

Impact of 4-Tertiary-butylpyridine in Imidazolium Iodide/Triiodide Redox Couple-Based Dye-Sensitized Solar Cells

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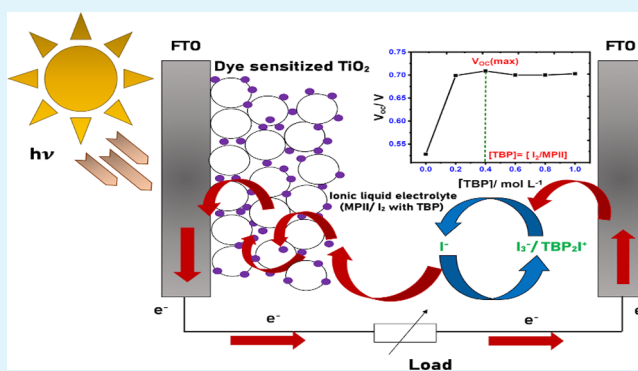
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ABSTRACT: The effect of 4-tertiary-butylpyridine (TBP) in improving the performance of imidazolium iodide/triiodide redox couple-based dye-sensitized solar cells (DSCs) is studied. The presence of N–I–N vibration is detected in the FT-IR spectrum, and the formation of TBT_2I^+ ion is predicted. The increased TBT_2I^+ concentration helps increase the transport number of iodide ions and consequently the ionic conductivity of the electrolyte. It is found that when TBP is introduced to a DSC utilizing 1-methyl-3-propylimidazolium iodide, the open-circuit voltage (V_{OC}), short-circuit current density (J_{SC}), and conversion efficiency (η) are significantly increased until the formal concentrations of TBP and triiodide ions are equal, beyond which the values are slightly lower. Increase in V_{OC} is due to the mixed potential of I^-/I_3^- and $\text{I}^-/\text{TBT}_2\text{I}^+$ redox couples and the maximum value at $[\text{TBP}] = [\text{I}_3^-]$ is due to the presence of only the $\text{I}^-/\text{TBT}_2\text{I}^+$ redox couple. Increase in J_{SC} is due to decreased recombination because of surface passivation by the adsorbed TBP molecules and increased ionic conductivity of the electrolyte. Consequently, maximum values are obtained when $[\text{TBP}] = [\text{I}_3^-]$, beyond which excess TBP tends to give slightly lower constant values. This is due to increased series resistance by the passivated TiO_2 surface. The mechanism proposed based on the chemistry of TBP and I_2 accounts for all the effects observed. The optimized DSC shows a conversion efficiency of 7.94%, with a high V_{OC} of 0.709 V and J_{SC} of 17.22 mA cm^{-2} , where the conversion efficiency has been increased by 35% from 5.15% when TBP is not present to 7.94% at this optimum TBP formal concentration.

KEYWORDS: ionic liquid dye-sensitized solar cell, 4-tertiary-butylpyridine, increased open circuit voltage, increased short circuit current density, increased conversion efficiency, increased ionic conductivity of electrolyte



INTRODUCTION

Current studies on dye-sensitized solar cells (DSCs) are mainly focused on developing low-cost and high-performance cells that utilize simple techniques for their fabrication. Liquid electrolytes used in ordinary DSCs are usually composed of a redox couple, additives, and a polar organic solvent such as acetonitrile. Low boiling points and high vapor pressures of organic solvents limit the long-term stability of DSCs. Concurrently, leakage of the solvent can completely dry the DSC, leading to the termination of the function of the solar cell. Therefore, attempts have been made to find alternatives to the currently used toxic and volatile solvents. Ionic liquids or low-temperature molten salts are defined as liquid electrolytes made up of ionic charge carriers.¹ Ionic liquids with a low melting point, below 100 °C, and reasonably low viscosity can freely flow at room temperature and are known as room-temperature ionic liquids (RTILs). RTIL electrolytes have several attractive characteristics such as good chemical and thermal stability, insignificant vapor pressure, nonflammability,

high ionic conductivity, and excellent environment compatibility.² They serve both as a source of redox couple and the solvent when integrated into DSCs. Ionic liquids are composed of organic cations linked with inorganic anions or organic anions and exist in the liquid state at room temperature. Papageorgiou et al., in 1996, reported long-term stable DSCs based on ionic liquid electrolytes and showed that when methyl-hexyl-imidazolium iodide is used as an involatile electrolyte, an assessed sensitizer redox turnover number over 50 million could be obtained.³ Thereafter, imidazolium salts and other ionic liquids have been extensively used as

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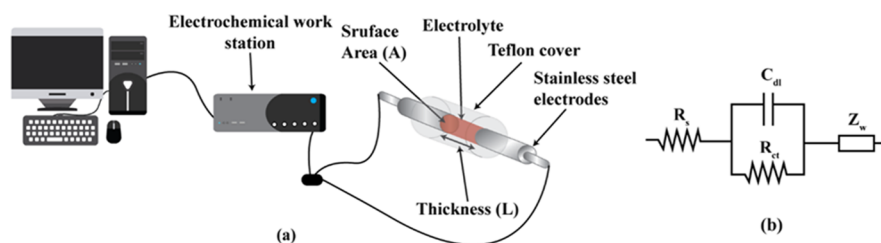


Figure 1. (a) Experimental setup used for the impedance studies of ionic liquid electrolytes with and without 4-tertiary-butylpyridine and (b) proposed equivalence circuit representing the Randles circuit.

