

# Effect of solvents in liquid electrolyte on the photovoltaic performance of dye-sensitized solar cells

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## Abstract

The effect of solvents in liquid electrolyte on the photovoltaic performance of dye-sensitized solar cells was investigated. The solvents with large donor number enhanced the open-circuit voltage but reduced the short-circuit current density. By mixing 30 vol.% NMP with 70 vol.% GBL, the open-circuit voltage increased from 0.55 to 0.632 V and the fill factor increased from 0.607 to 0.613 while the short-circuit current density decreased little. The further addition of 0.4 M pyridine into the above mixed solvent caused a huge increase of overall conversion efficiency from 5.73 to 6.70% under irradiation of 100 mW cm<sup>-2</sup>.

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**Keywords:** Dye-sensitized solar cell; Electrolyte; Solvent; Ionic conductivity; Donor number

## 1. Introduction

Dye-sensitized solar cells (DSSCs) are one of the promising candidates for the next generation of solar cells because of their simple structure with relatively high conversion efficiencies, inexpensive fabrication procedures in contrast with amorphous silicon solar cells [1–4]. The typical dye-sensitized solar cell consists of a dye-coated mesoporous TiO<sub>2</sub> nanoparticle film sandwiched between two transparent electrodes. A liquid electrolyte, traditionally containing the tri-iodide/iodide redox couple, fills the pores of the film and contacts the nanoparticles. Photoexcited dye molecules inject electrons into the conduction band of TiO<sub>2</sub>, and redox species in the electrolyte reduce the oxidized dyes back to their original state. The photoinjected electrons diffuse through the TiO<sub>2</sub> network, where they are collected at the back-contact (collecting electrode) unless they recombine with oxidized species at the TiO<sub>2</sub>/electrolyte interface. Redox species in the electrolyte transport the holes from the oxidized dye molecules to the counter electrode. In the past decade, much work has been done to improve the photovoltaic performance of DSSCs including optimizing nanostructured semiconductor electrodes [5–9], redox electrolytes [10–13] and electric addi-

tives [14–20]. But few attentions have been put in investigating the influence of organic solvents or mixed solvents in liquid electrolyte on the photovoltaic performance of DSSCs. However, it is very important to research the influence of solvents in liquid electrolyte on the photovoltaic performance of DSSCs either based on liquid electrolyte or based on gel electrolyte fabricated by solidifying liquid electrolyte with polymer materials or other materials [21–25]. This is because the physical characters of organic solvents including donor number, dielectric constants, viscosity, and so on, play important roles in determining the photovoltaic performance of DSSCs. For example, the donor number of solvents affects the data of open-circuit voltage of DSSCs and the dielectric constants of solvents influence their dissolution ability for inorganic iodide salts and the photocurrent in the cell [22,23,26,27].

Recently, we reported a short communication about preparation and application of a novel efficient liquid electrolyte absorbency for quasi-solid-state DSSCs based on poly(acrylic acid)–poly(ethylene glycol) (PAA–PEG) hybrid, the overall light-to-electricity efficiency is moderate due to the low liquid electrolyte absorbency of the PAA–PEG hybrid in pure  $\gamma$ -butyrolactone organic solvent [28]. It is known that the high content of liquid electrolyte in gel electrolyte is essential for fabricating high efficient quasi-solid-state DSSCs [29], so it is necessary to optimize the composition of liquid electrolyte for obtaining a high liquid electrolyte absorbency of the PAA–PEG

