A higher performance dye-sensitized solar cell based on the modified PMII/EMIMBF$_4$ binary room temperature ionic liquid electrolyte*

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Additives and iodine (I_2) are used to modify the binary room temperature ionic liquid (RTIL) electrolyte to enhance the photovoltaic performance of dye-sensitized solar cells (DSSCs). The short-circuit current density (J_{SC}) of 17.89 mA/cm^2, open circuit voltage (V_{OC}) of 0.71 V and fill factor (*FF*) of 0.50 are achieved in the optimal device. An average photoelectric conversion efficiency (*PCE*) of 6.35% is achieved by optimization, which is over two times larger than that of the parent device before optimization (2.06%), while the maximum *PCE* can reach up to 6.63%.

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Dye-sensitized solar cells (DSSCs) have attracted much attention because of high photovoltaic performance with low-cost production[1-3]. Although potential problems influence the stability of the electrolyte evidently due to leakage and volatilization of the traditional organic solvents[4], the room temperature ionic liquid (RTIL) can be used as an alternative choice to improve the lifetime and stability of DSSCs by replacing the organic solvent[5,6].

However, the photoelectric conversion efficiency (*PCE*) of the RTIL-DSSC is usually lower than that of the DSSC with volatile organic solvent due to the high viscosity of RTIL. To improve the *PCE* with easing mass transfer limitations brought by high viscosity of RTIL, researchers have developed a series of binary RTIL electrolyte systems[7-11]. Although these studies have shown that higher efficiency can be obtained with this binary RTIL system, there has been no report on the preferable modification of this binary RTIL system by the proper concentrations of additives and iodine (I_2) or the analysis of the effect on the performance of RTIL-DSSCs based on the 1-propyl-3-methylimidazolium iodide (PMII)/1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF$_4$) binary electrolyte with the dye N719 so far.

In this paper, the performance of the binary RTIL-DSSC is demonstrated. The photovoltaic performance of the RTIL-DSSC is studied at different volume ratios of the binary RTIL firstly. The photovoltaic performance is enhanced by modifying the binary RTIL system with appropriate concentrations of additives and I_2.

The solvents of electrolyte1 (E1) to electrolyte10 (E10) were prepared with the binary RTIL of PMII/ EMIMBF$_4$. Specific recipes of these electrolytes were shown in Tab.1. The concentration of 4-tert-butylpyridine (TBP) is fixed at 0.5 mol/L due to there is no doubt about its active effects on the *PCE* of DSSC [12-14]. I_2 and additives of lithium iodide (LiI) and guanidine thiocyanate (GuSCN) were added for obtaining DSSCs with better performance.

DSSCs were farbricated with the production process reported in Refs.[15]—[18], and the DSSCs obtained by using E1—E10 were marked as Device 1—Device 10, respectively. The active area of the assembled DSSC samples is 0.225 cm^2. Current density-voltage (*J*-*V*) curves of the devices were measured by a computer-controlled Keithley 2400 source meter under the AM 1.5G illumination (a solar simulator with illumination of

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100 mW/cm^2). Thickness of the photoanode was tested by a probe profilometer (Bruker Dektak XT).

Tab.1 Different binary RTIL electrolyte recipes

Electrolytes	Volume ratio of PMII to $EMIMBF_4$	TBP (mol/L)	I_2 (mol/L)	LiI (mol/L)	GuSCN (mol/L)
E1	40/60	0.5	0.15	-	-
E2	50/50	0.5	0.15	-	-
E3	60/40	0.5	0.15	-	-
E4	50/50	0.5	0.15	0.05	-
E5	50/50	0.5	0.15	0.1	-
E6	50/50	0.5	0.15	0.2	-
E7	50/50	0.5	0.30	0.1	-
E8	50/50	0.5	0.60	0.1	-
E9	50/50	0.5	0.30	0.1	0.1
E10	50/50	0.5	0.30	0.1	0.2