electrolytes in DSCs. Wang et al. achieved an unprecedented efficiency of 7.5–8.3% for the ionic liquid 1-ethyl-3-methylimidazolium selenocyanate, though the long-term stability of this system was not very promising.⁴ The efficient ionic liquid electrolytes commonly used for electrochemical applications are based on imidazolium cations.⁵ Other ionic liquids containing cations such as sulfonium, guanidinium, ammonium, pyridinium, and phosphonium have also been discovered as solvent-free electrolytes.^{6–9} However, due to high viscosity and mass-transport limitations, DSCs with these ionic liquids show low photocurrents and low conversion efficiencies. Xi et al. acquired high power conversion efficiencies of ~7% using a high-fluidity tetra-hydrothiophenium melt in DSCs, thus proving that nonimidazolium ionic liquids can also give high efficiencies.¹⁰ The photoelectrochemical properties of ionic liquids rely on the nature of the cation and the anion. The cations in ionic liquids are weak Lewis acids with electron-rich species. The halides/pseudohalides are famous Lewis bases that can connect with sensitizers allowing ligand exchange. However, other kinds of often-used cations are relatively weak Lewis bases. Son et al. discovered that when the cation of the ionic liquid is smaller, the diffusion coefficient of tri-iodide ions is larger and the consequent photocurrents of the DSCs are higher. They have also shown that larger cations contribute to enhanced photovoltage (V_{OC}). As such, the proper choice of cation and anion to give the right combination will have an important influence on the DSC performance.^{11,12} However, fairly high viscosity of ionic liquids leads to mass-transport limitations. The low-viscosity ionic liquids evade this limitation and the consequent photocurrent and fill factor (FF) losses.

Ionic liquids consisting of imidazolium salts have been commonly used as solvents for DSCs.^{13–16} Among these, 1-methyl-3-propylimidazolium iodide (MPII) has the lowest viscosity for room-temperature iodide salts. Efficient ionic liquids can be created by doping MPII with iodine.¹⁷ Likewise, some additives are used in liquid electrolytes for further optimization of the photovoltaic performance of DSCs. Even a small amount of electrolyte additives could improve the photovoltaic parameters by suppressing recombination losses. In 1993, Gratzel et al. first used 4-tertiary-butylpyridine (TBP) as an additive in the electrolyte and showed a significant improvement of V_{OC} .¹⁸ Thereafter, nitrogen-containing heterocyclic compounds, such as analogues and derivatives of pyridine, have been examined as additives in liquid electrolytes. As these nitrogen-containing heterocyclic compounds presented equivalent results to TBP, they are frequently used as additives in electrolytes in order to increase V_{OC} .^{2,19} Huang et al. discovered that the pyridine compounds may lower the recombination rate constant by 1–2 orders of magnitude.²⁰ Since then, extensive research studies have been carried out to

investigate the analogue derivatives of pyridine, alkylaminopyridine, alkylpyridine, benzimidazole, pyrazole, quinoline, and so forth for use as additives in liquid electrolytes.^{19,21–24} The nitrogen-containing heterocyclic additive is a kind of a base which has a cognate effect and mechanism based on the solvent donor number.^{21,22} Moreover, excessive additives will result in a lack of photovoltaic performance. In this research, low-viscosity ionic liquid MPII/0.4 M I_2 with TBP was used as an electrolyte for DSCs for improving their performances. We have also studied the effect of concentration of TBP on the ionic conduction of the electrolyte and the DSC performance. Herein, we explain the results based on the most plausible mechanism responsible for the increase in ionic conductivity due to TBP and the consequent effects on DSC parameters.

EXPERIMENTAL SECTION

Fabrication of TiO_2 Working Electrode. TiO_2 electrodes were prepared by the method described previously.²⁵ Titanium tetraisopropoxide (Sigma-Aldrich, USA, 97%, 8.0 mL) and acetic acid (Sigma-Aldrich, USA, 99.7%, 1.0 mL) were mixed with ethanol (VWR Chemicals, France, 99.9%, 8.0 mL), and steam was passed through the solution to aid rapid hydrolysis. The expulsion of ethanol by steaming produced a transparent solid mass consisting of TiO_2 nanoparticles. Then, the resultant solid mass was ground with 20.0 mL of deionized water in a mortar and sonicated for 10 min. Finally, the dispersion was autoclaved at 150 °C for 3 h. The TiO_2 colloidal solution (30.0 mL), acetic acid (8.25 mL), and Triton X-100 (8 drops) were mixed, and this colloidal solution was further diluted by ethanol (30.0 mL) to prepare the TiO_2 precursor suspension. The precursor suspension was sprayed on to preheated (150 °C) fluorine-doped tin oxide (FTO, Solaronix SA, Switzerland, 15 Ω /sq.) glass substrates using a purpose-built spray gun. Then, TiO_2 -sprayed plates were sintered at 500 °C for 30 min in air.

Preparation of an Ionic Liquid-Based Electrolyte. The ionic liquid-based electrolyte was prepared by mixing different amounts of TBP (Sigma-Aldrich, USA, 96%) with 0.40 mol dm^{-3} I_2 /MPII (TOYO GOSSEL, Switzerland). TBP amounts were selected as 0.20, 0.40, 0.60, 0.80, and 1.00 mol dm^{-3} , and a control electrolyte was prepared without adding TBP for comparison.

Fabrication of Counter Electrode. In this research, we used the FTO/Cr/Pt counter electrode (CE). The FTO glass was first cleaned with distilled water using teepol detergent. It was then thoroughly rinsed with distilled water and sonicated in ethanol for 10 min and allowed to dry in air. The cleaned FTO substrate was then fixed inside the vacuum chamber of a sputtering machine. Two source guns were used to hold the chromium (Cr) and platinum (Pt) targets. Then, chromium sputtering was carried out under an ultrahigh vacuum for 30 min in order to deposit a uniform, mirror-like Cr film with a thickness of 600 nm. Then, using the Pt target, sputtering was carried out for 3 min to obtain a 20 nm thick Pt layer deposited on the Cr layer.