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hybrid. Due to polyacid character of the PAA–PEG hybrid, it is feasible to obtain a high liquid electrolyte absorbency of the hybrid by using Lewis basic solvents or mixed solvents in liquid electrolyte. According to the definition of Lewis basic, the solvents with high donor number (DN) show high Lewis basicity. The experimental results show that the PAA–PEG hybrid can not swell in organic solvents with donor number lower than 15. So some conventional and popular solvents usually used in preparing DSSCs such as acetonitrile (DN: 14.1), methoxyacetonitrile (DN: 14.6) do not adapt to the PAA–PEG hybrid [22,23]. While the solvents with high basicity also affect the amount of absorbed dye on the surface of TiO<sub>2</sub> film or even fade the dye-coated TiO<sub>2</sub> film. So it is very important to select some suitable organic solvents or mixed solvents for optimizing the PAA–PEG hybrid. Taking the above factors into account,  $\gamma$ -butyrolactone (GBL) and *N*-methyl pyrrolidone (NMP) mixed solvents were selected as liquid electrolyte components for PAA–PEG hybrid. Furthermore, the donor number of organic solvents is an important parameter affecting the photovoltaic performance of DSSCs [22,23], it is necessary to investigate the influence of selected solvents on the photovoltaic performance of DSSCs.  $\gamma$ -Butyrolactone and propylene carbonate mixed solvents with lower donor number were also selected as components of liquid electrolyte for DSSCs in order to do research by the numbers. The core content of this paper is mainly about the influence of mixed solvents with different donor number on the photovoltaic performance of DSSCs. The liquid electrolyte for DSSCs contains NaI/I<sub>2</sub> and various selected organic solvents containing  $\gamma$ -butyrolactone, propylene carbonate, *N*-methyl pyrrolidone which all have low melting point, high boiling point and low volatility. Their dielectric constants are in the range of 30–65, which are sufficient for dissolving suitable amount of inorganic iodide such as NaI to afford appropriate ionic conductivity needed for operation of DSSCs. The pyridine was selected as electrolytic additive to further enhance the photovoltaic performance of DSSCs.

## 2. Experimental

### 2.1. Materials

Titanium isopropoxide, glacial acetic acid, propylene carbonate (PC),  $\gamma$ -butyrolactone, *N*-methylpyrrolidone, pyridine (PY), sodium iodide and iodine were all A.R. grade and all purchased from Sinopharm Chemical Reagent Co., Ltd., China. All reagents were used without further treating.

Conducting glass plates (FTO glass, fluorine doped tin oxide over-layer, sheet resistance 8  $\Omega$  cm<sup>-2</sup>, purchased from Hartford Glass Co., USA) were used as substrates for precipitating TiO<sub>2</sub> porous films. Sensitizing dye *cis*-[(dcbH<sub>2</sub>)<sub>2</sub>Ru(SCN)<sub>2</sub>] and optical diffuser paste Ti-Nanoxide 300 were purchased from Solaronix SA.

### 2.2. Preparation of electrodes and assembly of cells

The preparation of TiO<sub>2</sub> colloidal paste and double-layer film was according to the method reported by Wang et al. [30]. The

TiO<sub>2</sub> colloidal paste was used to fabricate the transparent film about 10  $\mu$ m. Then the optical diffuser film about 4  $\mu$ m was printed above the transparent film by using Ti-Nanoxide 300 paste. After sintering at 500 °C and cooling down to 80 °C, the double-layer nanostructured TiO<sub>2</sub> electrodes were dye-coated by immersing them into a 2.5  $\times$  10<sup>-4</sup> M absolute ethanol solution of *cis*-[(dcbH<sub>2</sub>)<sub>2</sub>Ru(SCN)<sub>2</sub>] for 24 h. Dye-sensitized solar cell was assembled by dropping a drop of liquid electrolyte above the dye-sensitized TiO<sub>2</sub> porous film electrode. A Pt plated counter electrode was placed above it. The two electrodes were clipped together and a cyanoacrylate adhesive was used as sealant to seal the solar cell.

### 2.3. Measurements

The ionic conductivity of liquid electrolyte containing different solvents or mixed solvents with 0.5 M NaI and 0.05 M I<sub>2</sub> was measured by using model DDB-6200 digitized conductivity meter (Shanghai Reici Instrument Factory, China). The instrument was calibrated with 0.01 M KCl aqueous solution prior to experiments. The donor numbers of the mixed solvents were estimated by the additivity rule, described by the following equation [22]:

$$D_{\text{mixed}} = \left(\frac{x}{100}\right) D_{\text{added}} + \left(\frac{100-x}{100}\right) D_{\text{GBL}} \quad (1)$$

where  $D_{\text{mixed}}$ ,  $D_{\text{added}}$  and  $D_{\text{GBL}}$  are the donor numbers of the mixed solvent, the added solvent and GBL, respectively.  $\chi$  is the volume percent of added solvent in the mixed solvent.