Among all reactions in the RTIL-DSSC, both of the diffusion process of ions in the electrolyte and the charge transfer process at interfaces play important roles in the performance of the DSSC[10]. The diffusion process of ions and the charge transfer process are markedly affected by the differences in viscosity, conductivity and other properties of the binary RTIL system. Fig.1 shows the *J-V* curves of binary RTIL-DSSCs without modification based on E1—E3 with different volume ratios of PMII/$EMIMBF_4$, and Tab.2 shows their performance parameters. The maximum *PCE* of 2.06% is achieved when the volume ratio of PMII/$EMIMBF_4$ is 50/50, where short-circuit current density (J_{SC}) and open circuit voltage (V_{OC}) reach 6.98 mA/cm^2 and 0.63 V, respectively. When the volume ratio of PMII/$EMIMBF_4$ is below or above 50/50, J_{SC} and V_{OC} both decrease compared with those of Device 2. The deteriorated photovoltaic performance is probably attributed to the lack of PMII in E1. The increased photocurrent is likely attributed to the improved diffusion coefficient of I_3^- and the reduced charge transfer resistance due to less viscosity compared with Device 2 and Device 3[10]. So the volume ratio of PMII/$EMIMBF_4$ in E2 (50/50) is chosen for the further modification to enhance the photovoltaic performance of DSSC. The diffusion process of ions and the charge transfer process can be preferably improved by modifying the electrolyte with additives and I_2.

Fig.2 and Tab.3 respectively show the *J-V* curves and performance parameters of the binary RTIL-DSSCs based on the electrolytes with different concentrations of LiI when the volume ratio of PMII to $EMIMBF_4$ is fixed at 50/50. The maximum *PCE* of 3.99% is achieved when the concentration of LiI is 0.1 mol/L. After adding LiI into the electrolytes, J_{SC} is improved when the concentration of LiI is no more than 0.1 mol/L, while V_{OC} changes in a small extent. This result may be due to the improvement of the electronic transportation in the TiO_2 films. On the other hand, both J_{SC} and V_{OC} are declined when the concentration of LiI is more than 0.1 mol/L, due to excessive Li^+ ions enter the nano-structured TiO_2 photoanode, causing the formation of Ti^{3+} species that trap the electrons in localized states[19]. Therefore, the concentration of LiI should be kept at 0.1 mol/L in the further modification to enhance the photovoltaic performance of DSSC.

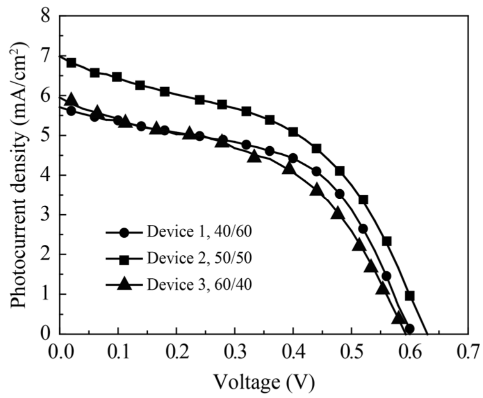

Fig.1 *J-V* curves of the binary RTIL-DSSCs based on E1—E3 with different volume ratios of PMII/$EMIMBF_4$

Tab.2 Performance parameters of the binary RTIL-DSSCs with different volume ratios of PMII/$EMIMBF_4$

Devices	J_{SC} (mA/cm^2)	V_{OC} (V)	*FF*	*PCE* (%)
Device 1 (E1)	5.71	0.61	0.52	1.80
Device 2 (E2)	6.98	0.63	0.47	2.06
Device 3 (E3)	5.95	0.59	0.46	1.63

Fig.3 and Tab.4 demonstrate the *J-V* curves and performance parameters of the binary RTIL-DSSCs based on the electrolytes with different concentrations of I_2[20]. The relatively high efficiency of 4.96% can be achieved when the concentration of I_2 reaches up to 0.3 mol/L. However, the *PCE* of binary RTIL-DSSC is decreased when the concentration of I_2 is further increased. This reduction may result from the notable visible light absorption of triiodide ions at 430 nm. The drop of absorption and the utilization of light for the dye lead to the decline in J_{SC} and *PCE* of the device[21]. Therefore, the concentration of I_2 should be kept at 0.3 mol/L in the further modification to enhance the photovoltaic performance of DSSC.

