



Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

High performance dye-sensitized solar cells containing 1-methyl-3-propyl imidazolinium iodide-effect of additives and solvents

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ARTICLE INFO

Article history:

Received 4 February 2009

Received in revised form 30 April 2009

Accepted 7 May 2009

Available online 19 May 2009

Keywords:

Dye-sensitized solar cell

1-Methyl-3-propyl imidazolinium iodide

Redox behavior

Additives and solvents

ABSTRACT

In this work, the influences of redox electrolyte, additives and solvents on the photovoltaic performance of dye-sensitized solar cells (DSSCs) containing 1-methyl-3-propyl-imidazolinium iodide (MPII) as the electrolyte were investigated. An optimum conductivity of 20.31 mS cm^{-1} for 0.6 M MPII in acetonitrile (AN) was found out from the conductivity measurement. Diffusion coefficient of I_3^- and photocurrent density (J_{SC}) of the DSSC varied with concentration of I_2 . Among the different inorganic and organic iodides as additives, the DSSC showed high performance with lithium iodide (LiI) and tetrabutylammonium iodide (TBAI), respectively. The performance of the DSSCs with different solvents was studied. From the EIS studies, it was inferred that the poor conversion efficiencies of the DSSCs were associated with high charge transfer resistance, noted along the $\text{TiO}_2/\text{solvent}$ interface. A high conversion efficiency of 6.7% (J_{SC} of 14.8 mA cm^{-2} , V_{OC} of 0.74 V, fill factor (FF) 0.62 under one sun (AM 1.5)) was obtained for the DSSC containing the electrolyte composition of 0.6 M of MPII/0.2 M of LiI/0.06 M of I_2 /0.5 M of TBP in AN along with the incorporation of light scattering particles (TiO_2 of 300 nm).

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1. Introduction

During the past decades, dye-sensitized solar cell (DSSC) has attracted much attention as an alternative to silicon solar cell since they use environmentally benign materials through low cost process and exhibits a commercially realistic energy-conversion efficiency [1–3]. In these devices, photon-to-electricity conversion is achieved by ultrafast electron injection from a photo-excited dye into the conduction band of TiO_2 and subsequently dye regeneration and hole transportation to the counter electrode. In order improve the performance of the DSSC, extensive research has been performed on semiconductor nano-crystalline TiO_2 electrodes [4–8], molecular dyes [9–12], supporting electrolytes [13–16] and counter electrodes [17–18].

The role of solvent-supporting electrolyte system is prominent in the operation of DSSCs. For, e.g., Kebede and Lindquist [19] and Hara et al. [20] investigated the spectrophotometric properties of I^-/I_3^- couple containing LiI based electrolytes in different solvents and postulated that various properties such as donor number, viscosity and dielectric constant had influenced strongly the

photo physical properties of the DSSC. In a recent work, photovoltaic properties of the DSSC containing mixture of solvents such as tetrahydrofuran (THF) and acetonitrile (AN) were studied in detail [21].

It has been demonstrated that cations of supporting electrolyte play an important role in improving the performance of the liquid electrolytes containing DSSCs [22–24]. Among the different cations, substituted imidazolinium iodides have been used as liquid [25–28] and quasi solid state electrolytes [29–33] in the solar cells. They contribute to the enhancement of conductivity of I^-/I_3^- electrolyte and their multilayer adsorption on the TiO_2 surface leads to the enhancement in electron diffusion coefficient [34].

The application of 1-methyl-3-propyl imidazolinium (MPII) iodide has widely been investigated in the DSSCs because of its low viscosity (865 MPa s) and high conductivity (0.8 mS cm^{-1}) [35]. Hence, the photovoltaic characteristics of the DSSC containing MPII as an electrolyte were investigated in this work as there is no detailed study in the literature on the comparison on the performance of the DSSCs containing the same in different solvents. On this basis, at first, the redox couple concentrations of I^-/I_3^- were optimized and a few organic and inorganic iodides were used to improve the photovoltaic performance of the DSSC containing MPII in AN. Further, the influence of different solvents on the redox behavior I^-/I_3^- was studied.

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2. Experimental

2.1. Materials

Anhydrous CH_3CN (AN), propylene carbonate (PC), methoxy propionitrile (MPN), γ -butyrolactone (GBL), N,N' -dimethylformamide (DMF), N,N' -dimethylacetamide (DMA), dimethylsulfoxide (DMSO) and tert. butanol were purchased from Merck and water molecules were removed by putting molecular sieves (4A) into the solvent. Anhydrous LiI , I_2 , poly(ethylene glycol) (PEG) and 4-tert. butyl pyridine (TBP) were obtained from Merck and titanium (IV) isopropoxide (98%) was from Acros. The N3 dye was the commercial product obtained from Solaronix (Aubonne, Switzerland). In the laboratory, 1-methyl-3-propyl imidazolinium iodide was synthesized from 1-methyl imidazole (Fluka) and propyl iodide (Fluka) [35]. The purity was confirmed by 400 MHz ^1H FT NMR instrument (Bruker Advance).