The photovoltaic tests of DSSCs were carried out by measuring the  $J$ - $V$  character curves under irradiation of white light from an AM 1.5, 100 W xenon arc lamp (XQ-100W, Shanghai Photoelectricity Device Company, China) under ambient atmosphere. The incident light intensity and the active cell area were 100 mW cm<sup>-2</sup> and 0.2 cm<sup>2</sup> (0.4 cm  $\times$  0.5 cm), respectively. The photoelectronic performance [i.e. fill factor (FF) and overall conversion efficiency ( $\eta$ )] were calculated by the following equations:

$$\text{FF} = \frac{V_{\text{max}} J_{\text{max}}}{V_{\text{OC}} J_{\text{SC}}} \quad (2)$$

$$\eta(\%) = \frac{V_{\text{max}} I_{\text{max}}}{P_{\text{in}}} = \frac{V_{\text{OC}} I_{\text{SC}} \text{FF}}{P_{\text{in}}} \times 100\% \quad (3)$$

where  $J_{\text{SC}}$  is the short-circuit current density (mA cm<sup>-2</sup>),  $V_{\text{OC}}$  the open-circuit voltage (V),  $P_{\text{in}}$  the incident light power, and  $J_{\text{max}}$  (mA cm<sup>-2</sup>) and  $V_{\text{max}}$  (V) are the current density and voltage in the  $I$ - $V$  curves, respectively, at the point of maximum power output.

## 3. Results and discussion

It is known that the role of electrolyte in DSSCs is significant and the solvents with different physical characters such as donor number (DN), dielectric constant ( $\epsilon_r$ ), viscosity ( $\xi$ ) affect the photovoltaic performance of DSSCs directly [22,23]. Table 1 shows the data of photovoltaic performance of DSSCs

Table 1  
Physical character of organic solvents and their influence on photovoltaic performance of DSSCs<sup>a</sup>

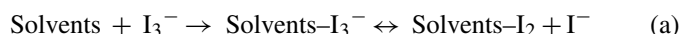
Solvent	GBL	PC	NMP	PY <sup>b</sup>
Physical character				
DN	18.0	15.1	27.3	33.1
$\epsilon_r$	42.0	65.0	32.2	12.3
$\xi$ (cP)	1.70	2.50	1.65	0.95
$\delta$ (mS cm <sup>-1</sup> )	9.60	5.95	7.76	–
$t_{mp}$ (°C)	–44.0	–49.0	–24.4	–42.0
$t_{bp}$ (°C)	204.0	242.0	203.0	115.5
Photovoltaic performance				
$J_{SC}$ (mA cm <sup>-2</sup> )	15.08 ± 0.55	14.54 ± 0.81	8.34 ± 0.39	–
$V_{OC}$ (V)	0.550 ± 0.003	0.510 ± 0.012	0.650 ± 0.004	–
FF	0.607 ± 0.025	0.554 ± 0.045	0.493 ± 0.026	–
$\eta$ (%)	5.03 ± 0.40	4.11 ± 0.65	2.67 ± 0.26	–

<sup>a</sup> Electrolyte contains 0.5 M NaI; 0.05 M I<sub>2</sub>. <sup>b</sup>The data of ionic conductivity and photovoltaic performance of DSSCs with electrolyte containing pure PY were not measured.

with different solvents. From Table 1, it is noticeable that by increasing donor number of solvents the values of open-circuit voltage ( $V_{OC}$ ) increased while the data of short-circuit current density ( $J_{SC}$ ) decreased except for the value of DSSCs with PC which is little lower than that of GBL. This is because the ionic conductivity of the former is much lower than that of the latter due to its higher viscosity compared with GBL. The maximum photoelectronic values were obtained when DSSCs containing liquid electrolyte with GBL. So GBL was chosen as basic component to fabricate mixed solvents with PC or NMP. It also can be seen from Table 1, the selected organic solvents of GBL, PC and NMP are all kind of high boiling point, low melting point and high dielectric constant organic solvents. The former two physical characters make for the long-term stability of DSSCs due to their low volatility. The latter physical character is good for dissolution and separation of iodide salts such as NaI to form free solvated ions, which give high transportation of I<sup>-</sup>/I<sub>3</sub><sup>-</sup> redox couples for good photovoltaic performance of DSSCs.