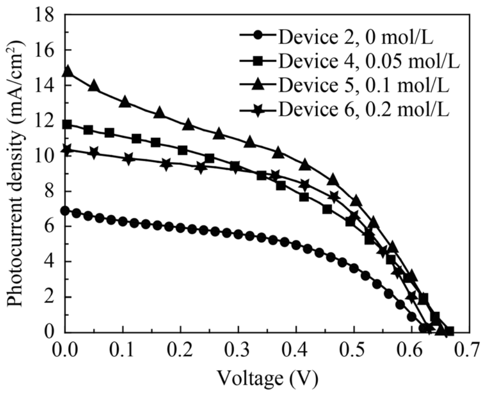

Fig.2 *J-V* curves of the binary RTIL-DSSCs based on E2, E4—E6 with different concentrations of LiI

Tab.3 Performance parameters of the binary RTIL-DSSCs with different concentrations of LiI

Devices	LiI (mol/L)	J_{SC} (mA/cm^2)	V_{OC} (V)	*FF*	*PCE* (%)
Device 2 (E2)	0	6.89	0.63	0.47	2.06
Device 4 (E4)	0.05	11.79	0.67	0.41	3.22
Device 5 (E5)	0.1	14.80	0.65	0.41	3.99
Device 6 (E6)	0.2	10.38	0.63	0.54	3.54

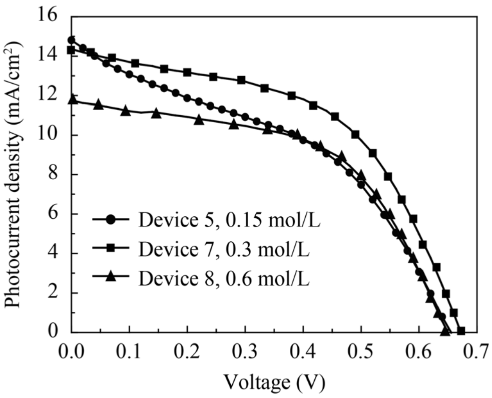

Fig.3 *J-V* curves of the binary RTIL-DSSCs based on E5, E7 and E8 with different concentrations of I_2

Tab.4 Performance parameters of the binary RTIL-DSSCs with different concentrations of I_2

Devices	I_2 (mol/L)	J_{SC} (mA/cm^2)	V_{OC} (V)	*FF*	*PCE* (%)
Device 5 (E5)	0.15	14.80	0.65	0.41	3.99
Device 7 (E7)	0.3	14.35	0.67	0.52	4.96
Device 8 (E8)	0.6	11.75	0.65	0.54	4.10

Fig.4 and Tab.5 illustrate the *J-V* curves and performance parameters of the binary RTIL-DSSCs based on the electrolytes with different concentrations of GuSCN. When the concentration of GuSCN is 0.1 mol/L, the device shows the excellent performance. The maximum *PCE* is 6.35%, which is over two times larger than that of Device 2 before optimization (2.06%). The *PCE* of RTIL-DSSC is declined when the concentration of GuSCN is more than 0.1 mol/L, due to J_{SC} and fill factor (*FF*) are both decreased, while V_{OC} is not so much affected. This phenomenon may indicate that an appropriate amount of GuSCN can promote the photovoltaic performance of the RTIL-DSSC. It may result from the strong binding of guanidinium cations to the N719 dyes and probably to many similar compounds. The binding of guanidinium cations competes with I_2 binding to the same molecule, reducing the surface concentration of dye-I_2 complexes. This in turn reduces the electron/ I_2 recombination rate constant, increasing the collection efficiency and improving the photocurrent[22].

