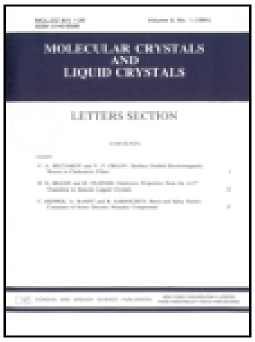

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Effect of Iodine Concentration in the Quasi-Solid State Electrolyte on the Photovoltaic Performance of Dye-Sensitized Solar Cells

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In the present study, the effect of iodine concentration on the photovoltaic properties of dye sensitized solar cells (DSSCs) based on the quasi-solid state electrolyte has been investigated. The electron transport properties and interfacial recombination kinetics have been evaluated by electrochemical impedance spectroscopy (EIS). It is found that increasing the concentration of iodine decreases the open-circuit voltage (Voc) whereas short circuit current density (Jsc) and fill factor (FF) shows improvement. The increment in Jsc for 0.05 M I_2 concentration is ascribed to the decreased charge transfer resistance value obtained by EIS analysis. In addition increasing the concentration of I_2 decreases the Voc which is attributed to the increased recombination with tri-iodide ions (I_3^-) as verified from the EIS analysis under dark condition.

Keywords Dye-sensitized solar cells; iodide/triiodide; photovoltage; exchange photocurrentdensity; photovoltaic performance.

Introduction

In recent years, search for renewable energy has received worldwide attention owing to the fast depletion of fossil fuel reserves and environmental pollution problems accompanying fossil fuel consumption. Since Grätzel made breakthrough in 1991 [1], dye-sensitized solar cells (DSSCs) have attracted considerable academic and industrial interest due to easy fabrication and their potential of low production costs, in contrast to conventional inorganic photovoltaic devices. DSSC mainly consist of four components: dye sensitizer, TiO_2 nano crystallites, a counter electrode and an electrolyte [iodide (I^-)/tri-iodide (I_3^-)]. Upon light irradiation, the sensitizer molecules get excited and the electrons are injected into the conduction band of TiO_2. The injected photoelectrons diffuse in TiO_2 semiconductor and reach the outer circuit through the back contact. The photo-oxidized dyes are regenerated by I^- ions resulting in the formation of I_3^- ions. Subsequently, oxidized component of the electrolyte redox couple (I_3^-) is reduced by the electrons reaching the counter electrode

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through the external circuit. In the device the charge-transfer process has to be controlled so that the photo-injected electrons do not recombine with acceptors but are transferred to the external circuit.

Up to now, the highest power conversion efficiencies for DSSCs have been achieved by using electrolytes based on volatile organic solvents [2–4]. However, the problems associated with the liquid electrolyte systems, such as desorption and degradation of the dye sensitizers, corrosion of the platinum counter electrode and more importantly the leakage and volatilization of the liquid solvent have blocked the commercial application of the DSSCs. Thus, solid state and quasi-solid state electrolytes have been proposed as alternatives to the liquid electrolytes.

Many groups have investigated the effect of electrolyte on the photovoltaic properties of DSSC, such as, redox species on interfacial energetics [5], the effect of adsorbed cations and I_2 on the back electron transfer of nano crystalline TiO_2 [6], the role of electrolyte on recombination kinetics of DSSC [7], the effect of different types of mixed solvents, [8], the charge recombination between TiO_2 electrode and the redox couple [9], the effect of electrolyte additives on the recombination kinetics of DSSC [10].

In this paper we have studied the effect of I_2 concentration on the photovoltaic properties of DSSCs for quasi-solid state electrolyte in acetonitrile using poly(vinylidenefluoride-*co*-hexafluoropropylene) [PVDF-HFV] as gelator. The effect of variation in the I_2 concentration on electron transfer process, and diffusion coefficient are studied through electrochemical impedance spectroscopy and stepped light-induced transient measurements (SLIM) analysis, respectively.

Experiment Details

Materials and Fabrication of the Quasi-solid State DSSC

4-*tert*-Butylpyridine (tBP), iodine (I_2), 1,2-Dimethyl-3-propylimidazolium iodide (PMII), 1-Butyl-3-methylimidazolium iodide (BMII), poly(vinylidenefluoride-*co*-hexafluoropropylene) [PVDF-HFP] and solvents were used as received from Sigma-Aldrich and TCI.