Assembly of DSC. Sintered TiO_2 films were heated to 80 °C and kept soaked overnight in a 0.3 mM solution of ruthenium-based N719 [di-tetrabutylammonium-cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium(II)] (Solaronix SA, Switzerland) dye,

Table 1. Room-Temperature Conductivity (σ) of the Ionic Liquid Electrolyte with Different Concentrations of TBP, Calculated from the Solution Resistance Values Obtained from the Data Given in Figure S1

[TBP]/mol dm ⁻³	0.00	0.20	0.40	0.60	0.80	1.00
conductivity at room temperature/ $\times 10^{-3}$ S cm ⁻¹	5.84	5.93	6.22	5.92	5.98	5.74

which was prepared by dissolving in a solution containing acetonitrile and tertiary-butyl alcohol in 1:1 v/v ratio.²⁵ Then, the dye-coated TiO₂ electrodes were rinsed with acetonitrile to remove excess dye molecules and dried. A lightly platinized FTO CE was clipped firmly with the dye-anchored TiO₂ working electrode, and the space between the two electrodes was filled with the prepared ionic liquid-based electrolyte. A mask with a window of 0.25 cm² was also clipped on the working electrode to complete the DSC configuration.

Characterization. The ionic conductivity (σ) of ILs was measured using Metrohm Autolab potentiostat/galvanostat PGSTAT 128 N by the AC complex impedance method at the frequency range of 100 Hz to 1 MHz. The experimental setup used to measure the impedance of ionic liquid electrolytes is shown in Figure 1a. As shown in Figure 1a, the electrolyte is sandwiched between two stainless steel electrodes tightly fitted in a uniform cylindrical glass tube with a cross-sectional area A . The electrochemical impedance spectrum of the system was then recorded for each electrolyte containing different concentrations of TBP, and the Nyquist plots were obtained. This system can be modeled as a simple Randles circuit comprising solution resistance, R_s , appearing as the x -axis intercept in the high-frequency region, a semicircle representing a possible double-layer resistance, R_{ct} , and capacitance, C_{ct} , provided that there are charge-transfer reactions occurring at the metal electrodes, and the Warburg impedance, W , due to ionic diffusion in the electrolyte which appears as a straight line with 45° inclination.

The equivalence circuit is shown in Figure 1b. As there are no charge-transfer reactions occurring at the electrodes, the semicircle that would appear after the x -axis intercept might not appear in this system. The Nyquist plots obtained for each electrolyte with different TBP concentrations that are given in Figure S1 clearly show the x -axis intercept with a hardly visible semicircle, followed by a straight line with 45° inclination. The x -axis intercept of the straight line obtained in the Nyquist plots corresponds to the solution resistance, R . The resistivity, σ , of an ionic liquid electrolyte can then be calculated using the equation $\sigma = L/RA$, where R is the resistance taken from the Nyquist plots, L is the thickness of the IL layer (2.23 nm), and A is the cross-sectional area of the IL layer (2.57 cm²), as clearly depicted in Figure 1a.

The Fourier transform infrared (FT-IR) spectra of the IL electrolyte, TBP, and IL with 0.40 mol dm⁻³ TBP were obtained using a Bruker Alpha FT-IR spectrometer. The wavenumber range used in measurements is from 500 to 2000 cm⁻¹. The samples were prepared by dripping one drop of the IL electrolyte/TBP/IL with 0.40 mol dm⁻³ TBP onto the KBr plate and sandwiching it with another KBr plate to form a uniform film. The plates were then placed on a sample holder, and the FT-IR spectra were taken.

EIS measurements were carried out on DSC devices using the same Metrohm Autolab potentiostat/galvanostat PGSTAT 128 N with a frequency response analyzer (FRA) 32 M FRA in the frequency range between 10⁻² and 10⁶ Hz. The impedance was obtained by applying the negative value of open-circuit voltage ($-V_{OC}$) as the bias voltage under the illumination of 100 mW cm⁻². The Bode plots for calculating the electron lifetime were also obtained from the aforementioned Autolab.

DSC device is characterized using current density–voltage (J – V) and incident photon-to-current conversion efficiency (IPCE) measurements. The J – V characteristics of the solar cells were obtained by exposing 0.25 cm² surface area of the completed cell to AM 1.5 at 100 mW cm⁻² simulated sunlight using an SPD SS-25 light-emitting diode solar simulator and a VK-PA-300 K PV power analyzer. The IPCE experimental setup includes a monochromatic light illumination from a Bentham PVE 300 unit with a TMC 300

monochromator and a 150 W xenon arc lamp covering the 300–800 nm wavelength range.

RESULTS AND DISCUSSION

Ionic Conductivity Measurement. The variation of ionic conductivity of an electrolyte at room temperature with TBP concentration is reported in Table 1. These data were obtained by converting the resistance values obtained from the EIS plots given in Figure S1.

