced by the choice of the electrolyte and can be suppressed or enhanced by optimisation of the electrolyte. In addition, these processes and their influence on the DSSC efficiency vary also with temperature. Usually investigations on DSSC-electrolyte properties and on DSSC performance are conducted only at 25 °C or even without controlling temperature. With respect to the later practical application of the DSSC and the expected thermal stress, a determination of electrolyte properties and DSSC performance over a typical temperature range seems to be appropriate [9,10].

Therefore, two of the above mentioned electrolyte related major processes for the efficiency of DSSCs, diffusion and recombination, were examined over broad temperature ranges in a potential DSSC-electrolyte system based on ILs. These IL-based electrolytes for DSSCs are normally made up of iodine, of an IL that is in addition the iodide source, such as an 1,3-dialkylimidazolium iodide, and, to lower the viscosity of the resulting electrolyte, of a second but low viscous 1,3-dialkylimidazolium salt. 1-Methyl-3-propylimidazolium iodide (MPII) was chosen as iodide source and 1-ethyl-3-methylimidazolium dicyanamide (EMIDCA) as "solvent IL", due to its high electrochemical stability [11], low viscosity, and broad liquid range [12] as well as its relatively low price. The diffusion of $I_3^-$ was investigated with two different measurement methods, steady-state cyclic voltammetry at microelectrodes (UMEs) and polarisation measurements at thin layer cells (TLCs), and with regard to two parameters, a variation of iodine concentration at constant mixing ratio of ILs and a variation of IL mixing ratio at constant iodine concentration, respectively. All diffusion measurements were conducted in the temperature range of 25–60 °C in addition to measurements of electrolyte viscosities. To clarify the influence on limitation of the efficiency of the DSSC by diffusion and recombination, PV-measurements were also conducted in a broad temperature range of 5–55 °C in mixtures of EMIDCA and MPII with varying iodine concentration at constant mixing ratio of ILs.

## 2. Experimental

### 2.1. Materials

Iodine was purchased from Riedel-de Haën (purity of ≥99.8%). The ILs MPII and EMIDCA, were synthesized according to Wachter et al. [13] NMR data ($^1H$, $^{13}C$) of all ILs described in this paper do not show any impurities. After synthesis the ILs were dried at high vacuum ($10^{-3}$ Pa). The resulting water contents were controlled by Karl–Fischer titration using a 756 KF Coulometer from Metrohm (Filderstadt, Germany), yielding 124 ppm water for MPII and 98 ppm for EMIDCA.

### 2.2. Viscosity measurements

Viscosity measurements were conducted under Argon atmosphere using a MCR 100 rheometer from Paar (Graz, Austria). Temperature control was maintained by a Peltier element (accuracy of ±0.02 °C). The viscosities given were averaged over the values obtained at shear rates from 10 to 1000 $s^{-1}$. The estimated errors are in the range of 3–5%.

### 2.3. Determination of triiodide diffusion coefficients

Triiodide diffusion coefficients were determined by polarisation measurements at TLCs [14,15] and steady-state cyclic voltammetry at microelectrodes [13,16–18]. A three electrode setup consisting of a Pt-wire as pseudo reference electrode, a second Pt-wire as counter electrode and a Pt-disk microelectrode with a radius of 5 μm as working electrode was used for steady-state cyclic voltammetry measurements. The TLCs used for polarisation measurements are described elsewhere [14,18,19]. The theoretical background for both measurement methods, their realisation for determination of triiodide diffusion coefficients in ionic liquids and the equipment used for this purpose were described in Refs. [13,18,19]. All measurements were conducted under inert-gas atmosphere at five different temperatures in a thermostat (RKS 20 or RK 8 KP thermostat from LAUDA, Königshofen, Germany), which was regulated to a minimum accuracy of ±0.05 °C.

To calculate diffusion coefficients, densities and hence molar concentrations of triiodide in all examined electrolyte mixtures were determined with the precision-densitometer DMA 60/DMA 602 from Paar (Graz, Austria) at five different temperatures controlled with a RK 8 KP thermostat from LAUDA (accuracy of ±0.02 °C).

### 2.4. DSSC

A fluorine-doped $SnO_2$ on glass (TCO glass) with a sheet resistance of 8 Ω was used as a substrate. The standard $TiO_2$ paste has been prepared by mixing 10 g of $TiO_2$ powder (P25, Degussa) in 12 mL of ethanol (98%, Riedel-de Haen) solution of 4-hydroxybenzoic acid (1 wt.%, Merck) together with 1 g of 5 wt.% ethyl cellulose (Fluka) in terpineol (Fluka). Furthermore, 10 g terpineol was added and mixed in a mortar grinder (RM 200, Retsch) for 1 h [20]. The paste was applied on the substrate using the "*doctor blading*" technique and afterwards sintered in open air at 450 °C for 1 h. The thickness of the resulting layer was about 13.5 μm, determined by surface profilometry (Taylor-Hobson Ltd.). The layers have been sensitised by immersing in an ethanol solution of the Ruthenium dye (Ru(2,2′bipyridyl-4,4′dicarboxylate)$_2$ (NCS)$_2$, Solaronix) for 12 h. For the counter electrode, platinum was sputtered onto a TCO glass substrate. Both electrodes were sealed with a 25 μm thick sealing foil (Surlyn, DuPont) and the cell was filled with an electrolyte through two holes, pre-drilled into the counter electrode. The electrolytes were binary IL mixtures of EMIDCA and MPII in a molar ratio of 60/40, while the concentration of $I_2$ (Fluka) varied between 0.004 and 0.260 mol $L^{-1}$. For each electrolyte three identical DSSCs with an active area of 0.7 $cm^2$ were assembled. Before characterisation, the cells were stored in the dark at open circuit conditions for 24 h to allow the electrolyte to penetrate the $TiO_2$ pores. Tungsten-halogen lamps were used as a light source as they mimic the black body spectrum with a colour temperature of 3200 K. We calculated the short circuit current mismatch parameter according to the IEC 60904-3 standard (Standard IEC 60904-3, *Measurements Principles for Terrestrial PV Solar Devices with Reference Irradiance Data,* International Electrotechnical Commission, Geneva, Switzerland) and in conjunction with a calibrated c-Si reference solar cell we determined the level of standard irradiance (AM1.5, 100 mW $cm^{-2}$). During irradiance and characterisation the cells were covered with a black mask fitting the active area of the cell. Applying a non-active area masking to the DSSC during characterisation is one of the most rigorous techniques and consequently the efficiencies are lower. If the mask size was smaller than the active cell area, the light could partly be reflected into the covered active area of the DSCC, if the mask size was larger than the active area of the cell, multiple reflections could enhance light intensity entering the cell. In both cases the measured efficiency is overestimated. More details of masking effect on conversion efficiency in a DSSC can be found in Ref. [21].