Kebede and Lindquist investigated the donor–acceptor reaction between the non-aqueous solvents and iodine [21]. The conclusion is that the donor number of the solvents is very important in solvents interaction with iodine. By controlling the donor number of the solvents or mixed solvents one can control the equilibrium of iodine and tri-iodide ions in given solvents or mixed solvents. Fukui et al. [22] further investigated the influence of the donor number of solvents or mixed solvents on the  $V_{OC}$  and  $J_{SC}$  of DSSCs and showed that solvents with large donor number dramatically enhanced the  $V_{OC}$ , but usually reduced the  $J_{SC}$ . The donor number of solvents or mixed solvents connects not only the photovoltaic performance of DSSCs but also the Lewis basicity of liquid electrolyte which is very important for fabricating high quality of gel electrolyte based on the novel absorbency [28], so it is necessary to investigate the influence of donor number of selected solvents and their mixed solvents on the data of photovoltaic performance of DSSCs. The results were shown in Fig. 1. It can be seen from Fig. 1, there exist trends that  $V_{OC}$  increases with increasing of donor number while  $J_{SC}$  has a totally reverse change tendency, which is the same as the reported results by Fukui [22].

These results can be explained by the electron donor–acceptor reaction between organic mixed solvents and tri-iodide [21]. The chemical reaction is written as:



When the electron pair donation ability of solvents increases, or, the DN of solvent increase, the above reaction equilibrium inclines to the left hand. On the contrary, the DN of solvent decrease, the above reaction equilibrium inclines to the right hand. Namely, with the increase of DN of solvent or mixed solvents, the free I<sub>3</sub><sup>-</sup> concentration decrease and free I<sup>-</sup> concentration increase, which improves the hole collection by I<sup>-</sup> [31,32] and increases the  $V_{OC}$  of the cell according to Eq. (4). Decreasing the I<sub>3</sub><sup>-</sup> concentration may also reduce the reaction

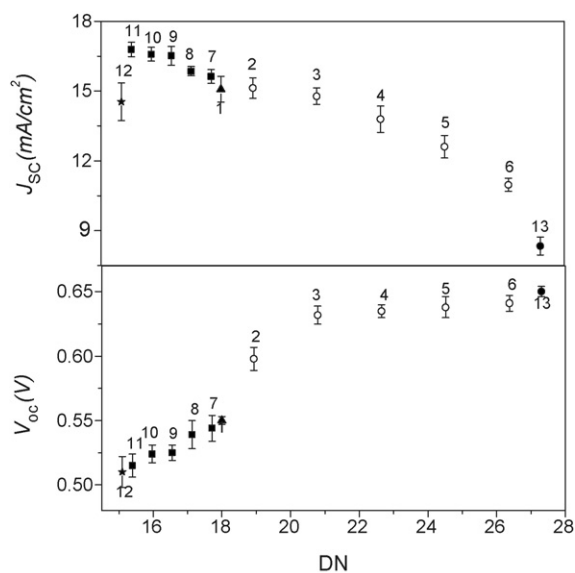


Fig. 1.  $V_{OC}$  and  $J_{SC}$  of DSSCs as function of donor numbers for different organic solvents and mixed solvents. (1: GBL; 2: 10 vol.% NMP/90 vol.% GBL; 3: 30 vol.% NMP/70 vol.% GBL; 4: 50 vol.% NMP/50 vol.% GBL; 5: 70 vol.% NMP/30 vol.% GBL; 6: 90 vol.% NMP/10 vol.% GBL; 7: 10 vol.% PC/90 vol.% GBL; 8: 30 vol.% PC/70 vol.% GBL; 9: 50 vol.% PC/50 vol.% GBL; 10: 70 vol.% PC/30 vol.% GBL; 11: 90 vol.% PC/10 vol.% GBL; 12: PC; 13: NMP).

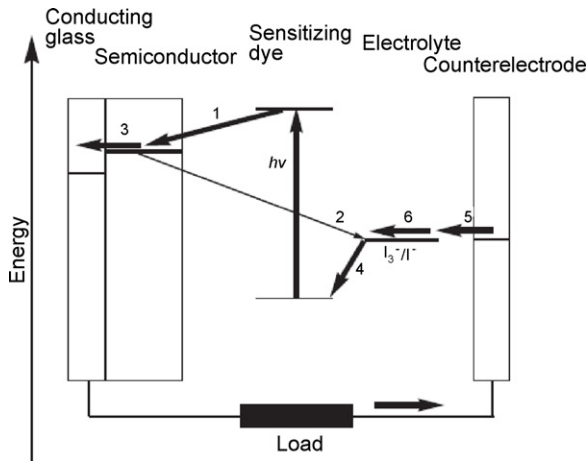


Fig. 2. Schematic description of a dye-sensitized solar cell that shows the principal processes involved.  $h\nu$ : photon absorption; (1) electron injection; (2) recombination; (3) electron transport and collection at the conducting glass; (4)  $I_3^-$  oxidation; (5)  $I_3^-$  reduction; (6) ion transport.