According to the data given in Table 1, the ionic conductivity of the ionic liquid electrolyte increases with the addition of TBP up to 0.40 mol dm⁻³ and then decreases with a further addition of TBP. This trend can be explained as follows. In nonaqueous polar solvents, the equilibrium (1) given below takes place with an equilibrium constant exceeding 776 dm³ mol⁻¹, and hence the equilibrium position lies toward far right, forming exclusively I₃⁻ ions. The reaction between pyridine (Py) and iodine forming the complex adduct Py*I₂ has been documented as early as 1954.^{26,27} It is, therefore, expected that when TBP is added to the I₂/IL mixture, TBP would react with I₂ in the system, forming the TBP*I₂ complex [equilibrium (2)] for which I₂ is supplied by shifting the equilibrium (1) to the left. TBP*I₂ then reacts with I⁻ ions, forming TBP and I₃⁻ ions [equilibrium (3)]. As represented by equilibrium (4), two molecules of TBP*I₂ react to form TBP₂I⁺ and I₃⁻. The reaction scheme is given below



The I₂ concentration of the ionic liquid solution was 0.40 mol dm⁻³, and, therefore, when TBP is not present in the system, the only redox couple present in the system is I⁻/I₃⁻. When the TBP concentration is less than the I₂ concentration, that is, 0.40 mol dm⁻³ in this system, two redox couples are present, which are I⁻/I₃⁻ and I⁻/TBP₂I⁺. When equal concentrations of TBP and I₂ are added (0.40 mol dm⁻³), there is no I₃⁻, and hence only the I⁻/TBP₂I⁺ redox couple is present in the system. The ionic conductivity is determined by the collective contributions from all the ions present in the system. However, smaller ions with high surface charge densities have higher mobilities and hence contribute more toward the conductivity of the electrolyte. Therefore, I⁻ ions present in this system would contribute mainly toward ionic conduction. The transport number of I⁻ ions will increase when the sizes of the other ions are relatively large. As TBP₂I⁺ is a bulky ion, its transport number is small; hence, as the TBP*I₂ concentration is increased, the transport number and hence the ionic conductivity of the iodide ion will increase progressively. As such, the highest conductivity of the electrolyte is expected when the TBP₂I⁺ concentration is maximum. This occurs when the TBP concentration is equal to the I₂ concentration at 0.40 mol dm⁻³. This explains the maximum conductivity of 6.22 $\times 10^{-3}$ S cm⁻¹ obtained when

the TBP formal concentration is 0.40 mol dm^{-3} . As the maximum concentration of I_2 present in the electrolyte is 0.40 mol dm^{-3} , further addition of TBP cannot generate more ions. However, the presence of bulky molecules in the solution can sterically hinder the ionic motion. Therefore, further increase in TBP concentration in the IL electrolyte results in the decrease of the conductivity. This gives evidence for the justification of the above mechanism, which is acceptable in terms of the chemistry of TPB and I_2 reaction, as shown by previous researchers.^{26,27}

FT-IR Analysis. The FT-IR spectra of the $0.4 \text{ M I}_2/\text{MPII}$ ionic liquid electrolyte, TBP, and the IL electrolyte with 0.4 mol dm^{-3} TBP are shown in Figure 2. The characteristic IR

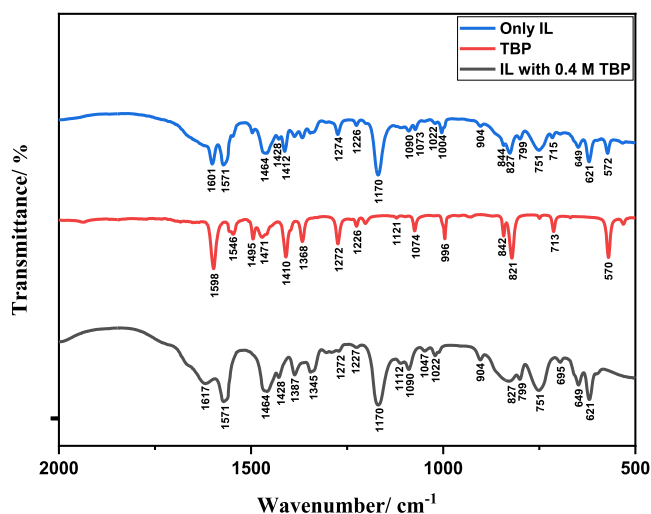


Figure 2. FT-IR spectra of $0.4 \text{ M I}_2/\text{MPII}$, TBP, and $0.4 \text{ M I}_2/\text{MPII}/0.4 \text{ mol dm}^{-3}$ TBP.

band positions of TBP and ionic liquid electrolyte with 0.4 mol dm^{-3} TBP are tabulated, respectively, in Tables S1 and S2. Comparison of the band positions of the IL electrolyte and the IL electrolyte containing TBP clearly shows that most of the bands of the IL electrolyte are present even when TBP is present. These include the bands centered at 621, 649, 751, 799, 827, 904, 1022, 1023, 1090, 1170, 1226, 1274, and 1424 cm^{-1} which are present at the identical positions in both electrolytes. This suggests that TBP does not interact with the 1-methyl-3-propylimidazolium ion. The broad band appearing in this region of spectrum of the IL with 0.40 mol dm^{-3} TBP is due to the merging of the band centered at 844 cm^{-1} of the spectrum of the IL only and 842 cm^{-1} in the spectrum of TBP. Other bands of the two materials near this spectral range are present in the mixture.

However, the comparison of the band positions of TBP and the mixture of IL electrolyte and TBP shows that the bands due to TBP have clearly shifted and a new band has appeared at 695 cm^{-1} . This shows that TBP should interact with some components present in the electrolyte. As it does not interact with the IL, these interactions should be between TBP and I_2 , as proposed earlier in the given reaction sequence. At the formal concentration of 0.4 mol dm^{-3} of TBP, the mechanism predicts that TBP is present exclusively as TBP_2I^+ , where the I^+ ion is coordinated by the lone pairs of the N atoms of two TBP molecules forming a new bond $\text{N}-\text{I}^+-\text{N}$ that is not present when TBP is not present. Therefore, the new band appearing at 695 cm^{-1} can be assigned to the asymmetric stretching

vibration of the $\text{N}-\text{I}^+-\text{N}$ moiety of the TBP_2I^+ ion when present in the MPII ionic liquid. Previous studies have shown that the asymmetric stretching of the $\text{N}-\text{I}^+-\text{N}$ moiety of TBP_2I^+ appears at 637 cm^{-1} in a polyethylene matrix.²⁸ The slightly higher energy of this vibration in the system containing 1-methyl-3-propylimidazolium ion indicates that TBP forms a stronger $\text{N}-\text{I}^+-\text{N}$ bond when present in this ionic liquid medium. Therefore, FT-IR studies also provide added evidence to the acceptability of the proposed mechanism for the reaction between TBP and iodine, creating more triiodide ions and bulky TBP_2I^+ ions.