To set the cell temperature to standard test conditions (25 °C), the temperature was stabilized with a cooling/heating Peltier setup designed specifically for solar cell characterisation. Current–voltage characteristics (*I*/*V*) were measured using a Keithley 238 source meter by applying a voltage and measuring the current. The *I*/*V* measurements were scanned from 0 V (short circuit condition) to 0.8 V (beyond open circuit voltage) in 10 mV steps.

Temperature dependent measurements were taken in steps of 5 °C from 5 to 55 °C. Before characterisation, each masked cell was placed and pressed with a contact tip to the copper plate to assure a good electrical and thermal contact. Subsequently, the cell was covered by a Styrodur®-box to insulate it from the heat produced by the lamps. The cell temperature was measured using two NTC resistors: one placed into the upper copper plate and the other directly on the cell. As soon as both temperatures were the same and the temperature inside the box was stabilized, the box was removed to perform the *I*/*V* characterisation of the DSSC under irradiance.

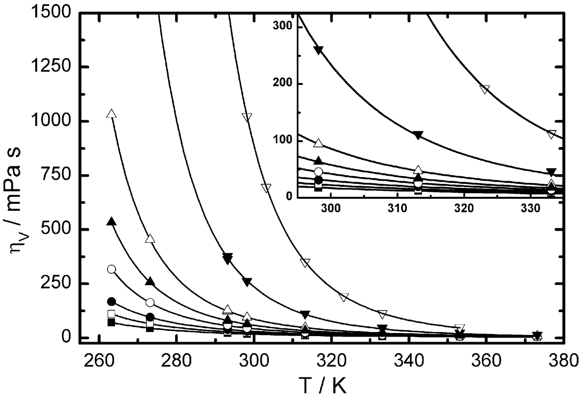

Fig. 1. Viscosities of mixtures consisting of 0.05 mol $L^{-1}$ $I_2$ in EMIDCA/MPII at varying molar mixing ratios of EMIDCA/MPII: (■) 91/9 mol%, (□) 80/20 mol%, (●) 70/30 mol%, (○) 60/40 mol%, (▲) 50/50 mol%, (△) 40/60 mol%, (▼) 20/80 mol%, (▽) 0/100 mol%. The solid lines are results of fitting the measurement data according to the VFT-equation.

## 3. Results and discussion

### 3.1. Viscosity and diffusion measurements

A simultaneous determination of viscosities and diffusion coefficients is essential for a complete understanding of the influence of MPII or iodine concentration on the $I_3^-$ diffusion coefficient. Additionally, viscosity data yield a first clue for a possible later application of an electrolyte mixture in electrochemical devices over wide temperature ranges. Therefore, viscosities of all electrochemical examined blends were determined over a broad temperature range, from −10 °C up to 80 °C or 100 °C in steps of 20 °C. The temperature dependence of the recorded viscosities was analysed by fitting the measurement data according the Vogel–Fulcher–Tamann (VFT) equation (Eq. (1))

$$\eta_V(T) = \eta_{V,0} \exp\left\{\frac{B}{T - T_0}\right\} \tag{1}$$

where $\eta_{V,0}$, $B$ and $T_0$ are fitting parameters, and $T$ is the measurement temperature.

The recorded viscosities of the blends of the system EMIDCA/MPII with 0.05 mol $L^{-1}$ $I_2$ and varying MPII concentration and resulting VFT plots are shown in Fig. 1. The fitting parameters for this system are summarised in Table 1. The enlargement in Fig. 1 shows the viscosities and VFT plots for the temperature region from 25 to 60 °C, the range where $I_3^-$ diffusion coefficients were measured. In general, the viscosities of the blends increase with rising MPII concentration at constant temperature. Reducing the MPII content from 100 to 80 mol% results in a viscosity-decrease of about 75%, a further reduction of the MPII content down to 40 mol% yields an overall viscosity-decrease of about 95%. The differences of viscosities for particular blends increase for lower temperatures.

Table 1
VFT equation parameters of viscosity data of mixtures consisting of 0.05 mol $L^{-1}$ $I_2$ in EMIDCA/MPII at varying molar mixing ratios of EMIDCA/MPII

| Mol% MPII | $\eta_{V,0}$ (mPa s) | $B$ (K) | $T_0$ (K) |
|---|---|---|---|
| 9 | 0.1878 ± 0.0324 | 698.94 ± 46 | 145.58 ± 4.49 |
| 20 | 0.1912 ± 0.0293 | 703.83 ± 38 | 152.61 ± 3.43 |
| 30 | 0.1299 ± 0.0333 | 837.25 ± 67 | 146.24 ± 5.25 |
| 40 | 0.1247 ± 0.0249 | 836.88 ± 47 | 156.42 ± 3.29 |
| 50 | 0.0825 ± 0.0225 | 957.25 ± 64 | 154.05 ± 3.98 |
| 60 | 0.0623 ± 0.0143 | 1045.68 ± 53 | 155.50 ± 2.92 |
| 80 | 0.0124 ± 0.0039 | 1536.85 ± 77 | 143.99 ± 3.12 |
| 100 | 0.0222 ± 0.0067 | 1463.50 ± 82 | 161.87 ± 3.87 |