2.2. Preparation of TiO_2 thin films and the cell assembly

The TiO_2 colloids were prepared by the method reported in our previous study [36]. Titanium (IV) isopropoxide (72 ml, 98%) was added to 430 ml of 0.1 M nitric acid solution with constant stirring and the colloidal solution was heated to 85 °C simultaneously for 8 h. The mixture was cooled down to room temperature and filtered. Then the filtrate was heated in an autoclave at 240 °C for 12 h in order to allow the TiO_2 particles to grow uniformly. The solution was then concentrated to 13 wt% and two types of pastes namely P1 and P2 were prepared by the addition 30 wt% (with respect to TiO_2) of PEG with the corresponding molecular weights of 20,000 and 200,000, respectively, to the above solution in order to control the pore diameters and to prevent the film from cracking during drying.

Thus, the TiO_2 photoelectrode was prepared by the uniform initial coating of P2 TiO_2 followed by P1 TiO_2 pastes (named as P2P1 TiO_2) on a fluorine-doped tin oxide (FTO) glass plate by glass rod method (The sheet resistivity of FTO is 20–25 $\Omega/\text{sq.}$); after this, the TiO_2 photoelectrode was dried in the air at room temperature for 30 min followed by sintering at 500 °C, in a hot-oven at a rate of 20 °C/min for another 30 min. An active area of 0.25 cm^2 was selected from sintered electrode and the electrodes were immersed in 3×10^{-4} M solution of cis-di(thiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium (II) (N3) containing acetonitrile and tertiary butanol (in the volume ratio of 1:1) for 12 h.

In this work, MPPII and I_2 were used as redox couple and were dissolved in different solvents along with 0.5 M of 4-tert. butyl pyridine (TBP). It is assumed that I^- and I_2 immediately formed I_3^- in this solution. The specified composition of the electrolyte solution was sprayed on both the dye immobilized photoanode and Pt sputtered (thickness of Pt is 100 nm) FTO glass and they were physically sandwiched together using cell holders.

The photoelectrochemical characterizations of the DSSCs were carried out by using an AM 1.5 simulated light radiation. The light source was a 450 W Xe lamp (#6266, Oriel) equipped with a water-based IR filter and AM 1.5 filter (#81075, Oriel).

Conductivity measurement of solution was performed by electrochemical impedance spectroscopy (EIS) with two Pt electrodes conductance cell where the area of the each Pt electrode is 1 cm^2 and the distance between the two electrodes is 1 cm. The cell constant is 0.555 cm^{-1} , as calibrated from the standard aqueous KCl solution. Photoelectrochemical characteristics and the ac-impedance measurements of the DSSCs were recorded with a potentiostat/galvanostat (PGSTAT 30, Autolab, Eco-Chemie, Netherland) under different light illumination. The EIS of the DSSC was performed under constant light illumination and under open-circuit

conditions. The applied bias voltage and ac amplitude were set at open-circuit voltage of the DSSC at 10 mV between the FTO/Pt counter electrode and the FTO/ TiO_2 /dye working electrode, respectively [37]. Besides, the frequency range explored was 10 mHz to 65 kHz.

3. Results and discussion

3.1. Effect of different concentrations of MPPII/ CH_3CN and I_2

The conductivity of the electrolyte in this study was first examined as it provides information on the mobility of ions and their interaction with solvent molecules. From the conductivity measurements, a high conductivity of 20.31 mS cm^{-1} for MPPII/AN at a concentration of 0.6 M was obtained and hence, this concentration was taken as an optimum value for further investigations on the photovoltaic studies of the DSSC.

From steady-state voltammograms obtained using Pt electrode, the apparent diffusion coefficient (D_{app}) values of I_3^- at different concentrations of I_2 containing 0.6 M of MPPII were calculated. Anodic and cathodic currents are not affected with higher sweep rates, suggesting that the steady-state currents controlled by the diffusion of iodide (I^-) and triiodide (I_3^-) have been attained. The D_{app} values of I^- and I_3^- were obtained from the anodic and cathodic steady-state currents (i_s) according to the following equation:

$$i_s = 4nFD_{\text{app}}r_oC$$

where i_s is the peak current, n is the number of electron transfer taking place in the electrochemical reaction, D_{app} is the apparent diffusion coefficient, r_o is the radius of the Pt micro electrode and C is the concentration of the reactive species.