Photocurrent Density–Photovoltage Characteristics. Figure 3 depicts the J – V curves for the DSCs fabricated with

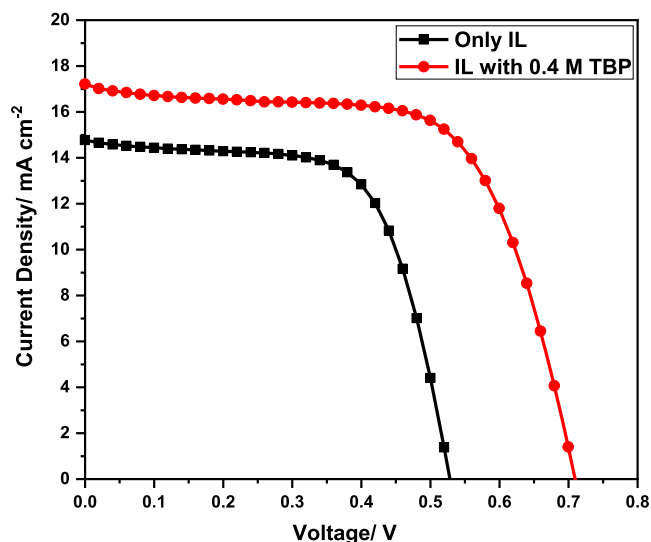


Figure 3. Photocurrent–voltage characteristics of DSCs fabricated with only ionic liquid electrolyte and ionic liquid electrolyte with 0.4 mol dm^{-3} TBP.

the IL electrolyte without TBP and that at 0.40 mol dm^{-3} formal concentration. The J – V curves of all the DSCs studied are shown in Figure S2. The photovoltaic parameters obtained from the J – V characteristics of DSCs fabricated using the IL electrolyte with different concentrations of TBP are given in Table 2.

Table 2. Photovoltaic Parameters of DSCs Employing Ionic Liquid Electrolyte Prepared with Different Concentrations of TBP

[TBP] (mol dm^{-3})	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF	η (%)
0.00	14.77	0.528	0.66	5.15
0.20	16.58	0.699	0.64	7.42
0.40	17.22	0.709	0.65	7.94
0.60	16.39	0.700	0.63	7.23
0.80	16.40	0.700	0.64	7.35
1.00	16.28	0.703	0.64	7.32

As clearly shown in Table 2, V_{OC} , J_{SC} , and the conversion efficiency, η , data are significantly higher in the presence of TBP in the IL electrolyte than that without TBP. The DSC made with 0.40 mol dm^{-3} TBP shows the highest J_{SC} , V_{OC} , and η values. The DSC prepared without TBP showed an efficiency of 5.15%, and the addition of 0.4 mol dm^{-3} TBP to the IL electrolyte resulted in an optimized conversion efficiency of

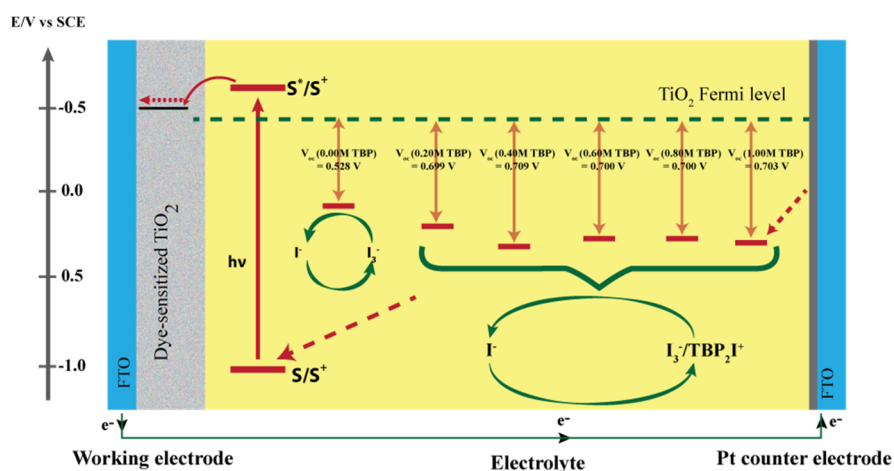


Figure 4. Schematic representation of the change in V_{OC} with the added TBP in the ionic liquid electrolyte of the DSCs fabricated using FTO/Cr/Pt CE.