FTO was glass cleaned by sequential sonication in methanol, distilled water and acetone. A thin first layer of TiO_2 was deposited by "doctor-blade" technique. The film was dried at 70°C for 30 min, followed by heating to 450°C for 30 min. Then, a second layer of 200 nm-sized light scattering particles was coated on the top of the first layer, also followed by heating to 450°C for 30 min. The electrodes were treated in 40 mM $TiCl_4$ solution at 70°C for 30 min, then rinsing in distilled water and heated at 450°C for 30 min. The TiO_2 electrodes were immersed in a 0.3 mM solution of **N**719 in ethanol at room temperature for 24 h before being removed and rinsed in ethanol immediately before cell fabrication. Cells were fabricated by sandwiching the sensitized TiO_2 electrode and a thermally platinized FTO counter electrode together with a hot-melt polymer (Surlyn, 60 μm). The electrolyte contains 0.01/0.05/0.1 M I_2, 0.5 M 4-*tert*-butylpyridine, 0.5 M 1,2-dimethyl-3-propylimidazolium iodide and 0.3 M 1-butyl-3-methylimidazolium iodide in acetonitrile. Herein, a polymer, poly(vinylidenefluoride-*co*-hexafluoropropylene) was used to solidify a acetonitrile-based liquid electrolyte to prepare a quasi-solid state electrolyte for DSSCs.

Transient measurements were performed by a same method to O'Regan et al. [11] and as illustrated elsewhere [12]: a white light bias was generated from an array of diodes (Abet, LS Series light source) with red-light pulsed diodes (Thorlabs HNL210L system) as

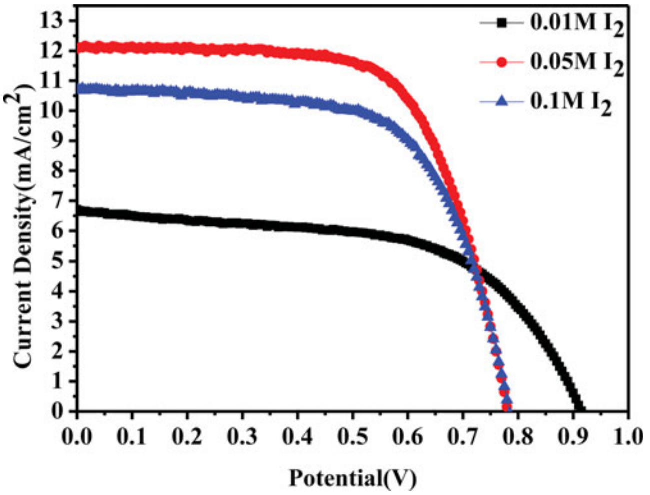

Figure 1. Currentdensity-voltage (J-V) curves for DSSCs based on different I_2 concentrations.

the perturbation source, controlled by a fast solid-state switch. The voltage dynamics were measured on a 1 GHz Tektronix oscilloscope (DPO4102B-L) across the high impedance (1 MΩ) port. The perturbation light source was set to a suitably low level such that the voltage decay kinetics were mono-exponential. Small perturbation transient photocurrent measurements were performed in a similar manner to the open-circuit voltage decay measurement. For the voltage decay measurements in the short-circuit regime, a Keithley 2600B source meter was connected in series with the solar cell and parallel with the oscilloscope which was set on the high impedance port. The Keithley sourced the current through the solar cell which was under bias illumination in such a way that the voltage was kept at 0 V (i.e., short-circuit). In this way no extra current is allowed to flow through the device following the light pulse, therefore the decay of the measured perturbation signal is entirely governed by the charge recombination within the cell. For the current decay measurements, while the charge is being collected the charges are also simultaneously recombining within the cell.