Fig. 1 shows the variations in the diffusion coefficient values of I_3^- obtained from the CV and the photocurrent density of the DSSC (containing 0.6 M of MPPII with P1 TiO_2 electrode at a constant illumination of 100 mW cm^{-2}) with respect to the change in the concentrations of I_2 . It was found that both the D values of I_3^- and J_{sc} increased with increase in the concentration of I_2 (from 0.03 to 0.06 M) and subsequent additions resulted in the decrease of J_{sc} . An optimum diffusion coefficient values of $4.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for I_3^- and $9.2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for I^- were found out for a $\text{I}^- : \text{I}_3^-$ ratio of 10:1 (0.6 M of MPPII and 0.06 M of I_2). The results show that diffusion coefficient of the electrolyte and the J_{sc} of the DSSC depend strongly on the concentrations of I_2 . The reason for this behavior can be accounted below.

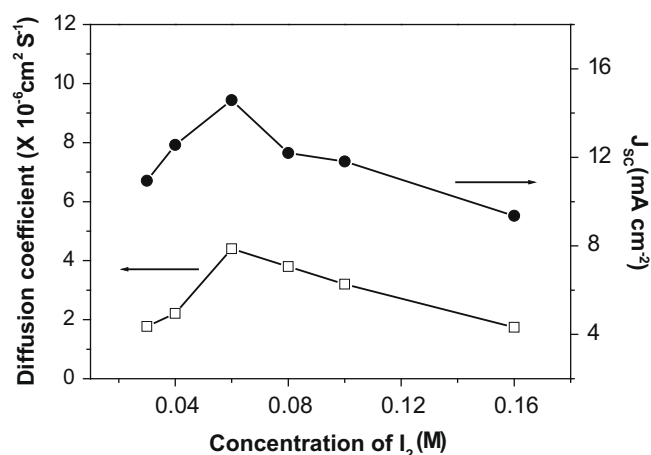


Fig. 1. The dependence of concentration of I_2 vs. diffusion coefficient of I_3^- (at 25 °C) and photocurrent density (J_{sc}) of the DSSC containing MPPII.

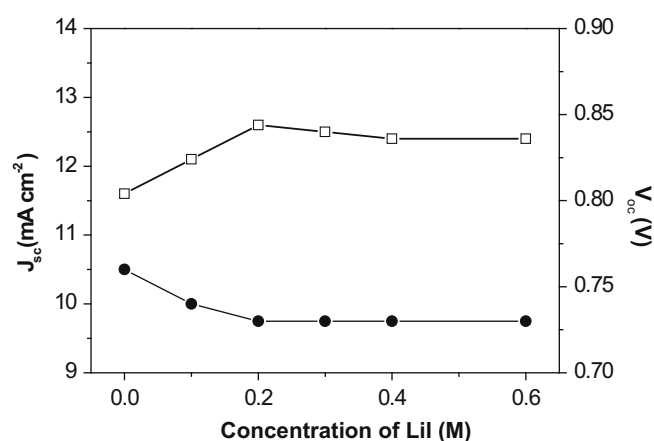
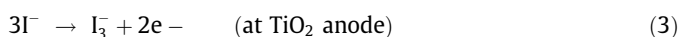
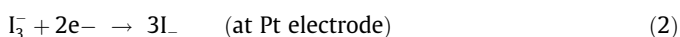


Fig. 2. The dependence of photocurrent density (J_{sc}) and open-circuit voltage (V_{oc}) of the DSSC as a function of concentration of LiI; conditions are: TBP = 0.5 M in AN, $[I^- : I_3^-] = 10 : 1$.

When the concentration of I_2 increases, the viscosity of the electrolyte solution increases. As a result of this, the ionic mobility and diffusion coefficient of I_3^- decreases. This leads to low J_{sc} value of the DSSC. Further, explanation may also be given by considering the following redox reactions:



According to reaction (1), increase of the concentration of I_2 acts in favor of I_3^- as the concentration of I^- is much higher than that of I_2 . Since a critical concentration level of I_3^- is necessary for the cell functioning at the beginning, reaction (2) and (3) proceeds effectively and the J_{sc} increases and saturates at once. However, further increase in the concentration of I_2 results in favor of reaction (4) leading to a decrease in the performance of the DSSC. In addition to this, I_2 also absorbs visible light from 400 to 500 nm, suppressing the visible light absorption by the N3 dye [24].