7.94%, which shows a remarkable efficiency enhancement of 35% due to the addition of TBP at this formal concentration. This is due to 14% enhancement of J_{SC} and 26% enhancement of V_{OC} due to TBP at this formal concentration. There is a trend in the progressive increase of J_{SC} , V_{OC} , and η values up to 0.40 mol dm⁻³ formal concentration of TBP in the IL electrolyte. Further increase in TBP formal concentration tends to give lower but constant values of both J_{SC} and V_{OC} values. Interestingly, FF shows no significant change due to the presence of TBP, and the FF value of all the DSCs containing TBP in the IL electrolyte is slightly lower compared to that without TBP. This is because the FF is primarily influenced by the characteristics of the photoanode; the electronic conductivity of TiO₂ surfaces of the photoanode tend to decrease due to the adsorbed TBP molecules, though this effect seems small suggesting that the amount of TBP molecules adsorbed on the TiO₂ surfaces is low at 0.40 mol dm⁻³ concentration. This is because TBP is not present as TBP molecules in this system due to the large equilibrium constants of all the equilibria depicted in the reaction sequence given above. Instead, TBP is present exclusively as TBP₂I⁺ when the formal concentration of TBP is 0.40 mol dm⁻³. However, there is a possibility for some TBP molecules to get adsorbed onto the TiO₂ surface as the equilibria can be shifted when TBP molecules are removed from them due to adsorption. Below and above this concentration, both TBP and TBP₂I⁺ are present. At these concentrations, the adsorbed TBP molecules may tend to lower the electronic conductivity of the TiO₂ electrode, thus giving a slightly lower FF value. When TBP is not present as in the first row of Table 2, there is no such effect from the adsorbed TBP, and hence the FF obtained is the highest.

The change in V_{OC} due to TBP can be explained as follows. As explained earlier, when only the IL electrolyte is used, the redox couple present in the electrolyte is I⁻/I₃⁻, and V_{OC} is determined by the difference between the potential of the Fermi level of the photoanode under illumination and the redox couple at the Pt CE. This value is 0.528 V in this DSC which is very much similar to that of the DSC with the I⁻/I₃⁻ redox couple present in the acetonitrile solvent, as shown in the Grätzel cell. When TBP is added to the IL electrolyte, up to 0.40 mol dm⁻³ formal concentration, there are two redox couples, namely, I⁻/I₃⁻ and I⁻/TBP₂I⁺, present in the

electrolyte, and the potential at the CE is then determined by the mixed potential at the Pt CE. However, when the TBP formal concentration is 0.40 mol dm⁻³, only the I⁻/TBP₂I⁺ redox couple is present to determine the potential at the CE. Thus, V_{OC} is determined by the potential difference between the Fermi level of the illuminated photoanode and the Pt/TBP₂I⁺/I⁻ redox couple which is 0.709 V. Although the same V_{OC} is expected even when more TBP is present, the change in the properties of the photoanode due to some adsorbed TBP molecules seems to slightly decrease its value. The variation of the V_{OC} values of the DSCs is schematically shown in Figure 4.

The trend of increasing current density, J_{SC} , up to the 0.40 mol dm⁻³ formal concentration of TBP is clearly due to two effects: (i) increase in V_{OC} , as shown in Figure 4, and decrease in solution resistance, R_s , as J_{SC} can be represented as V_{OC}/R_s and (ii) decrease in recombination due to the coverage of recombination sites of the dyed photoanode due to adsorbed TBP. At this critical concentration, the effect (i) works to its full strength, and the highest J_{SC} of 17.22 mA cm⁻² is therefore obtained. Although slightly lower than this value, the J_{SC} values of DSCs with more than this critical TBP concentration are significantly higher than that of the DSC without TBP. The decrease in ionic conductivity due to the presence of more TBP molecules in the IL electrolyte may account for this effect.

Analysis of the Incident Photon-to-Current Conversion Efficiency Curves. The IPCE spectra of DSCs fabricated using the IL electrolyte with and without 0.40 mol dm⁻³ TBP are depicted in Figure 5. The DSC made with IL electrolyte with 0.40 mol dm⁻³ TBP shows higher IPCE than that made with only IL electrolyte for each wavelength. The IPCE exceeds 50% in a wide spectral range of 450–641 nm in DSCs fabricated using IL electrolyte with 0.40 mol dm⁻³ TBP, which supports its J_{SC} measurements. This is due to the enhancement of the electron injection ability of the excited electrons by TBP, attached on the surface of TiO₂.

Analysis of the Electrochemical Impedance Plots. The processes taking place in DSCs include several steps: (i) the absorption of photons by the dye molecules and the corresponding excitation of electrons from the highest occupied molecular orbital (HOMO) levels, (ii) injection of electrons from the LUMO levels of dye molecules to the conduction band (CB) of the interconnected TiO₂ nanoparticles, (iii)

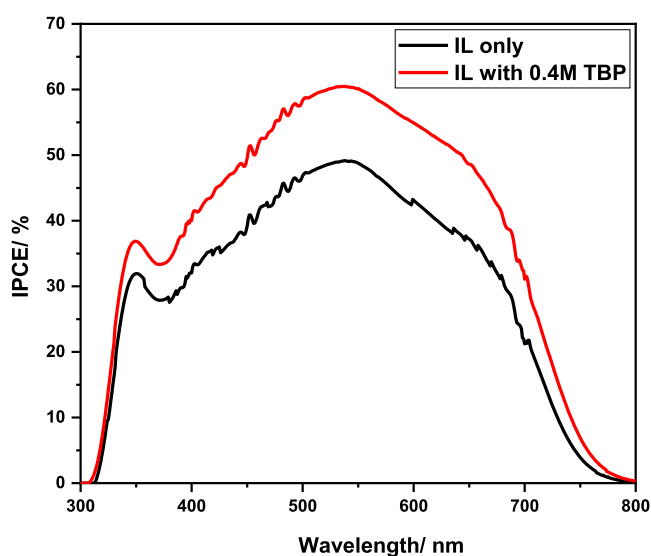


Figure 5. Incident photon-to-current conversion efficiency (IPCE) spectra of DSCs fabricated using ionic liquid electrolyte with and without 0.40 mol dm^{-3} TBP.

random diffusion of electrons in the CB of TiO_2 particles to the FTO surface of the photoelectrode, (iv) recombination of electrons present in the CB of TiO_2 particles with the oxidized dye molecules and the oxidized species of the redox couple, (v) transport of electrons along the external circuit to the CE, (v) reduction of the oxidized species to reduced species taking place at the CE.