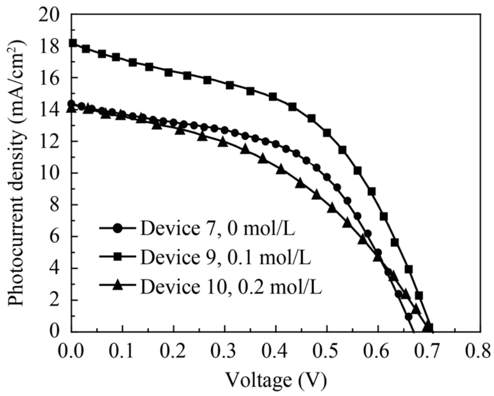

Fig.4 *J-V* curves of the binary RTIL-DSSCs based on E7, E9 and E10 with different concentrations of GuSCN

More devices were fabricated to confirm the repeatability of Device 9. Tab.6 lists the performance parameters of corresponding 15 binary RTIL-DSSCs employing the electrolyte E9. As can be seen from Tab.6, it is found that V_{OC} values of these devices are all 0.71 V. The averages of V_{OC}, J_{SC}, *FF* and *PCE* are 0.71 V, 17.89 mA/cm^2, 0.50 and 6.35%, respectively. Standard deviations of J_{SC}, *FF* and *PCE* are 0.42 mA/cm^2, 5.2×10^{-3} and 0.13%, respectively. Therefore, a conclusion can be drawn that these devices employing the electrolyte E9 not only indicate high photovoltaic performance, but also manifest that the device technology has good repeatability.

Tab.5 Performance parameters of the binary RTIL-DSSCs with different concentrations of GuSCN

Devices	GuSCN (mol/L)	J_{SC} (mA/cm^2)	V_{OC} (V)	*FF*	*PCE* (%)
Device 7 (E7)	0	14.35	0.67	0.52	4.96
Device 9 (E9)	0.1	18.20	0.71	0.49	6.35
Device 10 (E10)	0.2	14.36	0.71	0.41	4.23

Tab.6 Performance parameters of corresponding 15 binary RTIL-DSSCs employing the electrolyte E9

Devices	V_{OC} (V)	J_{SC} (mA/cm^2)	*FF*	*PCE* (%)
9-1	0.71	17.33	0.50	6.18
9-2	0.71	18.18	0.49	6.29
9-3	0.71	17.40	0.50	6.19
9-4	0.71	17.51	0.50	6.25
9-5	0.71	18.06	0.50	6.38
9-6	0.71	17.75	0.51	6.38
9-7	0.71	18.20	0.49	6.35
9-8	0.71	18.10	0.50	6.39
9-9	0.71	17.73	0.50	6.29
9-10	0.71	17.52	0.50	6.21
9-11	0.71	17.25	0.50	6.13
9-12	0.71	18.55	0.50	6.55
9-13	0.71	18.55	0.50	6.63
9-14	0.71	17.88	0.51	6.44
9-15	0.71	18.35	0.50	6.54
Average	0.71	17.89	0.50	6.35

In conclusion, the *PCE* of the binary RTIL-DSSCs based on PMII/EMIMBF$_4$ is greatly enhanced by modification with the proper concentrations of additives and I_2 into the binary RTIL electrolyte. The average values of J_{SC} of 17.89 mA/cm^2, V_{OC} of 0.71 V and *FF* of 0.50 are achieved in the best device consisting of 0.5 mol/L TBP, 0.3 mol/L I_2, 0.1 mol/L LiI, 0.1 mol/L GuSCN with the PMII/EMIMBF$_4$ volume ratio of 50/50. The highest *PCE* is up to 6.63%, while the average *PCE* of 6.35% is obtained, which is over two times larger than that of the parent device before optimization (2.06%). Further work concerning on the mechanism of modified optimization is under progress.

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