3.2. Effect of additions of organic and inorganic iodides

In this section, the effect of additions of different inorganic and organic iodides on the photovoltaic performance of the DSSC was investigated. Prior to this study, the effect of different concentrations of one such additive such as LiI on the performance of the DSSC was examined. Fig. 2 depicts such dependence of photovoltaic parameters on the effect of addition of LiI. The J_{sc} increased initially with the increase in the concentration of LiI and saturated with further addition (0.2 M). On the other hand, V_{oc} decreased to a smaller extent and also saturated at the same concentration

of LiI. Therefore, the concentration of LiI should be in between 0.1 and 0.2 M, in terms of the cell performance. In the same manner, with the addition of 0.2 M of LiI, the conductivity of 0.6 M MP11/CH₃CN increased about 12% and further addition of LiI produced no effect. Hence, in subsequent studies, 0.2 M of different iodides were taken and investigated.

Table 1 shows the photo voltaic and impedance parameters (see later) of the DSSC obtained by the addition of inorganic iodides such as NaI and KI (for comparison, the results obtained with the addition of 0.2 M LiI is also included) and organic iodides such as tetraalkylammonium iodides ($R_4N^+I^-$ where $R = C_2H_5$, C_3H_7 and C_4H_9) on the photovoltaic performance of the DSSC (Here, the effect of addition cesium and rubidium iodides (CsI and RbI) were not studied due to their poor solubility in AN). From Li^+ to K^+ cation, the V_{oc} increased from 0.73 to 0.75 V and the J_{sc} decreased from 12.6 to 10.6 mA cm⁻², leading to a decrease in the cell performance. A similar trend was also observed from $C_2H_5^+$ to $C_4H_9^+$ cations (Table 1).

The reason for this characteristic behavior may be correlated with ionic radius of the different cations [38]. As we know that cation radius increases from Li^+ to K^+ and the adsorption of cationic species onto the TiO₂ surface leads to potential drop in the Helmholtz layer, which depends on adsorbed cations and this decreases with the increase of cation radius. This causes the potential of conduction band of the TiO₂ shifts negatively decreasing the energy gap between the LUMO level of the N3 dye and the conduction band of the TiO₂ leading to the increase of photovoltage [38]. When the conduction band shifts negatively, the driving force for the injection of electrons from the excited dye to the conduction band decreases and hence, injection efficiency decreases. Therefore, the J_{sc} decreased with the increment of cation radius [38].

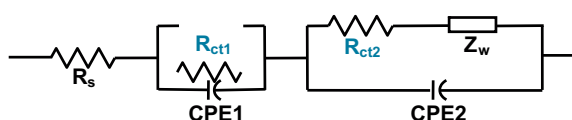
In the case of organic iodides, the V_{oc} of the DSSC in contact with an iodine redox electrolyte is derived from the energy gap between the conduction band level of the TiO₂ and the I^-/I_3^- redox potential of alkyl cations. As a result of this, the conduction band of the TiO₂ shifted negatively from $C_2H_5^+$ to $C_4H_9^+$, leading to the increase of the V_{oc} and the vice-versa [20].

The photoelectrochemical behavior of the DSSC containing different iodides can also be followed successfully using EIS spectroscopy. Because of a non uniform distribution of current due to non-smooth surface of TiO₂ film and Pt electrode, the constant phase element (CPE) acting as the capacitance, is used to fit the experimental data more accurately. It is a non ideal frequency dependent capacitance, used for fitting depressed semicircles in Nyquist plots obtained by the equation $Z = 1/[T(i \times \omega)^P]$, where T , P are the constant phase element parameters, and i represents the complex conjugate, ω is the angular frequency of the ac signal, respectively, [37]. For convenience, the serial resistance (R_s) values were shifted to identical value of a DSSC having the lowest value of R_s . The general equivalent circuit for the EIS studies of the DSSC is shown in Scheme 1. The ohmic serial resistance (R_s) corresponds to the series resistance and the resistances R_{ct1} and R_{ct2} relate to charge-transfer processes occurring at the solvent interfaces of Pt counter electrode and TiO₂ film, respectively, [39,40]. The third semicircle

Table 1

Photovoltaic and EIS parameters of DSSCs obtained with the addition of inorganic and organic iodides. The conditions are the same as in Fig. 2.