between the injected electrons and  $I_3^-$  at the semiconductor electrolyte junction, i.e. recombination in Fig. 2. Moreover, this reaction also decreases the  $I_3^-$  concentration, which also decreases the rate of dark reaction:



which would increase the electron concentration  $n_{cb}$  in the  $TiO_2$  film and improve the  $V_{OC}$  [33–36].

$$V_{OC} = \left[ \frac{kT}{e} \right] \ln \left\{ \frac{I_{inj}}{n_{cb} k_{et} [I_3^-]} \right\} \quad (4)$$

where  $k$  is Boltzmann constant,  $T$  the absolute temperature,  $e$  the electronic elementary charge,  $I_{inj}$  the flux of charge resulting from sensitized injection,  $n_{cb}$  the concentration of electrons at the  $TiO_2$  surface,  $k_{et}$  reaction rate constant of  $I_3^-$  dark reaction on  $TiO_2$ , and  $[I_3^-]$  is the concentration of  $I_3^-$  in electrolyte. Solvents or mixed solvents with higher donor number make for easier formation of complex between solvents and iodine, so the  $V_{OC}$  increases with increasing donor number of solvents or mixed solvents.

On the other hand, according to the Nazeetuddin and Gratzel's hypothesis [8], the reaction between the bare Lewis acidic  $TiO_2$  surface and the Lewis basic solvents blocks the active surface sites of  $TiO_2$  electrode which is responsible for tri-iodide reduction as the above reaction. The increasing order of donor number and Lewis basicity of solvents is  $PC < GBL < NMP$  [37]. Therefore, the solvents or mixed solvents with higher donor number are more Lewis basicity and easier reacting with the bare Lewis acidic  $TiO_2$  surface which shows higher efficient for blocking the active sites of  $TiO_2$  electrode and decreasing the rate of tri-iodide reduction. According to Eq. (4), the open-circuit voltage increases with decreasing of  $k_{et}$ .

Kim and co-workers proposed that the influence of the additives on  $V_{OC}$  and  $J_{SC}$  was due to an increase in the flatband potential ( $V_{FB}$ ) of the  $TiO_2$  photoelectrode [38]. Owing to the Lewis basic character of additives which also have high donor

number, so the theory also can be used to explain the  $V_{OC}$  and  $J_{SC}$  change trends with the change of donor number of solvents or mixed solvents. Absorbing high donor number of solvents or mixed solvents in liquid electrolyte on the  $TiO_2$  surface may raise  $V_{FB}$  of the  $TiO_2$  electrode [39]. Under Fermi level pinning, these two parameters are linked by the following equation:

$$V_{OC} = |V_{FB} - V_{red}| \quad (5)$$

where  $V_{red}$  is the standard reduction potential of a redox coupling. It remains constant upon the change of donor number of solvents or mixed solvents [40], while  $V_{FB}$  of the  $TiO_2$  electrode is sensitive to the characteristics of absorbed solvents on the  $TiO_2$  surface, so the increase of  $V_{FB}$  by absorbing high donor number of solvents on the  $TiO_2$  surface should increase the  $V_{OC}$ . Raising the  $V_{FB}$  also causes a negative shift in the conduction band edge of  $TiO_2$ , which decreases the driving force for excited dye to inject electrons into the conduction band of  $TiO_2$  and leads to the decrease of  $J_{SC}$  as shown in Fig. 2. Furthermore, the change of dielectric constants also response for the change of  $J_{SC}$ . For the selected organic solvents or mixed solvents, the dielectric constants decrease with increasing donor number, the lower the dielectric constants of the solvents or mixed solvents, the less photocurrent in the cell [26,27].