The electronic excitation and injection take place in ultrafast timescales, as determined by several researchers. According to Teuscher et al., the electron injection in IL-based DSCs shows two different trends: ultrafast timescale in femtoseconds, followed by relatively slower decay in picoseconds (26.9 ps).²⁹ However, these timescales translate to 10^{12} – 10^{15} Hz frequencies which are not attainable in EIS experiments. The X-axis intercept represents the series resistance, R_s , of the DSC, which is the overall resistance between the two electrodes of the device under illumination. This appears in the frequency range of 31200–16,000 Hz in the EIS experiments. The semicircle, appearing after the X-axis intercept, represents the sum of the resistance for the electron transport, R_{et} , along the interconnected nanoparticles of TiO_2 and that for the recombination of electrons, R_r , in parallel combination with the chemical capacitance C_μ . These processes appear in the timescale of 31,200–140 Hz in the EIS experiments. The next feature of EIS is the straight line with 45° inclination representing the Warburg impedance corresponding to the ionic diffusion in the electrolyte.

This process appears in the timescale of 1700–400 Hz. The last feature appearing in the lowest frequency domain (200–0.50 Hz) used is a semicircle representing the charge-transfer resistance at the CE for the reduction of the triiodide ion to iodide ions in parallel combination with the electrical double-layer capacitance at the CE. Figure 6 shows the Nyquist plots obtained for the illuminated DSCs without any TBP in the electrolyte and with 0.40 mol dm^{-3} of TBP with other identical parameters. The features described above are clearly visible in both Nyquist plots. The corresponding data extracted from the Nyquist plots are given in Table 3.

Analysis of the data given in Table 3 shows that R_s for the DSC containing 0.40 mol dm^{-3} TBP in the IL electrolyte is

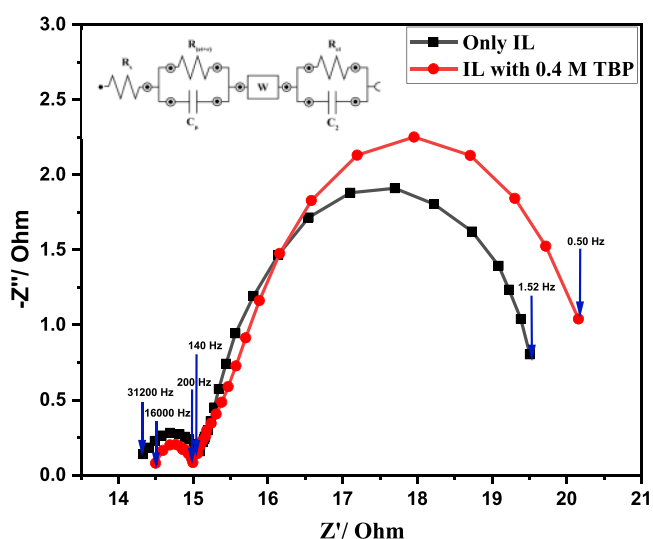


Figure 6. Nyquist plots obtained for the DSCs fabricated using ionic liquid electrolytes with (black curve) and without (red curve) 0.40 mol dm^{-3} TBP measured between 1×10^{-2} – 1×10^6 Hz under 1 sun illumination (AM 1.5, 100 mW cm^{-2} ; the corresponding equivalent circuit is given as an inset).

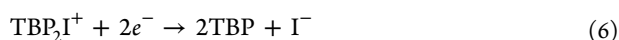
14.45Ω , whereas that without TBP is only 14.23Ω , although the former is expected to be lower than that of the latter as the electrolyte conductance in the former is higher than that of the latter. There is another effect due to the adsorption of TBP molecules on the available sites of TiO_2 nanoparticles that tends to passivate the TiO_2 surface, thus corresponding to the increase in the series resistance. The trend observed is due to the combination of the two opposing effects which seems to almost cancel each other. Interestingly, the combined resistance for the electron transport and recombination is lower in the DSC with 0.40 mol dm^{-3} TBP present in the electrolyte than that without TBP. The lowered resistance in the DSC with TBP is mainly due to the facilitation of the electron transport along the interconnected TiO_2 nanoparticles with reduced recombination as the recombination sites are covered with adsorbed TBP molecules. The fast transport of electrons to the FTO surface of the working electrode with reduced recombination allows the DSC to give a higher conversion efficiency and is in line with the data given in Table 2. The chemical capacitance of the electrical double layer formed at the photoanode is also higher in the DSC with TBP than that without TBP, indicating that the double layer shrinks due to the presence of TBP. As the recombination is reduced due to the presence of TBP, the charge of the photoanode should be higher than that without TBP. This effect is clearly shown in the dark J – V curves given in Figure S3. The improvement of the rectification properties, that is, the shift of the onset of the dark current at positive potentials is an indication that recombination is suppressed.

The higher charge of the photoanode attracts counterions present in the electrolyte to a closer distance, thus affecting the shrinkage of the electrical double layer. This result also gives an indirect evidence to the decreased recombination in the DSC when TBP is added to the electrolyte. The reduced Warburg impedance due to the presence of TBP is clearly due to the increase in conductivity of the electrolyte that matches well with the data given in Table 1. Ironically, the charge-transfer resistance at the CE, R_{ct} , has been increased by 20.7% in the DSC containing TBP from that without TBP. The redox

Table 3. Data Extracted from Nyquist Plots of the Illuminated DSCs Without Any TBP and 0.40 mol dm^{−3} TBP Present in the Electrolyte

[TBP]/mol dm ^{−3}	R_s/Ω	$R_{(et+)}/\Omega$	$C_\mu/\mu\text{F}$	W/Ω	R_{ct}/Ω	C_2/mF
0.00	14.23	0.91	108.64	15.01	4.73	7.34
0.40	14.45	0.55	133.73	14.93	5.71	25.08

couple present in the DSC without TBP is I^-/I_3^- while that present in the DSC with 0.40 mol dm^{−3} TBP is $\text{I}^-/\text{TBP}_2\text{I}^+$. It is expected that the kinetics of the reduction of I_3^- ion to I^- ion is faster, owing to the simplicity of the reaction mechanism than that of the reduction of TBP_2I^+ to I^- , as shown in eqs 5 and 6, respectively.