Type of iodides (0.2 M)	Name of iodides	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF	η (%)	R_{ct1} (Ω)	R_{ct2} (Ω)
Inorganic	LiI	0.73	12.6	0.65	5.98	2.6	11.6
	NaI	0.74	12.0	0.66	5.80	5.8	11.9
	KI	0.75	10.3	0.64	5.01	6.6	16.0
Organic	TBAI	0.73	11.61	0.62	5.23	4.6	11.7
	TPAI	0.74	9.60	0.66	4.77	5.9	13.9
	TEAI	0.75	8.80	0.67	4.45	6.7	14.8



Scheme 1.

in both the conditions represents the Warburg resistance coefficients. Figs. 3A and B show the EIS spectra of the DSSC obtained with the addition of different inorganic iodides and organic iodides, respectively, and the corresponding values of R_{ct1} and R_{ct2} of the DSSC obtained from the spectra are tabulated (Table 1). The solid line shows the experimental curve, while straight line corresponds to the fitting. From the table, it is understandable that both the J_{SC} and the conversion efficiency of the DSSC depend strongly on R_{ct1} and R_{ct2} values. As shown in the Table 1 and Fig. 3, the charge transfer resistances along the Pt and TiO_2 /solvent interfaces (R_{ct1} and R_{ct2}) increase from Li^+ to K^+ and TBA^+ to TEA^+ ionic species and hence, the performance of the DSSC decreases.

3.3. Effect of different solvents

The dependence of the MPII concentration in different solvents vs. the corresponding ionic conductivity is shown in Fig. 4 and for comparison, 0.6 M of MPII/AN is also included. Among the different solvents, 1.3 M of MPII in DMF showed high conductivity next to AN. In others solvents such as MPN, GBL, DMF and DMSO, the MPII exhibited almost the same conductivity (an average of 13.1 mS cm^{-1} at 1.3 M of MPII) and in PC, the least conductivity of 9.6 mS cm^{-1} was observed (Fig. 4).

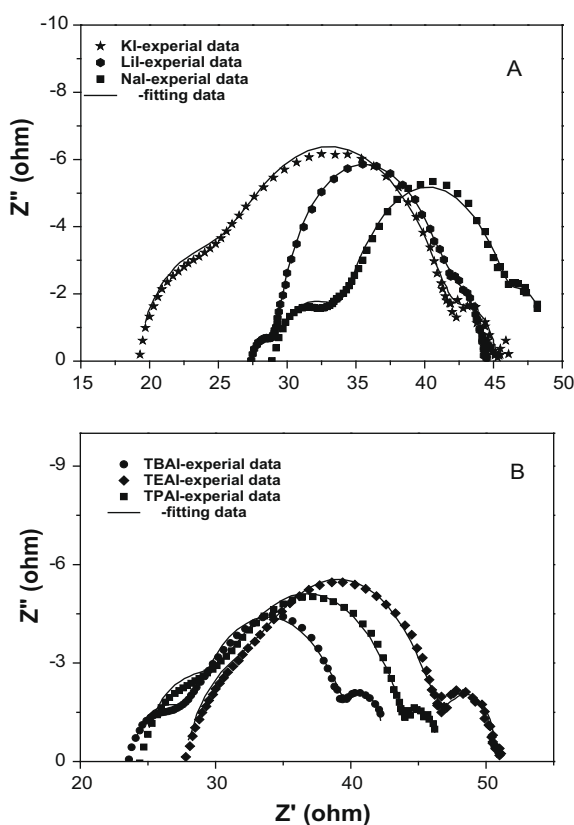


Fig. 3. EIS plots of the DSSC containing (A) inorganic iodides and (B) organic iodides and the other conditions are the same as in Fig. 2.

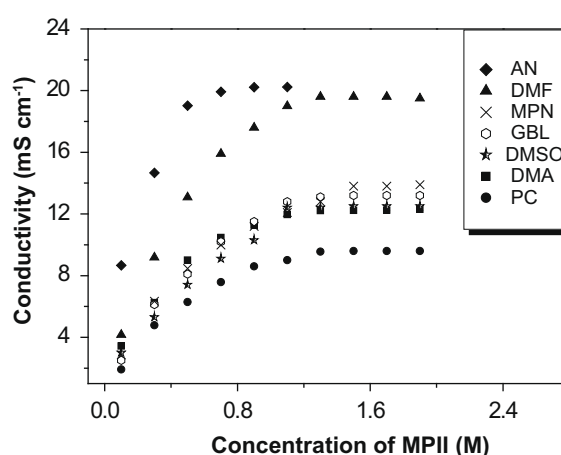


Fig. 4. The relationship between the ionic conductivities and concentrations of MPII in different solvents at 25 °C.

Fig. 5 shows the steady-state cyclic voltammograms (CV) of the Pt micro electrode in AN containing 0.6 M of MPII/0.06 M of I_2 and other solvents containing 1.3 M/0.13 M of I_2 . The D_{app} values of I^- and I_3^- obtained from the CV were tabulated (Table 2). The method of calculations of D_{app} values for I^- and I_3^- has already been described in Section 3.1. Once again, in AN, high D_{app} values for both I^- and I_3^- were observed and the other solvents such as DMF, MPN, GBL, DMA and DMSO had approximately identical D_{app} values (an average D_{app} value $4.72 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$). The lowest D_{app} value was found out in PC.