Thus the transient measurements were performed on stepwise light induced transient measurements (SLIM-PCV) and photocurrent voltage measurements measurements and then obtained using opti data then applied into the photo

The photocurrent-voltage measurement was performed using a Keithley model 2400 Source Meter and a Newport 91192 solar simulator system (equipped with a 1 kW xenon arc lamp, Oriel). Light intensity was adjusted to 1 sun (100 mW/cm^2) with a Radiant Power

Table 1. Photovoltaic parameters of DSSCs at various I_2 concentrations in the quasi-solid state electrolyte

[I_2] (M)	Jsc(mA/cm^2)	Voc(V)	F.F(%)	η (%)
0.01M	6.71	0.92	59.36	3.48
0.05M	12.07	0.78	64.53	6.11
0.1M	10.71	0.78	64.31	5.34

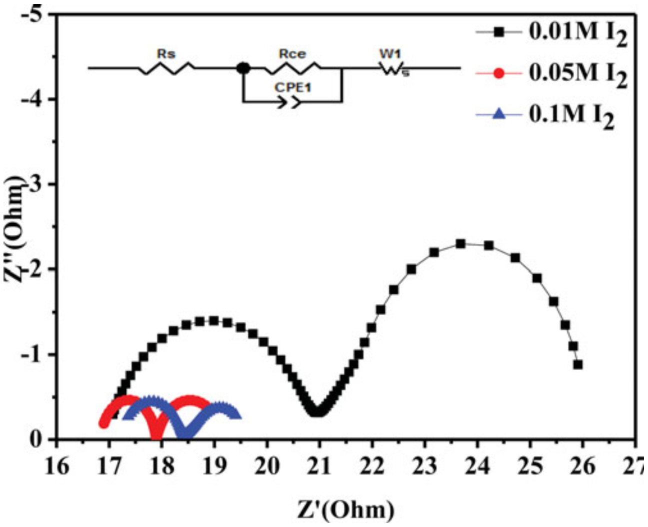

Figure 2. Conductivity measurements for DSSCs based on different I_2 concentrations using electrochemical impedance analysis.

Energy Meter (model 70260, Oriel). The incident photon-to-current conversion efficiency (IPCE) results were acquired from IPCE G1218a (PV Measurement). This system applies monochromatic light from a 75 W xenon arc lamp (Ushio UXL-75XE) filtered by a dual-grafting monochromator and individual filters onto the test devices. An ellipsoidal reflector collects light from the lamp and focuses on the monochromatic entrance slit via a mechanical chopper to create a small modulated signal. While the modulated, monochromatic light was applied to the test devices, a continuous bias light (ca. 1 sun) was also applied. Electrochemical impedance spectroscopy (EIS) was performed using an electronic-chemical analyzer (Iviumstat Tec.) and the data were recorded under forward bias condition from 10 kHz to 100 mHz with an A.C amplitude of 10 mV. Data were recorded under dark and A.M 1.5 illumination conditions applying corresponding open circuit potential (Voc) for each electrode. The impedance measurements were carried out under forward bias of −0.70 V in the dark. The data were analyzed using Zview2 commercial software (Scribner Associates Inc.). The conductivity of the electrolyte system was derived from the complex impedance measurements.

Results and Discussions

The role of the iodide (I^-) in the redox couple in a DSSC is to regenerate the oxidized dye by electron donation according to the reaction: $3I^- + 2D^+ \rightarrow 2D + I_3^-$ (D = Dye

Table 2. Conductivity analysis at various I_2 concentrations

$[I_2]$ (M)	R1(Ohm)	R2(Ohm)	W1-R(Ohm)	Conductivity
0.01M	16.94	3.84	5.22	1.20E-05
0.05M	16.84	1.01	1.15	5.45E-05
0.1M	17.06	1.20	1.24	5.06E-05

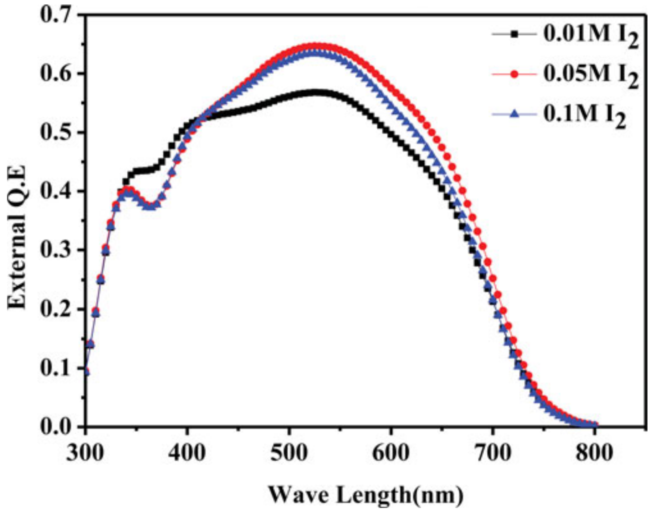

Figure 3. IPCE curves of DSSCs employing different concentrations of I_2.