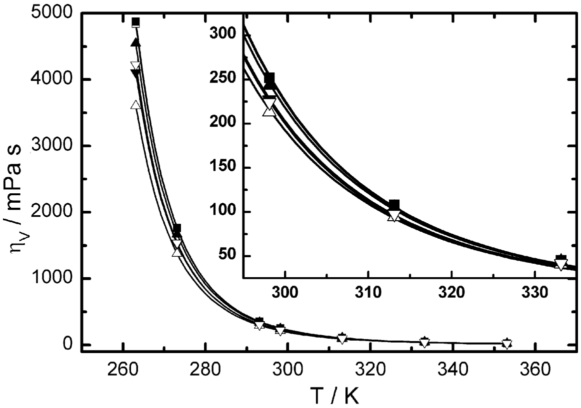

Fig. 2. Viscosities of blends of $I_2$ in a mixture of EMIDCA/MPII = 20/80 at $I_2$ concentrations of: (■) 0.05 mol L$^{-1}$, (□) 0.10 mol L$^{-1}$, (▲) 0.20 mol L$^{-1}$, (△) 0.30 mol L$^{-1}$, (▼) 0.40 mol L$^{-1}$, (▽) 0.49 mol L$^{-1}$. The solid lines are results of fitting the measurement data according to the VFT-equation.

To investigate a possible influence of the iodine concentration on the $I_3^-$ diffusion coefficient, viscosities of six blends with fixed EMIDCA/MPII ratio of 20/80 mol% and varying iodine concentrations, ranging from 0.05 to 0.49 mol L$^{-1}$, were determined. The recorded viscosities of these blends and their VFT plots are shown in Fig. 2, the enlargement shows again both functions for the temperature region from 25 to 60 °C, the temperature range of $I_3^-$ diffusion coefficient determination. The resulting fitting parameters for these blends are summarised in Table 2. In general, the viscosities of these mixtures show a small decrease with increasing iodine concentration over the whole investigated temperature range. Therefore, the viscosities of the investigated electrolyte mixtures are not only clearly MPII concentration and temperature dependent, but also slightly dependent on the iodine concentration.

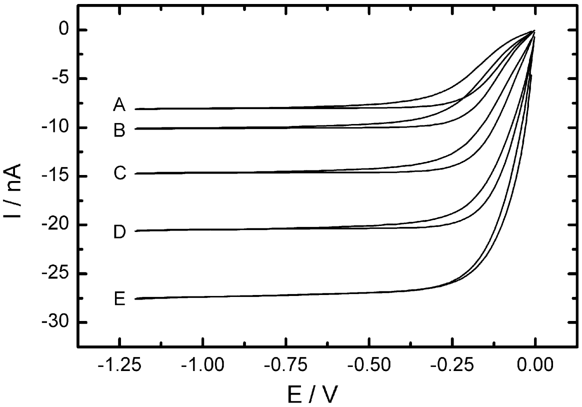

Fig. 3. Steady-state cyclic voltammograms recorded at a 5 μm Pt-disk microelectrode, using a Pt wire as pseudo-reference electrode and a scan rate of 5 m/s$^{-1}$, of 0.05 mol L$^{-1}$ iodine in EMIDCA/MPII with 50 mol% MPII at different temperatures; $\theta$: (A) 25 °C, (B) 30 °C, (C) 40 °C, (D) 50 °C, and (E) 60 °C.

Typical steady-state cyclic voltammograms which were recorded at microelectrodes at five different temperatures are shown in Fig. 3 for a mixture with 0.05 mol L$^{-1}$ $I_2$ and a molar ratio of EMIDCA/MPII of 50/50. The $I_3^-$ diffusion coefficients were obtained by evaluation of these steady-state cyclic voltammograms according to Eq. (2) [22–24]

$$I_l = 4nFDcr \tag{2}$$

where $I_l$ is the limiting current, $n$ is the number of electrons transferred per molecule, $F$ is the Faraday constant, $D$ is the diffusion coefficient, $c$ is the bulk concentration of the electroactive species and $r$ is the radius of the disk microelectrode. Since $F$, $n$, $c$ and $r$ are known, it is possible to calculate $D$ from the limiting current $I_l$ measured under steady-state conditions.

Table 2
VFT equation parameters of viscosity data of blends of $I_2$ in a mixture of EMIDCA/MPII = 20/80 at varying $I_2$ concentrations

| $c(I_2)$ (mol L$^{-1}$) | $\eta_{V,0}$ (mPa s) | $B$ (K) | $T_0$ (K) |
|---|---|---|---|
| 0.05 | 0.0168 ± 0.0039 | 1430.14 ± 54 | 149.43 ± 2.26 |
| 0.10 | 0.0167 ± 0.0038 | 1438.15 ± 54 | 148.82 ± 2.26 |
| 0.20 | 0.0177 ± 0.0041 | 1423.61 ± 54 | 148.88 ± 2.28 |
| 0.30 | 0.0186 ± 0.0047 | 1416.01 ± 61 | 146.86 ± 2.65 |
| 0.40 | 0.0190 ± 0.0049 | 1395.03 ± 61 | 149.59 ± 2.58 |
| 0.49 | 0.0190 ± 0.0057 | 1378.51 ± 70 | 151.19 ± 2.95 |

Fig. 4 shows typical polarisation studies with a TLC for six blends with fixed EMIDCA/MPII ratio of 20/80 mol% and varying iodine concentrations, ranging from 0.05 to 0.49 mol L$^{-1}$, to exemplify the characteristics of the measurement. The small hysteresis of the plot in Fig. 4 demonstrates the achievement of the steady-state condition [14], which is essential for the determination of a limiting current density and therefore a diffusion coefficient, too. The polarisation measurements were evaluated according to Eq. (3) [25]

$$D = \frac{j_l l}{2nFc^0} \tag{3}$$

where $j_l$ is the limiting current density, $l$ is the electrode distance and $c^0$ is the molar initial concentration of the investigated species.