Table 3 shows the different photovoltaic parameters of the DSSC containing MPII in different solvents with other additives of optimal concentrations. Naturally, the DSSC containing MPII/AN showed highest performance among the others solvents in terms of their J_{SC} (12.6 mA cm^{-2}), V_{OC} (0.73 V) and conversion efficiency ($\eta = 5.98$) whereas in other solvents, the performance decreases in the order: GBL > MPN > PC > DMA. Surprisingly, in the case of DMF and DMSO, the total performance was very low ($\eta = 1.13$ and 1.37%, respectively).

The dependences of the J_{SC} against various factors such as donor number of solvents, conductivity and diffusion coefficients of MPII measured in the above solvents are shown in Fig. 6A–C, respectively. A better correlation is found out between the donor number of solvents and the J_{SC} of the DSSC containing these solvents rather than the diffusion coefficient and conductivity of MPII measured in

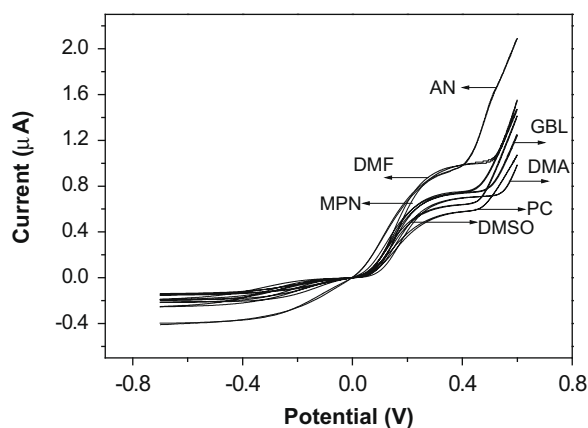


Fig. 5. Steady-state voltammograms of MPII in different solvents at a scan rate of 0.05 mV s^{-1} ; the condition is $[I^- : I_3^-] = 10 : 1$.

Table 2
Apparent diffusion coefficient of triiodide and iodide ions in different solvents.

(MPII + LiI)/I ₂ in different solvents	Diffusion coefficient of I ⁻ (10 ⁻⁶ cm ² s ⁻¹)	Diffusion coefficient of I ₃ ⁻ (10 ⁻⁶ cm ² s ⁻¹)
AN	9.12	4.40
DMF	5.85	1.00
MPN	4.48	1.01
GBL	4.42	1.00
DMA	4.13	0.69
DMSO	3.79	0.67
PC	2.73	0.66

Table 3
Photovoltaic performances of the DSSCs containing MPII in different solvents. The conditions are I⁻/I₃⁻ = 10/1, LiI = 0.2 M and TBP = 0.5 M.

Solvents	V _{OC} (V)	J _{SC} (mA cm ⁻²)	FF	η (%)
AN	0.73	12.6	0.65	5.98
GBL	0.73	12.0	0.66	5.80
MPN	0.65	11.6	0.65	5.01
PC	0.67	10.3	0.61	4.22
DMA	0.69	5.72	0.69	2.65
DMSO	0.70	3.18	0.63	1.37
DMF	0.66	3.12	0.55	1.13

different solvents. This reveals that higher the donor number of solvents, lesser will be the conversion efficiencies of the DSSC.

Fig. 7A shows the typical EIS spectroscopy of the DSSC containing AN, MPN, GBL, PC and DMA and Fig. 7B for DMSO and DMF. The

solid line shows the experimental curve, while straight line corresponds to the fitting. For convenience and clarity, all the impedance plots taken had been overlapped and put together under the same value of the R_s , corresponding to the lowest R_s value of a DSSC. The obtained R_{ct1} (charge transfer resistance across Pt/electrolyte-solvent interface) values of the DSSC containing different solvents were almost identical; however, R_{ct2} values (charge transfer resistance across TiO₂/electrolyte-solvent interface) of the DSSCs containing the two solvents (DMF and DMSO) varied significantly. Fig. 8 shows the plot of R_{ct2} values of DSSC against their conversion efficiency η (%) for different solvents. From the figure, once again it is confirmed that the η (%) values of the DSSC greatly depend on the R_{ct2} values of the DSSC and the increase of the R_{ct2} values of the DSSC containing the solvents, particularly, for DMF and DMSO, was very much higher than the other solvents. The reason for this anomalous behavior may be correlated with the presence of solvent-dye interaction on the surface of the TiO₂ photoelectrode.