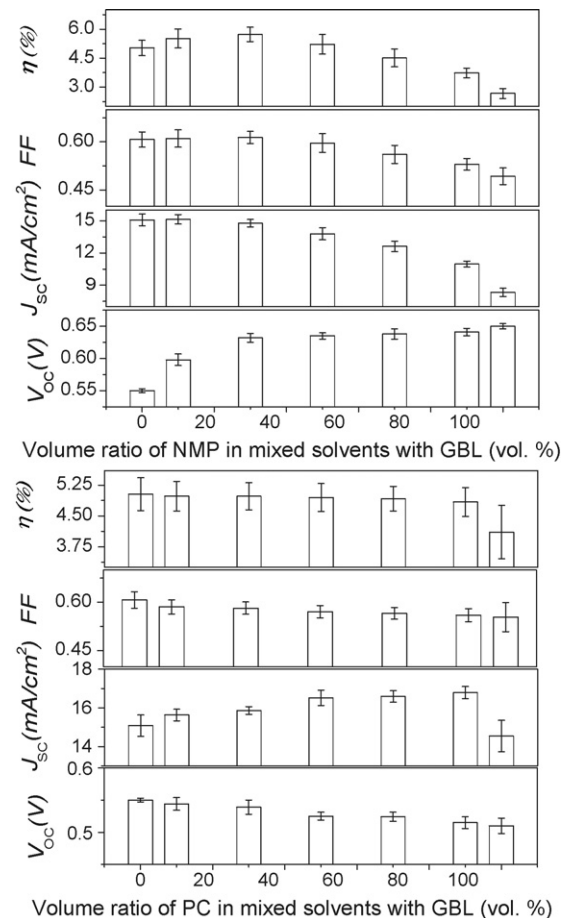


Fig. 3. Dependence of photovoltaic characters of DSSCs on the mixing ratio of NMP/GBL and PC/GBL. Electrolyte compositions: 0.5 M NaI + 0.05 M  $I_2$ .

Fig. 3 shows the dependence of photovoltaic characters of DSSCs on the NMP volume ratio in mixed solvents. With increasing of NMP volume ratio in mixed solvents,  $V_{OC}$  increases and  $J_{SC}$  decreases. While both the fill factor (FF) and overall conversion efficiency ( $\eta$ ) increase firstly when the NMP volume ratio in mixed solvent in the range of 0–30 vol.% and then decrease with the further increasing of the NMP volume ratio. The increase of  $V_{OC}$  is caused by the increase of donor number with increasing of NMP volume ratio as afore mentioned. And the decrease of  $J_{SC}$  is caused on the same reason. The increase of FF in the range of 0–30 vol.% is due to the larger donor number of NMP molecules showing high efficiency of suppressing the dark reaction on the surface of  $TiO_2$ . It causes the lower loss of electrons due to dark reaction, so the  $I-V$  curve shows more similar with rectangle. Higher FF can be obtained [8]. When further increasing the volume ratio of NMP in mixed solvents, the effect of NMP on suppressing the dark reaction on the surface of  $TiO_2$  becomes saturation, while the dielectric constant decreases which causes the lower concentration of free solvated ions in liquid electrolyte and lower ionic conductivity of liquid electrolyte as shown in Fig. 4. It means the transportation of  $I^-/I_3^-$  redox couples becomes poorer than former, so the  $I-V$  curve departs from rectangle. Lower FF is obtained [38]. The change tendency of overall conversion efficiency is caused by the change of  $V_{OC}$ ,  $J_{SC}$  and FF.

Fig. 3 also shows the dependence of the photovoltaic characters of DSSCs on the volume ratio of PC in mixed solvents. The increase of volume ratio of PC in mixed solvents causes the decrease of  $V_{OC}$  and the increase of  $J_{SC}$ . This is due to the same reasons as aforementioned. FF decreases with the volume ratio of PC in mixed solvents in the range of 0–100 vol.%. This is caused by lower Lewis basicity property of PC, which is bad for suppressing dark current on the bare  $TiO_2$  surface. On the other hand, the viscosity of PC is highest in the three selected solvents, the increase of volume ratio of PC in mixed solvents causes the increase of viscosity of mixed solvents and decrease of ionic conductivity as shown in Fig. 4, which is bad for transportation of  $I^-/I_3^-$  redox couples in electrolyte, the above two factors lead

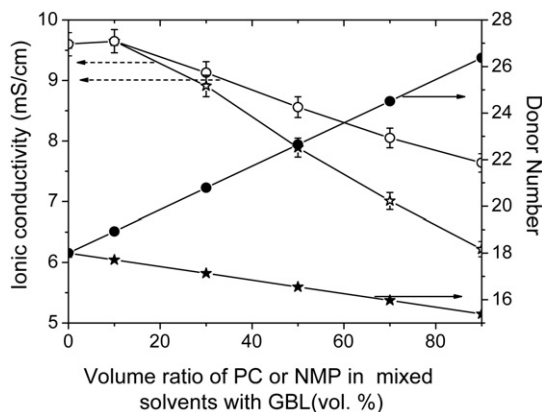


Fig. 4. Dependence of ionic conductivity and donor numbers of electrolyte on the mixed ratio of PC with GBL (open squares: ionic conductivity; filled squares: donor numbers) and NMP with GBL (open circles: ionic conductivity; filled circles: donor numbers).

to the decrease of FF. The values of overall conversion efficiency keep almost unchanged in the range of 0–90 vol.%. It is because of the compensation effect of changes of  $V_{OC}$ ,  $J_{SC}$  and FF in this range.