The $I_3^-$ diffusion coefficients of the six blends with fixed EMIDCA/MPII ratio of 20/80 mol% and varying iodine concentrations which were determined with microelectrodes are

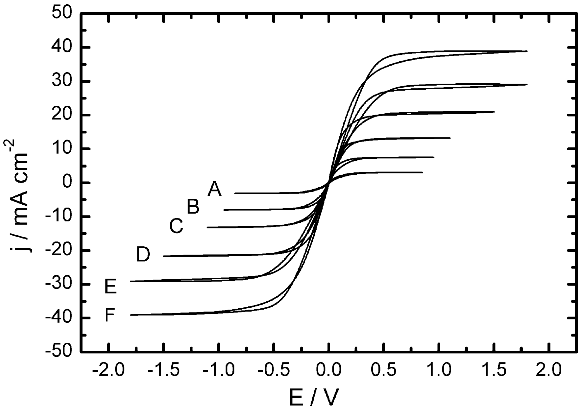

Fig. 4. Polarisation measurements recorded at a TLC, in mixtures of EMIDCA/MPII with 80 mol% MPII and varying iodine concentrations, at 25 °C and with a scan rate of 5 mV s$^{-1}$; (A) $c(I_3^-)$ = 0.05 mol L$^{-1}$, (B) $c(I_3^-)$ = 0.10 mol L$^{-1}$, (C) $c(I_3^-)$ = 0.20 mol L$^{-1}$, (D) $c(I_3^-)$ = 0.30 mol L$^{-1}$, (E) $c(I_3^-)$ = 0.40 mol L$^{-1}$, and (F) $c(I_3^-)$ = 0.49 mol L$^{-1}$.

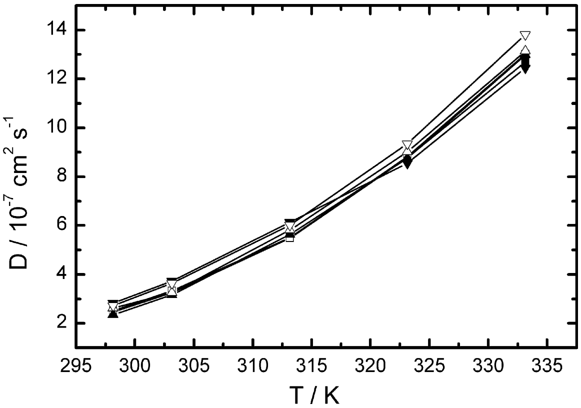

Fig. 5. Comparison of triiodide diffusion coefficients determined with UMEs of blends of $\mathrm{I_2}$ in a mixture of EMIDCA/MPII = 20/80 at $\mathrm{I_2}$ concentrations of: (■) 0.05 mol L$^{-1}$, (□) 0.10 mol L$^{-1}$, (▲) 0.20 mol L$^{-1}$, (△) 0.30 mol L$^{-1}$, (▼) 0.40 mol L$^{-1}$, (▽) 0.49 mol L$^{-1}$.

shown in Fig. 5. In general, diffusion coefficients are reciprocally related to viscosities (Stokes–Einstein rule). Therefore, the $\mathrm{I_3}^-$ diffusion coefficients show a strong increase with increasing temperature and simultaneously decreasing viscosity. The difference between the diffusion coefficients of particular blends at constant temperatures correlates strongly with the difference in the viscosity of these blends at the same temperatures. Therefore, the slight enhancement in diffusion is not directly related to the increasing iodine concentration, but again to the viscosity, which itself is dependent on the iodine concentration.

The $\mathrm{I_3}^-$ diffusion coefficients of the six blends with fixed EMIDCA/MPII ratio of 20/80 mol% and varying iodine concentrations which were determined at TLCs (Fig. 6) show a complete different behaviour compared to the diffusion coefficients determined at microelectrodes. The increase of the diffusion coefficients flattens with increasing iodine concentration at higher temperatures, only the blend with 0.05 mol L$^{-1}$ iodine shows the expected behaviour and yields a diffusion coefficient at 60 °C which is comparable to that determined at microelectrodes. Additionally, this is the only blend where the increase in diffusion is in the same magnitude, with increasing temperature, as the decrease in viscosity. The reason for this unexpected behaviour may be the corrosion of Pt by triiodide. Such corrosion reaction was suggested by Kay and Grätzel [26] and verified by Olsen et al. [27]. The oxidation of Pt to $\mathrm{PtI_4}$ and $\mathrm{PtI_6}$ in solutions containing iodine was observed for Pt, plated on TCO-glass, whereas massive Pt-electrodes showed no corrosion. This matches with the results of impedance measurements [19] where the received nyquist-plots are distorted for elevated temperatures and triiodide concentrations, which may be also a result of the discussed side reaction.

Thus, at high temperatures an exclusive determination of diffusion coefficients with TLCs is not suitable for blends with high iodine concentrations in low viscous ionic liquids. Complementary viscosity measurements or steady-state measurements at microelectrodes should be conducted, to get more reliable measurement data by calculation or comparison.

The blends of the system EMIDCA/MPII with varying MPII concentration were examined at an iodine concentration of 0.05 mol L$^{-1}$, since the $\mathrm{I_3}^-$ diffusion coefficient is not iodine concentration dependent and to get reliable results for measurements at TLCs over the whole mixing and temperature range. Fig. 7 shows the diffusion coefficients versus the MPII concentration from polarisation measurements at TLCs and Fig. 8 from steady-state cyclic voltammetric measurements at microelectrodes. For both measurement methods the determined values tend downwards for increasing MPII concentration due to the simultaneously rising viscosity. The diffusion coefficients determined with microelectrodes are typically about 10% lower than the ones determined at TLCs. Steady-state measurements at microelectrodes are normally more precise than measurements at TLCs, due to the comparatively exact determination of the microelectrode radius and its continuous control with SEM [18]. However, for mixtures with high EMIDCA concentrations the measurements at microelectrodes show larger relative standard deviations than the measurements at TLCs because of some kind of passivation of the microelectrode surface.