In order to characterize such interaction, dye immobilized TiO₂ electrodes were washed repeatedly with AN till the excess dye had been removed and each electrode was dipped separately in 2 ml of the solvents (DMSO, DMF and DMA) for one hour and the absorption spectra of these solvents were recorded immediately. Surprisingly, UV-visible spectra taken for these solvents showed absorption characteristics for the N3 dye molecules, which revealed that the solvent molecules desorbed the N3 dye molecule from the surface of the TiO₂ to some extent. The intensity of the absorption spectra reveals that the desorption characteristics follows the order: DMSO > DMF > DMA. The study indicates that both

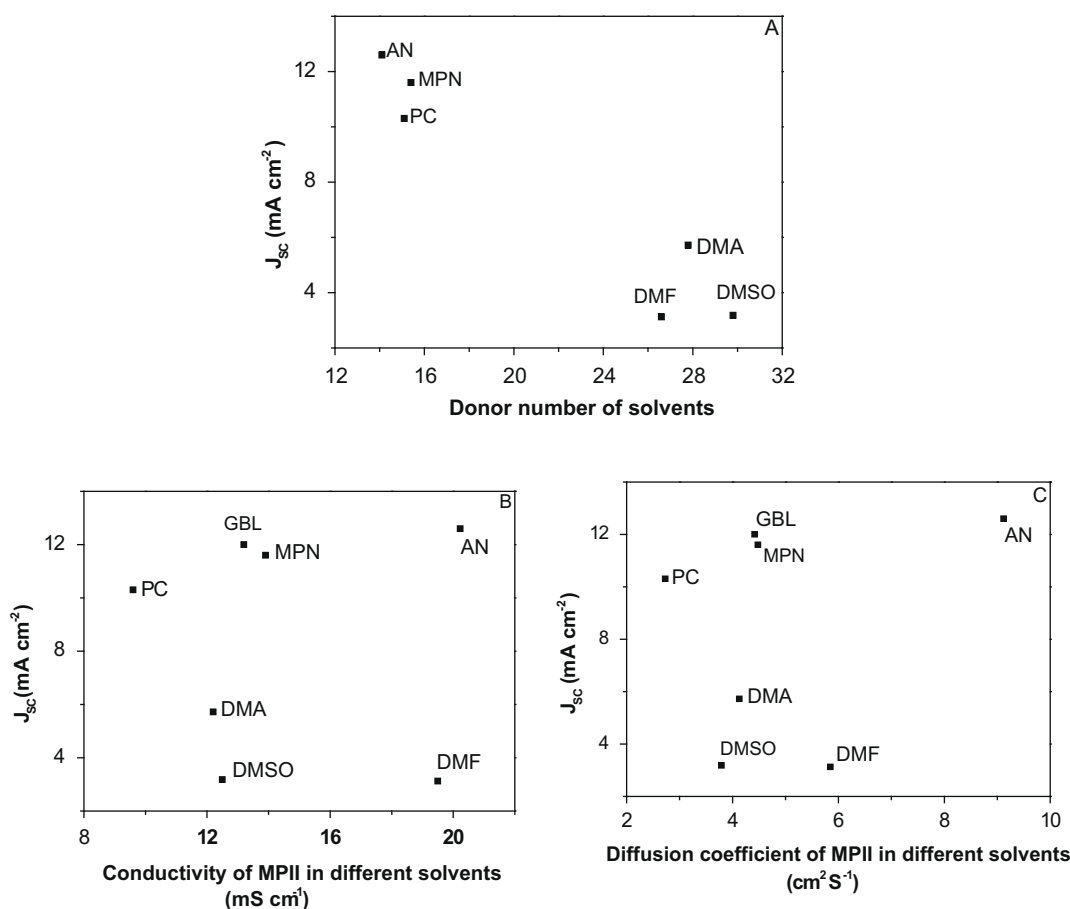


Fig. 6. Dependence of J_{sc} of the DSSC with (A) donor number of solvents (B) conductivity and (C) diffusion coefficient of MPII in different solvents; the conditions are the same as in Fig. 2.