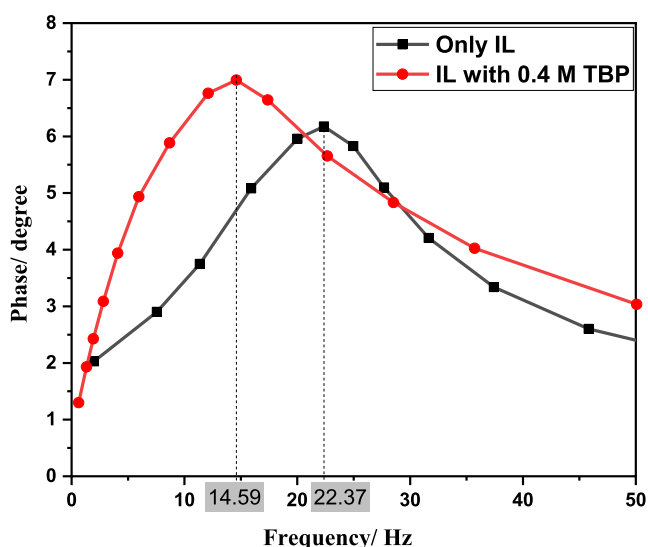


As the I^+ ion is covered by two bulky TBP molecules coordinated to the I^+ ion, it is expected that electron transfer at the CE is slower (6) than that for (5). Further, the diffusion coefficient of the bulky TBP_2I^+ ion should be lower than that of the I_3^- ion, giving some transport limitation also. However, the positively charged TBP_2I^+ ion is expected to be attracted to the CE by electrostatic attractions better than that of the negatively charged I_3^- ion when the ions have reached the close proximity of the CE. With all these effects, it seems that the rate of electron transfer to the TBP_2I^+ ion is slower overall than that to the I_3^- ion. The increased capacitance of the electrical double layer formed at the CE when TBP is present in the electrolyte is due to the shrinkage of the electrical double layer as positively charged TBP_2I^+ ions can reach the cathode to a closer distance than negatively charged I_3^- ions. It is important to note that there are several positive aspects of the presence of the TBP_2I^+ ion in the electrolyte as the bulky TBP_2I^+ helps increase the transport number of I^- ions, thus increasing the electrolyte conductivity and giving higher V_{OC} due to the higher positive potential of the $\text{I}^-/\text{TBP}_2\text{I}^+$ redox couple than that of the I^-/I_3^- redox couple, both of which contribute positively to increase the conversion efficiency of the DSC.

Figure 7 depicts the Bode plots of EIS spectra of the DSCs made using IL electrolytes with and without TBP. The electron lifetime can be calculated using the equation, $\tau_e = 1/2\pi f$, where f is the maximum frequency of the Bode plot. Therefore, τ_e values were calculated by obtaining f values from the Bode plots. The maximum frequency values were used to calculate the lifetime of electrons (τ_e) in the photoanode and are 7.11 and 10.91 ms, respectively, for the DSCs without and with TBP. The increased lifetime of the electrons in the photoanode of the DSC with TBP gives further evidence for reduced recombination.

CONCLUSIONS

Ionic liquids owing the properties such as nonvolatility, electrochemical stability, and reasonably high ionic conductivity stand out as practical electrolytes for DSCs. We have shown that both V_{OC} and J_{SC} increased up to the 0.40 mol dm^{−3} TBP which is equal to the formal concentration of iodine in the electrolyte. We have proposed an explanation based on a novel mechanism by which the redox couples present in the electrolytes are different when TBP is absent and present, which are only I^-/I_3^- when there is no TBP and both I^-/I_3^- and $\text{I}^-/\text{TBP}_2\text{I}^+$ up to the TBP formal concentration of 0.40

**Figure 7.** Bode phase plots for the DSCs fabricated using an ionic liquid electrolyte without TBP and ionic liquid-based electrolyte with 0.40 mol dm^{−3} TBP.

mol dm^{−3}. When the formal concentration of TBP is equal to or greater than 0.40 mol dm^{−3}, only the $\text{I}^-/\text{TBP}_2\text{I}^+$ redox couple is present. The latter $\text{I}^-/\text{TBP}_2\text{I}^+$ redox couple has a higher potential than that of the I^-/I_3^- redox couple, thus increasing V_{OC} . The increased conduction of the electrolyte and the reduced recombination of electrons contribute to increased J_{SC} . The conclusions were made by carrying out several independent analyses including electrolyte conductivity measurement, FT-IR spectroscopy, J – V measurements of DSCs as a function of TBP formal concentration of the electrolyte, IPCE studies, and EIS studies. The DSC made of IL electrolyte with 0.40 mol dm^{−3} TBP offers a high efficiency of 7.94% with high V_{OC} of 0.709 V and J_{SC} of 17.22 mA cm^{−2}.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsaem.1c01587>.

Impedance spectra of ionic liquid electrolytes; photo-current–voltage characteristics of all cells; dark photo-current voltage curves of solar cell; and IR band positions (PDF)

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Notes

The authors declare no competing financial interest.

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