The relative difference between diffusion coefficients of blends with low MPII concentration and high MPII concen-

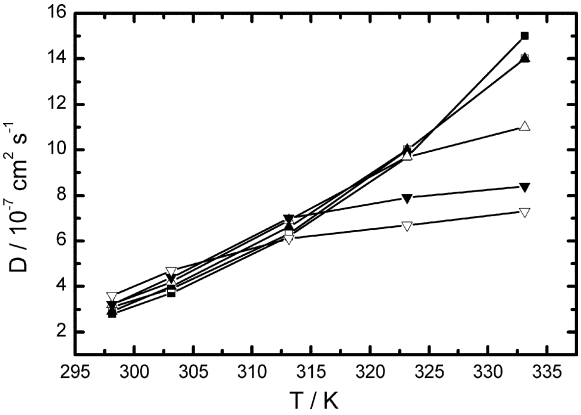

Fig. 6. Comparison of triiodide diffusion coefficients determined with TLCs of blends of $\mathrm{I_2}$ in a mixture of EMIDCA/MPII = 20/80 at $\mathrm{I_2}$ concentrations of: (■) 0.05 mol L$^{-1}$, (□) 0.10 mol L$^{-1}$, (▲) 0.20 mol L$^{-1}$, (△) 0.30 mol L$^{-1}$, (▼) 0.40 mol L$^{-1}$, and (▽) 0.49 mol L$^{-1}$.

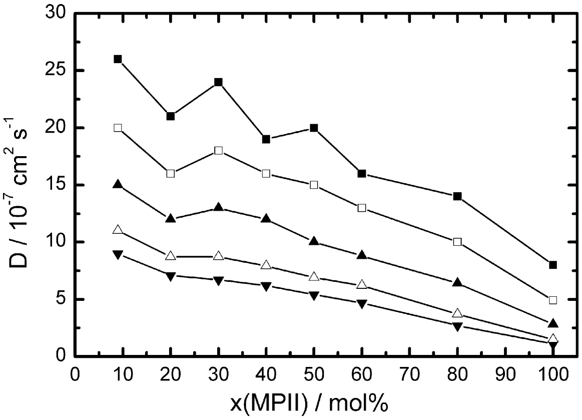

Fig. 7. Comparison of triiodide diffusion coefficients determined with TLCs of 0.05 mol L$^{-1}$ $\mathrm{I_2}$ in blends of EMIDCA/MPII as a function of molar fractions of EMIDCA/MPII at different temperatures; $\theta$: (▼) 25 °C, (△) 30 °C, (▲) 40 °C, (□) 50 °C, and (■) 60 °C.

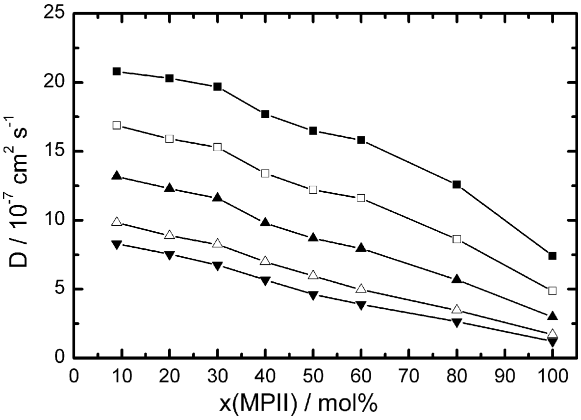

Fig. 8. Comparison of triiodide diffusion coefficients determined at UMEs of 0.05 mol L$^{-1}$ $I_2$ in blends of EMIDCA/MPII as a function of molar fractions of EMIDCA/MPII at different temperatures; $\theta$: (▼) 25 °C, (△) 30 °C, (▲) 40 °C, (□) 50 °C, and (■) 60 °C.

tration becomes smaller for increasing temperature, e.g. the diffusion coefficient at 25 °C of the blend with 11 mol% MPII, is eight times larger than the one of the blend with 100 mol% MPII, but at 60 °C it is just three times larger.

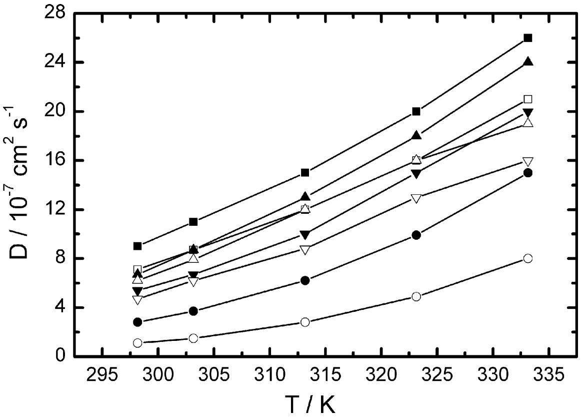

Fig. 9. Comparison of triiodide diffusion coefficients determined with TLCs of 0.05 mol L$^{-1}$ $I_2$ in a mixture of EMIDCA/MPII at varying molar mixing ratios of EMIDCA/MPII: (■) 91/9 mol%, (□) 80/20 mol%, (▲) 70/30 mol%, (△) 60/40 mol%, (▼) 50/50 mol%, (▽) 40/60 mol%, (●) 20/80 mol%, and (○) 0/100 mol%.

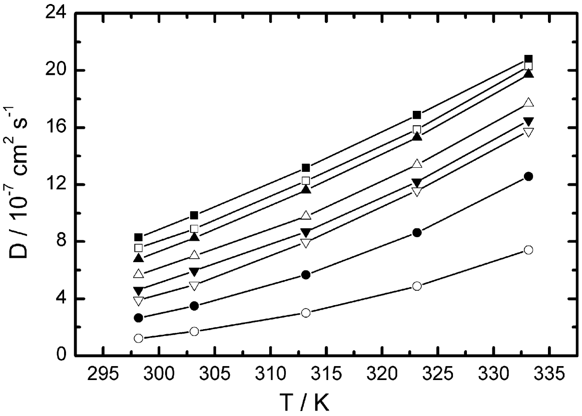

Fig. 10. Comparison of triiodide diffusion coefficients determined at UMEs of 0.05 mol L$^{-1}$ $I_2$ in a mixture of EMIDCA/MPII at varying molar mixing ratios of EMIDCA/MPII: (■) 91/9 mol%, (□) 80/20 mol%, (▲) 70/30 mol%, (△) 60/40 mol%, (▼) 50/50 mol%, (▽) 40/60 mol%, (●) 20/80 mol%, and (○) 0/100 mol%.