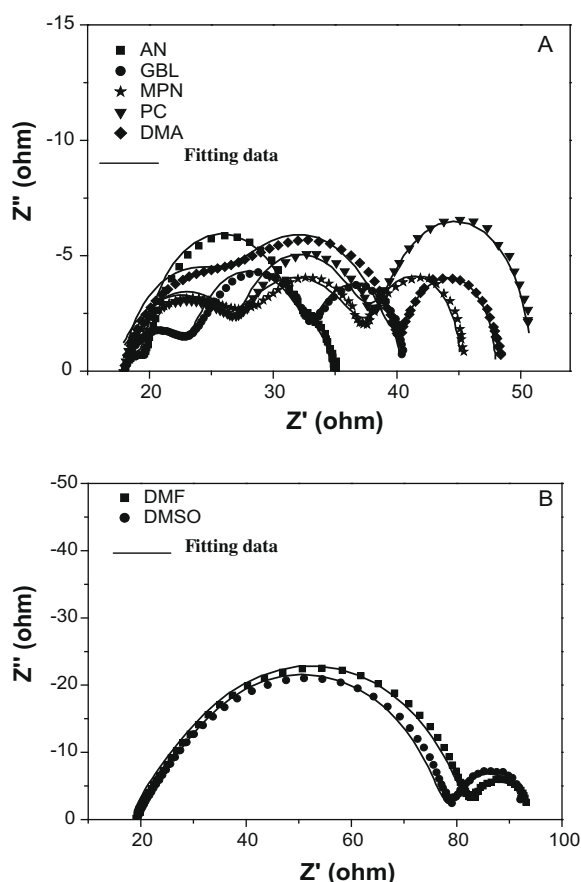


Fig. 7. EIS plots of the DSSC containing MPII in (A) AN, GBL, MPN, PC and DMA. (B) DMF and DMSO; the conditions are the same as in Fig. 2.

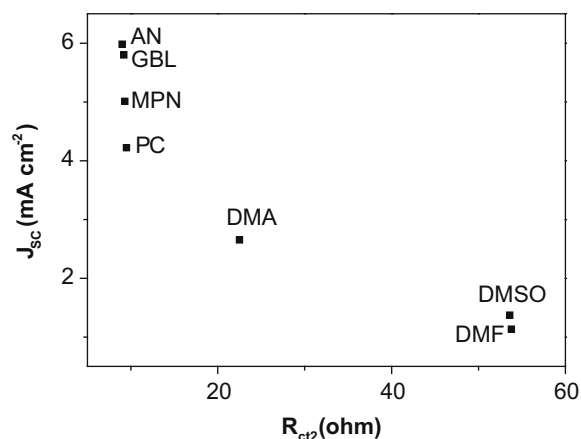


Fig. 8. Plot of R_{ct2} vs. J_{sc} of the DSSCs containing MPII in different solvents.

the donor number and desorption properties of the solvents play an important role in tuning the performance of the DSSC [36].

The scattering of light increases the path length of the photon inside the cell and increases the probability to interact with the dye molecule in the red light region where the dye is not efficient [4]. The DSSC containing the electrolyte composition (0.6 M of MPII, 0.2 M of LiI, 0.06 M of I_2 , 0.5 M of TBP in CH_3CN) incorporated with light scattering particles (TiO_2 of 300 nm) under AM 1.5 irradiation (100 mW cm^{-2}) shows a high solar energy-conversion efficiency of 6.7% along with J_{sc} of 14.8 mA cm^{-2} , V_{oc} of 0.74 V and fill factor (FF) 0.62. Further studies are in progress in order to under-

stand the detailed mechanism involving the use of the solvents in the DSSC.

4. Conclusions

The effects of addition of redox electrolyte (I^-/I_3^-), different additives and solvents on the solar cell performance of the DSSC containing MPII were investigated. The J_{sc} of the DSSC containing 0.6 M of MPII/AN varied with different concentrations of I_2 and diffusion coefficient of I_3^- played an important role in directing the performance of the DSSC. The performance of the DSSCs with the incorporation of different additives decreases in the order: LiI > NaI > KI; and TBAI > TPAI > TEAI. The DSSC performance depended strongly on the nature of the solvent. The AN containing MPII had highest diffusion coefficient and conductivity than the other solvents and the performance of the DSSCs containing the different solvents decreases in the order: AN > GBL > MPN > PC > DMA > DMSO > DMF. Better correlation was found out between J_{sc} of the DSSC containing different solvents and the donor number rather than the measured conductivity and diffusion coefficient of the MPII in different solvents. The reason for the low performance of the DSSC containing DMA, DMSO and DMF could be ascribed with high R_{ct2} values, as noted from EIS studies and this may be correlated with the desorption of dye molecules by these solvents. A high solar energy-conversion efficiency of 6.7% was attained for the DSSC incorporated with light scattering particles (TiO_2 of 300 nm) containing MPII in AN under AM 1.5 irradiation (100 mW cm^{-2}).

Acknowledgements

The authors appreciate the financial support provided by Academia Sinica, Taipei, Taiwan, under Grant AS-97-TP-A08. This work was also partially supported by the National Science Council (NSC) of Taiwan. The author also thanks Director, CECRI, Karaikudi for his keen encouragement of this work.

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