sensitizer). At the counter electrode the tri-iodide (I_3^-) is reduced to I^- ($I_3^- + 2e \longrightarrow 3I^-$). Therefore, physical diffusion of I^- and especially of I_3^- in the redox couple is an essential parameter that can impact the performance of DSSC. This process becomes often a limiting process in a DSSC with quasi-solid state or ionic liquid based electrolytes, particularly, if the I_2 concentration and consequently the I_3^- concentration is low. Besides, at high I_2 concentration the diffusion of I_3^- does not limit the performance of DSSC, but stimulates recombination reactions in DSSC. The recombination mainly occurs at the interface of TiO_2/electrolyte, where the excited electrons react with the oxidized electrolyte (I_3^-). If the recombinations are fast, they become the governing process in DSSC. In this direction, the DSSC based different iodine concentrations have been assembled. Their

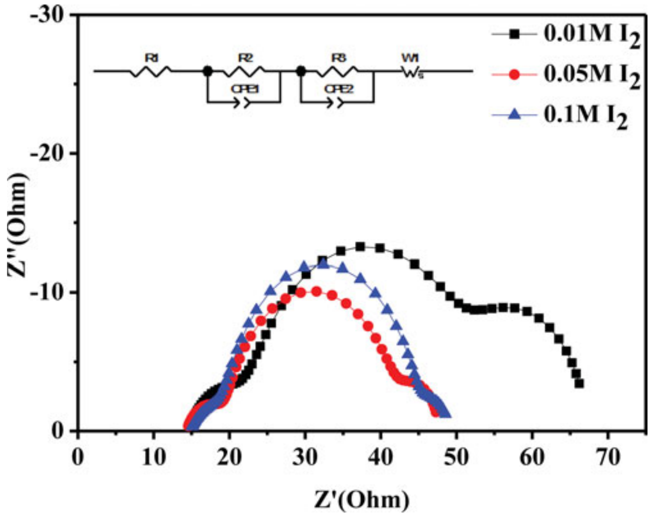

Figure 4. Nyquist plots showing the effect of I_2 concentration under illumination condition.

Table 3. EIS analysis at various I_2 concentrations under illumination condition

$[I_2]$ (M)	R1(Ohm)	R2(Ohm)	R3(Ohm)
0.01M	14.70	7.67	25.39
0.05M	14.38	5.25	21.34
0.1M	14.79	5.35	23.87

current density to voltage characteristics (J-V) under 1 sun illumination are presented in Fig. 1.

Table 1 shows the photovoltaic behaviors of DSSC containing different concentration of I_2. It can be seen that the cell efficiency and current density (Jsc) increase on addition of a small quantity of I_2 (Fig. 1 and Table 1). When the concentration of I_2 is 0.01 M in the quasi-solid state electrolyte, the cell efficiency 3.48%. Jsc increases with increasing concentration of I_2 up to 0.05 M, where a power conversion efficiency of 6.1% is achieved. However, device efficiency and Jsc decreases for I_2 concentration greater than 0.05 M due to increased recombination in the device. Another reason may be that the higher concentration of I_2 absorbs some of the incident light, thus lowering the light absorption of the dye sensitizer. It is thus evident that there exists an optimum concentration of I_2 below or above which the quasi-solid electrolyte loses its optimum performance. The increase in the Jsc values as more I_2 is added into the electrolyte may be a direct result of increased conductivity of the redox electrolyte (Fig. 2 and Table 2). This could be a consequence of increased mobility of the redox species in the quasi-solid state electrolyte. The conductivity of the electrolytes (σ) is derived from the complex impedance measurements using: $\sigma = L/R_mA$; where R_m is the resistance determined from the equivalent circuit obtained from the EIS spectra, L is the thickness of the film, and A is the area of the sample.