It can be seen from Fig. 3 that the photovoltaic characters of DSSCs with liquid electrolyte containing NMP and GBL mixed solvents are better than that of using PC and GBL mixed solvents. Although DSSCs with former electrolyte have lower  $J_{SC}$ , they have much higher  $V_{OC}$  and relatively high FF in the range of 0–50 vol.% than that of latter electrolyte. Therefore, the DSSCs with NMP and GBL mixed solvents show better photovoltaic performance. A short-circuit current density of  $14.78 \text{ mA cm}^{-2}$ , an open-circuit voltage of 0.632 V, a fill factor of 0.613, and an overall conversion efficiency of 5.73% were obtained using an electrolyte composition of 0.5 M NaI, 0.05 M  $I_2$  in 30 vol.% NMP and 70 vol.% GBL mixed solvent. Whether the composition of mixed solvents with 30 vol.% NMP and 70 vol.% GBL is the optimized composition is further validated by results of overall light-to-electricity conversion efficiency of DSSCs containing above mixed solvents with volume ratio of NMP in mixed solvents changing from 15–45 vol.% as shown in Fig. 5. The result is that the mixed solvents with 30 vol.% NMP and 70 vol.% GBL composition show the highest light-to-electricity conversion efficiency. So this composition is used for following experiments.

Kusama et al. investigated the influence of nitrogen-containing heterocyclic additives on the photovoltaic characters of DSSCs by the numbers [14–20] and found that pyridine and 4-*tert*-butylpyridine which is usually used as additive in liquid or ionic liquid electrolyte showed high efficient for enhancing the photovoltaic performance of DSSCs [8]. In terms of the lower molecular weight and viscosity of pyridine than that of 4-*tert*-butylpyridine, the amount of pyridine used as electrolyte additive is lower and its influence on changing character of liquid electrolyte is small. Therefore, pyridine was chosen as additive for further optimizing the electrolyte containing NMP and GBL mixed solvent. As shown in Fig. 5, the  $V_{OC}$  and FF of DSSCs increase greatly with the increase of pyridine concentration. The working mechanism of pyridine in the cell is the same as 4-*tert*-butylpyridine. Namely, the absorption of pyridine in the bare  $TiO_2$  surface affects the surface charge of  $TiO_2$  by decreasing the amount of absorbed protons and decreases the recombination of electrons in  $TiO_2$  surface with tri-iodide in the electrolyte

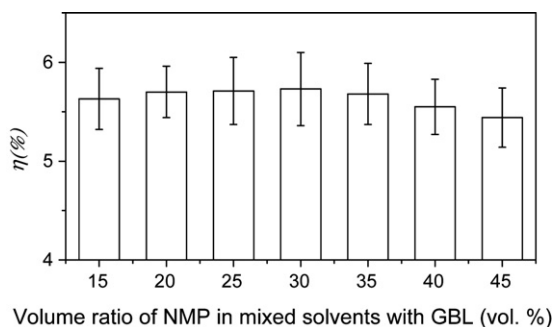


Fig. 5. Dependence of light-to-electricity conversion efficiency of DSSCs on the mixing ratio of NMP in NMP/GBL mixed solvents.