The temperature dependence of the $I_3^-$ diffusion coefficients of the blends with varying MPII concentration and fixed iodine concentration of 0.05 mol L$^{-1}$ which were determined with TLCs is shown in Fig. 9, for those determined at microelectrodes it is shown in Fig. 10. Similar to the blends with an EMIDCA/MPII ratio of 20/80 mol% and varying iodine concentrations the diffusion coefficients show a strong increase with increasing temperature and decreasing viscosity. The increase in diffusion with increasing temperature is largest for the systems with the highest viscosities at 25 °C. Therefore, with regard to a typical operating temperature for the solar cell, even these mixtures with comparably slow diffusion at 25 °C are promising electrolytes for a later application in DSSCs, due to high iodide concentrations and diffusion coefficients in the region of $10^{-6}$ cm$^2$ s$^{-1}$ at 60 °C. The temperature dependence of the diffusion coefficients shown in Figs. 9 and 10 shows, that diffusion measurements have to be performed in thermostatted cells, due to comparative large relative errors of about 14% which are already caused by temperature fluctuations of ±1 K.

As mentioned above, the diffusion coefficient is reciprocally proportional to the viscosity as described by the Einstein–Stokes equation (Eq. (4)) [28,29]:

$$D = \frac{kT}{6\pi\eta_V r} \tag{4}$$

where $k$ is the Boltzmann constant, $T$ the temperature and $r$ the radius of the sphere. The product of viscosity and diffusion coefficient (the Walden product) is approximately constant [28,30], therefore the Einstein–Stokes ratio $D\eta_V/T$ should also be constant for a constant temperature. The first deviation reported in literature was the high mobility of protons in water, where according to Grotthus [28] an alternative transport mechanism has been postulated. In the meantime, there are several electrolyte systems consisting of ionic liquids where the determined diffusion coefficient is much higher than expected according to viscosity data [13,18,31]. For the triiodide anion in ionic liquid electrolytes containing iodide, which is one of the systems mentioned before, a mechanism has already been suggested [8,15]. This mechanism depends on the assumption that the triiodide transport is not only created by an ordinary diffusion process, but also by a Grotthus-type charge-exchange mechanism, increasing at increasing iodide concentration [18].

The values of the Einstein–Stokes-ratios of the $I_3^-$ diffusion coefficients of the blends with varying MPII concentration and fixed iodine concentration which were determined at UMEs (Fig. 11), as well as for the diffusion coefficients determined with TLCs, do not show a Stokesian behaviour for the three analysed temperatures. Instead of staying constant with increasing MPII concentration and increasing viscosity, the values grow by a factor of 5 (60 °C) up to a factor of 10 (25 °C). The impact of the non-Stokesian transport mechanism on the overall mass- and charge-transport is obvious for the three temperatures shown in Fig. 11. It decreases with increasing temperature.

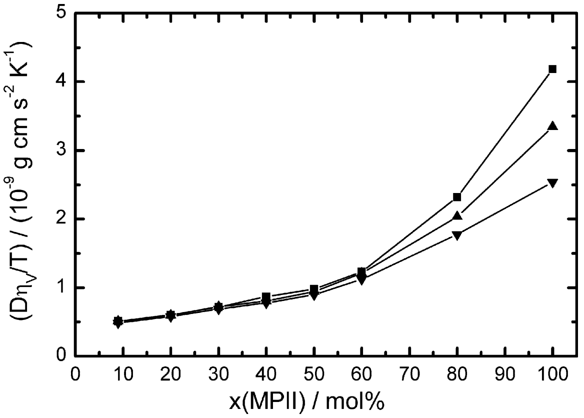

Fig. 11. Einstein–Stokes-ratio calculated with diffusion coefficients determined with steady-state cyclic voltammetry at UMEs vs. mol% MPII at different temperatures; *θ*: (■) 25 °C, (▲) 40 °C, and (▼) 60 °C.

### 3.2. PV-measurements of DSSC

The electrolytes based on binary IL mixtures of EMIDCA/MPII (molar ratio 60/40) were also tested in DSSCs, where ionic liquids are used as a solvent and a source of iodide while iodine is added to form triiodide. The role of the iodide in the electrolyte is to regenerate the positively charged photo-excited dye by electron donation according to the redox reaction: $3I^- + 2Dye^+ \rightarrow 2Dye + I_3^-$. At the counter electrode the triiodide is reduced back to iodide ($I_3^- + 2e^- \rightarrow 3I^-$). Therefore, physical diffusion of iodide and especially of triiodide in the electrolyte is an important parameter that can influence the performance of DSSC. This process often becomes a limiting process in a DSSC when IL-based electrolytes are used, especially when the $I_2$ content and consequently the triiodide concentration in the electrolyte is low. On the other hand, at a high $I_2$ concentration the diffusion of triiodide does not limit the performance of the DSSC, but promotes recombinations in the DSSC. The recombinations mainly appear at the interface between $TiO_2$ and the electrolyte, where the photo-generated electrons react with the triiodide. If the recombinations are strong, they become the limiting process for the performance of DSSCs. Beside the $I_2$ concentration in the electrolyte, the cell temperature also influences both processes, diffusion as well as recombination. As shown in Fig. 5, the diffusion coefficient increases with increasing temperature. Therefore, it is expected that the short circuit current ($J_{SC}$) of the DSSC, based on this electrolyte would increase with temperature. On the other hand a higher temperature increases the probability of recombinations leading to a decrease of $J_{SC}$. In order to evaluate the influence of these two limiting processes DSSCs with electrolytes based on EMIDCA/MPII having different $I_2$ concentrations have been assembled and their *I*/*V* characteristics have been measured under one sun illumination for different cell temperatures. In Fig. 12, the *I*/*V* characteristics of DSSCs with different $I_2$ concentrations that were measured at low, high and standard test temperatures (5, 55 and 25 °C) are presented, respectively. We observed that the $V_{OC}$ decreases with increasing $I_2$ concentration and/or when the cell temperature is increased. The influence of the temperature and $I_2$ concentration on the value of $J_{SC}$ is more complex. At a specified temperature the $J_{SC}$ can either increase or decrease with increasing $I_2$ concentration. The same behaviour is found when the $J_{SC}$ for specific iodine concentration and varying cell temperature (Fig. 12) is compared. These results are in a good agreement with already published results in Ref. [21], where a