Incident photon-to-current efficiency (IPCE) is a useful method to evaluate the light absorption in the DSSC device. The IPCE action spectra of the DSSCs are shown Fig. 3.

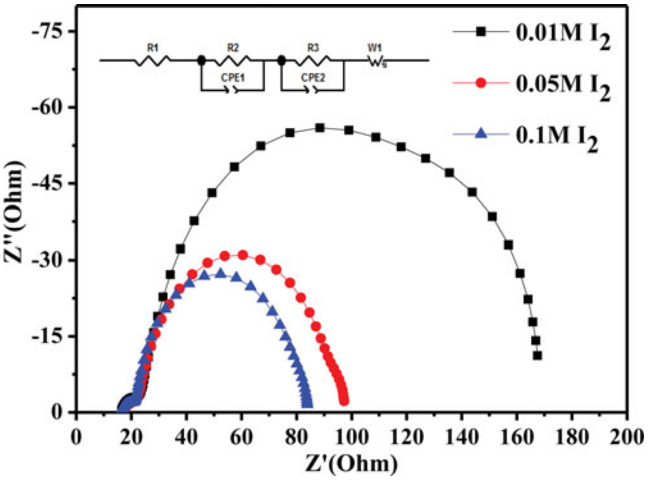

Figure 5. Nyquist plots showing the effect of I_2 concentration under dark condition.

Table 4. EIS analysis at various I_2 concentrations under dark condition

$[I_2]$ (M)	R1(Ohm)	R2(Ohm)	R3(Ohm)
0.01M	16.38	6.723	95.93
0.05M	17.09	6.293	68.89
0.1M	16.13	5.893	56.70

IPCE obtained for the higher I_2 content added electrolyte is higher than that with lower I_2 content electrolyte in the wavelength region of 440–700 nm. But, decreased absorption below the 400 nm regions is observed for the higher I_2 content electrolyte, which could be due to the light absorption of iodine in that region. However, the evidence of the improvement in IPCE further confirms the higher Jsc achieved for the moderate iodine content electrolyte.

The variation of photovoltage is shown in Fig. 1 and Table 1. As increasing the concentration of I_2 decreases the Voc. In general, in DSSC the Voc is controlled mainly by the recombination process occurring at TiO_2/electrolyte interface. There are mainly two recombination reactions at the interface. The electrons in the conduction-band of TiO_2 injected from the excited dye molecules may recombine with oxidized dye molecules (D^+) or react with redox species in the electrolyte (I_3^-). If the electrolyte contains sufficient amount of I^- ions, the rate of reduction of the ionized dye molecules by I^- ions, will be fast and hence the contribution of this energy-loss channel to the recombination current can usually be ignored [13]. The net recombination process, controlling the photo voltage in DSSC is represented by the reaction

$2e^-$(TiO_2 conduction band) + I_3^- (electrolyte) → $3I^-$ The Voc in DSSC is represented as [9]:

$$Voc = \frac{kt}{q} In(\eta\Phi_0|n_0k_{et}[I_3^-]) \tag{1}$$

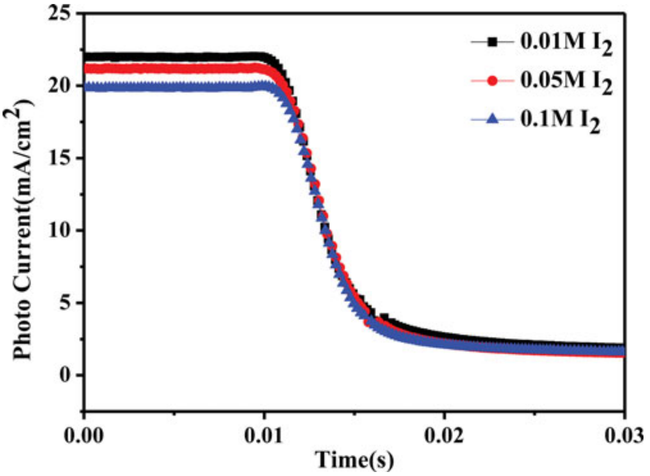

Figure 6. Typical current responses of DSSCs against the different stepped laser intensities.