Table 2  
Effect of pyridine concentration on the photovoltaic performance of DSSCs

Concentration of PY (M)	$J_{SC}$ (mA cm <sup>-2</sup> )	$V_{OC}$ (V)	FF	$\eta$ (%)
0.0	14.78 ± 0.35	0.632 ± 0.007	0.613 ± 0.019	5.73 ± 0.35
0.1	14.61 ± 0.31	0.642 ± 0.006	0.625 ± 0.018	5.86 ± 0.32
0.2	14.22 ± 0.34	0.656 ± 0.009	0.643 ± 0.024	6.00 ± 0.42
0.3	13.84 ± 0.28	0.685 ± 0.006	0.680 ± 0.020	6.45 ± 0.34
0.4	13.34 ± 0.25	0.705 ± 0.008	0.712 ± 0.022	6.70 ± 0.38
0.5	12.33 ± 0.30	0.725 ± 0.011	0.730 ± 0.029	6.53 ± 0.49

by preventing tri-iodide access to the TiO<sub>2</sub> surface and by complexation with iodine in the electrolyte [41]. On the other hand, Kebede and Lindquist thought the pyridine played a key role to decrease the conduction band electron acceptor such as I<sub>2</sub> by efficiently converting iodine to less efficient electron acceptor of PY<sub>2</sub>I<sup>+</sup>, which also decreased the dark reaction [21]. All the above factors lead to the increase of  $V_{OC}$ .

It is different between the solvent effect and the additives effect, the former is the basic component for liquid electrolyte, which gives a channel for iodide/tri-iodide in liquid electrolyte. The additives play the role to optimize the liquid electrolyte and their main function is to suppress the dark reaction. The solvent percentage is larger, and the additives percentage is smaller. The solvent characteristics such as donor number, dielectric constants, viscosity are more important for dissolving iodide salts and photovoltaic performance of DSSC than additives.

From Table 2, the  $J_{SC}$  of DSSCs decreases slowly with increasing pyridine concentration in mixed solvent. The reason is that the complexes between pyridine and iodine play as obstacles to retard the diffusion of tri-iodide/iodide redox species in electrolyte. Due to the low viscosity character of pyridine and low amount of pyridine added in liquid electrolyte, its influence on the  $J_{SC}$  is inapparent, so the decrease of short-circuit current density is little. The optimized electrolyte with highest overall conversion efficiency was obtained by adding 0.4 M pyridine into 30 vol.% NMP and 70 vol.% GBL mixed solvent. The data of photovoltaic performance of DSSCs with liquid electrolyte containing pyridine additive are listed in Table 2.

Fig. 6 shows the photocurrent–photovoltage curves for DSSCs with liquid electrolyte containing different solvent com-

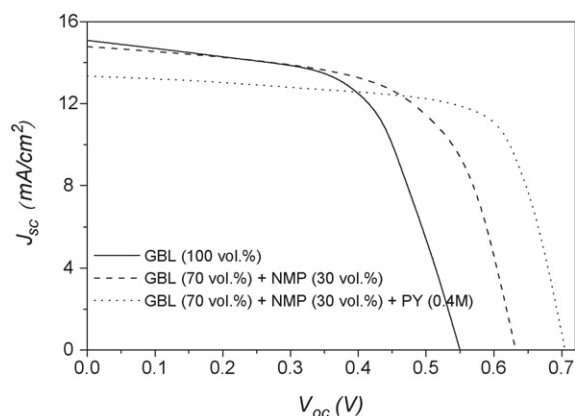


Fig. 6. Photocurrent–photovoltage curves for DSSCs with liquid electrolyte containing different solvent components.

ponents. By adding NMP in GBL, the  $J_{SC}$  of DSSCs changes little while the  $V_{OC}$  largely increases from 0.550 to 0.632 V and the fill factor also increases, which cause the great increase of overall conversion efficiency. By further addition of pyridine into NMP and GBL mixed solvent, although the short-circuit current density decreases, the large increase of open-circuit voltage and fill factor still cause the huge increase of the overall conversion efficiency from 5.73 to 6.70%.

#### 4. Conclusions

The effect of solvents in liquid electrolyte on photovoltaic performance of dye-sensitized solar cells was investigated. The donor numbers of solvents or mixed solvents plays an important role in determining the values of open-circuit voltage and short-circuit current density. Solvents with large donor number enhance the  $V_{OC}$  but usually decrease the  $J_{SC}$ . The photovoltaic characters of DSSCs with liquid electrolyte containing NMP and GBL mixed solvents are better than that of using PC and GBL mixed solvents because their high donor number cause high open-circuit voltage and fill factor. Otherwise their relatively high ionic conductivity maintains high short-circuit current density. By adding 30 vol.% NMP into 70 vol.% GBL, the overall conversion efficiency of DSSCs enhances from 5.03 to 5.73%. The large increase of open-circuit voltage and fill factor causes the huge increase of overall conversion efficiency from 5.73 to 6.70% by further addition of 0.4 M pyridine into the above mixed solvent.

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