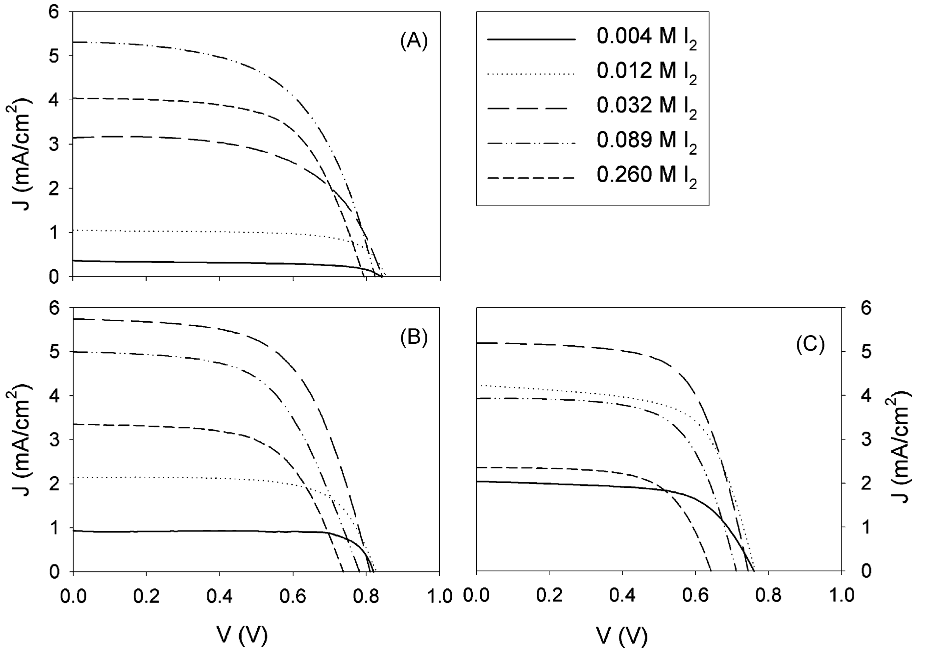

Fig. 12. Current to voltage characteristics for iodine concentration between 0.004 and 0.260 M measured at different cells temperatures (A, 5 °C; B, 25 °C and C, 55 °C). The molar ratio of EMIDCA/MPII was 60/40.

detailed analysis of the influence of the temperature for MPII based electrolyte with different iodine content on the DSSC performance can be found.

In order to gain more information on the influence of $I_2$ concentration and cell temperature for the EMIDCA/MPII electrolyte on the performance of the DSSC, the DSSCs with different $I_2$ concentrations (between 0.004 and 0.260 mol $L^{-1}$) were measured in a temperature range from 5 to 55 °C. Furthermore, the $J_{SC}$, $V_{OC}$ and conversion efficiency ($\eta_{CE}$) have been extracted for each DSSC. The results are shown in Fig. 13.

The influence of $I_2$ concentration in an EMIDCA/MPII electrolyte based DSSC on $J_{SC}$ is presented in Fig. 13A. In general when $J_{SC}$ is measured in the temperature range from 5 to 55 °C, the $J_{SC}$ initially increases with increasing temperature and then reaches a maximum, while a further increase of temperature leads to a small decrease of $J_{SC}$, e.g. 0.032 mol $L^{-1}$ $I_2$ in Fig. 13A. Such behaviour of $J_{SC}$ could be explained by assuming that at different cell temperatures different limiting processes are dominant. At a low cell temperature the diffusion of triiodide limits the $J_{SC}$ while an increase of the cell temperature improves the diffusion as presented in Fig. 5, but it also stimulates the recombination that becomes the dominating limiting process at higher cell temperatures leading to a small decrease of $J_{SC}$. An increase of $I_2$ concentration in the electrolyte shifts the maximum of $J_{SC}$ to lower temperature s therefore a monotonic decrease in the $J_{SC}$ is observed for $I_2$ concentrations >0.089 mol $L^{-1}$ within the measured temperature range.

Temperature dependence of the open circuit voltage $V_{OC}$ of the DSSC for different iodine contents at 1 sun illumination is presented in Fig. 13B with corresponding linear fits. The results reveal that an increase in the iodine concentration lowers the $V_{OC}$ value. This follows a prediction for an ideal semiconductor/liquid junction [32]. A monotonic decrease in $V_{OC}$ with temperature was found for all electrolytes, regardless of the iodine concentration while the absolute value of the open circuit voltage temperature coefficient $dV_{OC}/dT$ increases with increasing iodine concentration in the electrolyte. An increase in the $dV_{OC}/dT$ at higher iodine concentrations is, according to Kron et al. [33], associated with a higher probability of recombinations. Kron et al. measured the temperature dependence of the open circuit voltage of both the liquid electrolyte based DSSC and the solid-state hole conductor based DSSC ($dV_{OC}/dT = -1.5$ mV °$C^{-1}$—liquid electrolyte DSSC, $dV_{OC}/dT = -1.7$ mV °$C^{-1}$—solid-state hole conductor DSSC, extracted from Fig. 3 in [33]). In each case, a linear decrease in $V_{OC}$ with temperature was observed, where the slope $dV_{OC}/dT$ depends on recombination probability. In our case, the $dV_{OC}/dT$ values for 1 sun irradiance vary between $-1.5$ and $-2.9$ mV °$C^{-1}$ for the defined iodine concentration window.