Table 5. SLIM-PCV analysis at various I_2 concentrations

$[I_2]$ (M)	D(cm^2/s)	L(μm)
0.01M	4.31E-05	16
0.05M	6.37E-05	23.2
0.1M	5.35E-05	20.1

where k is the Boltzmann constant, q is the magnitude of the electron charge, T is the absolute temperature, η is the quantum yield for photogenerated electrons, Φ_0 is the incident photon flux, n_0 is the electron density on the conduction band of the TiO_2 in the dark, k_{et} is the rate constant for recombination, and $[I_3^-]$ is the concentration of I_3^- in solution. I_3^- is formed instantaneously when I_2 is added in solution which contains I^- *via* the equation $I^- + I_2 \rightarrow I_3^-$. Apparently, from eq 1, Voc increases as $[I_3^-]$ decreases; this is consistent to the J-V parameters listed in Table 1.

To understand the fate of the photogenerated electrons, detailed electrochemical impedance spectroscopy was performed on the DSSCs fabricated using these systems. Nyquist plots of the DSSCs measured under illumination and dark conditions are displayed in Fig. 4 (Table 3) and Fig. 5 (Table 4), and display three semicircles for all DSSCs. R1 is the series resistance, R2 is the resistance of electron transport in the counter electrode and R3 is the electron transfer/recombination resistance between the TiO_2 film and electrolyte.

The values of charge transfer resistance (R3) obtained under illumination condition for three different I_2 concentration are in the order of 0.01 M $>$ 0.1 M $>$ 0.05 M. Clearly lower R3 values were obtained for the device with 0.05 M $[I_2]$. The increase of $[I_2]$ from 0.01 to 0.05 M decreased the electron transfer resistance. However, further increasing the $[I_2]$ resulted in increased electron transfer resistance. For 0.05 M $[I_2]$, the value of R3 was 21.34 Ω, whereas the R3 value of 0.01 and 0.1 M were 25.39 and 23.87 Ω, respectively. The decrease of R3 value would result in the better performance, i.e., photoregeneration is more efficient. The fitting data of EIS agreed well with the cell efficiency shown in Fig. 1 and Table 1. To understand the Voc values EIS was measured under dark condition and results were summarized in Fig. 5 and Table 4. The value of recombination resistance (R3) under dark condition for three different I_2 concentrations are in the order 0.01 M $>$ 0.05 M $>$ 0.1 M. Clearly higher R3 values obtained for the device with 0.01 M I_2 concentration. The increase of I_2 concentration from 0.01 to 0.1 M decreased the recombination resistance. For 0.01 M $[I_2]$, the value of R3 was 95.93 Ω, whereas the R3 value of 0.05 and 0.1 M were 68.89 and 56.7 Ω, respectively. The decrease of R3 would result in the decrease of photovoltage values. The fitting data of EIS agreed with the photovoltage values shown in Fig. 1 and Table 1, which is in agreement with the literature results [14, 15].

The electron diffusion length (L_n) is a useful tool to reflect the electron collection efficiency (η_c). Typical photocurrent transients from the stepped light-induced transient (SLIM) measurements for DSSCs are shown in Fig. 6 and Table 5. L_n values of 23.2, and 20.1 μm were obtained for the 0.05, and 0.1 M- based devices, respectively, which are higher than the 0.01 M based device (16 μm), implying that electron collection is efficient in concentrated iodine based devices. These results agree with the variation in current density of the corresponding cells.

Conclusions

In summary the effect of I_2 concentration on the photovoltaic properties of dye sensitized solar cell based on TiO_2 nanoparticles is studied. It is found that the Voc decreases with increase in the I_2 concentration whereas Jsc and FF increases initially and decreases for iodine concentration above 0.05 M. From electrochemical impedance spectroscopy, it is found that the charge transfer resistance (R3) decreases with an increase in concentration of I_2 which accounts for the increase in current density (Jsc). SLIM results indicate improved electron collection efficiency with the increase in I_2 concentration. In addition using EIS under dark condition it is found that the recombination reaction rate increases with an increase in I_2 concentration which account for decrease in photovoltage (Voc).

Acknowledgment

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