Conversion efficiency ($\eta_{CE}$) is proportional to the $J_{SC}$, $V_{OC}$ and the fill factor (FF). The temperature has a strong influence on $J_{SC}$, while the relative temperature dependence of $V_{OC}$ and FF is smaller showing contrary trends, therefore the temperature dependence of $\eta_{CE}$ almost resembles the behaviour of $J_{SC}$. The results of $\eta_{CE}$ versus $T$ for the DSSC are presented in Fig. 13C. They confirm an increase in $\eta_{CE}$ with $T$ for a DSSC when the diffusion of the triiodide limits the $J_{SC}$ (low iodine concentration, low temperature). The temperature where a maximal $\eta_{CE}$ is reached shifts to a lower temperature with an increase in the $I_2$ content in the electrolyte, as it is the case for the $J_{SC}$.

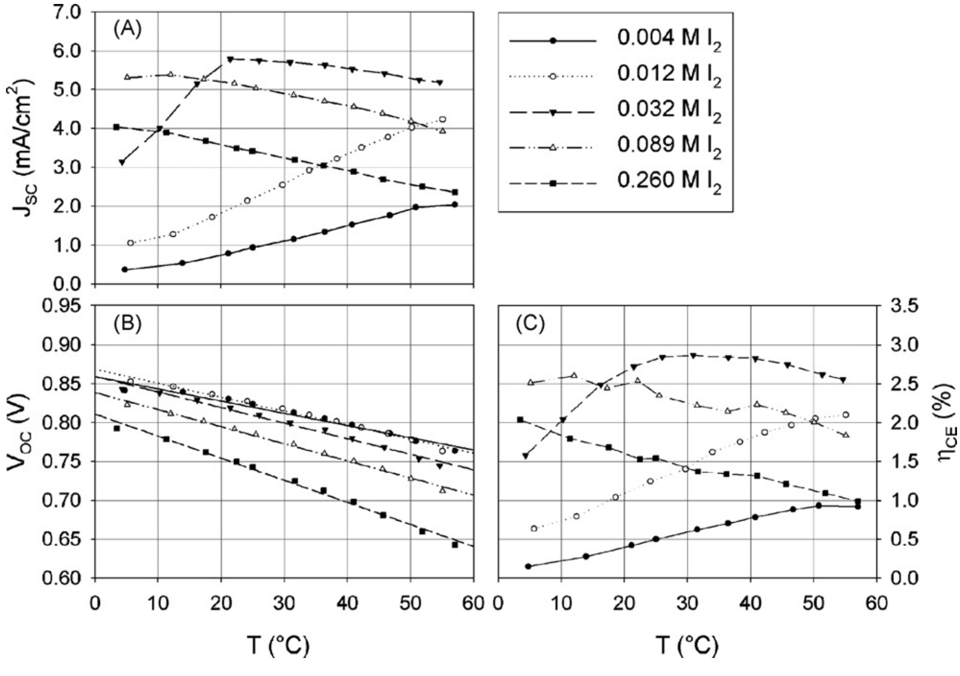

Fig. 13. Temperature dependence of the DSSC parameters measured at 1 sun (100 mW $cm^{-2}$). All lines are a guide to the eyes, except in graph B, where the lines represent a linear fit of the measured data. The molar ratio of EMIDCA/MPII was 60/40.

## 4. Conclusions

A simultaneous determination of triiodide diffusion coefficient and electrolyte viscosity is a fast and reliable procedure for search and optimisation of ionic liquid electrolytes for DSSCs. The electrolyte system EMIDCA/MPII with $0.05\,\mathrm{mol\,L^{-1}}$ $I_2$ shows increasing triiodide diffusion coefficients with decreasing MPII concentration or increasing temperature, in both cases related to the decreasing electrolyte viscosity. Additionally it shows strong non-Stokesian behaviour over the whole mixing range with decreasing magnitude at higher temperatures. The small increase of triiodide diffusion with increasing iodine concentration for the electrolyte mixtures with fixed molar ratio of EMIDCA/MPII and varying iodine concentration is also related to a small decrease of the viscosity. Therefore, the triiodide diffusion coefficient is not directly iodine concentration dependent. The importance of the limiting processes within the DSSC exchanges with a variation of iodine concentration or temperature. Due to the strong increase of the $J_{SC}$ and therefore DSSC efficiency with increasing iodine concentration at low temperatures, the triiodide diffusion is the dominating limiting process at low iodine concentrations in this temperature region. Higher temperatures not only enhance the triiodide diffusion but also recombination processes. Increasing temperature leads to increasing $J_{SC}$ and therefore DSSC efficiency until a maximum for both parameters is reached. A further increase in temperature leads to a decrease of both, $J_{SC}$ and DSSC efficiency, despite a further enhancement of triiodide diffusion. An increase of $I_2$ concentration in the electrolyte shifts the maximum of $J_{SC}$ and DSSC efficiency to lower temperatures. The reason for this unusual behaviour is the rising influence of recombination processes on $J_{SC}$ and DSSC efficiency with increasing temperature as well as with increasing iodine concentration. Thus, for high temperatures or high iodine concentrations recombination processes are the dominating limiting factor for $J_{SC}$ and DSSC efficiency, since limitation by triiodide diffusion would yield a monotonic increase and no maximum for both parameters with increasing temperature or iodine concentration. With respect to the results of diffusion measurements (Section 3.1), photovoltaic measurements (Section 3.2) and impedance measurements [19] an optimised ionic liquid electrolyte for DSSCs, which is based on EMIDCA, MPII an $I_2$, has an EMIDCA/MPII mixing ratio of 91/9 to 70/30 mol% and an iodine concentration in the range between 0.032 and $0.089\,\mathrm{mol\,L^{-1}}$.

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