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Effect of electrolyte conductivity, co-additives and mixed cation iodide salts on efficiency enhancement in dye sensitized solar cells with acetonitrile-free electrolyte

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ABSTRACT

Electrolyte modifications in dye-sensitized solar cells (DSSCs) provide a convenient way to enhance their photovoltaic performance. In this work, the synergistic effect of the two mixed cation iodide salts KI and Pr4NI and the two co-additives 4-tertiary butyl pyridine (TBP) and guanidinium thiocyanate (GuSCN) has been used successfully to enhance the photovoltaic performance of DSSCs fabricated with non-volatile propylene carbonate (PC) solvent based electrolyte. The reference DSSC made with electrolyte using only TPAI as the iodide salt exhibited an efficiency of 5.26 % while the DSSC made with optimized electrolyte with TPAI and KI exhibited an efficiency of 6.43 %. This efficiency increase of 22 % has been attributed to the mixed cation effect. It was observed that, the addition of TBP alone to the electrolyte increases the photovoltage of the cells but decreases their photocurrent density. However, the addition of GuSCN increases both the photocurrent density and the photovoltage. While the addition of TBP to the mixed cation electrolyte increased the efficiency from 6.43 % to 6.84 %, the addition of GuSCN increased the cell efficiency from 6.43 % to 6.76 %. However, the addition of the combination of TBP and GuSCN as co-additives in the optimized ratio of 65:35 enhanced the cell efficiency to 7.70 %. After compensating for the loss of iodine due to complexation with TBP the efficiency of DSSCs with coadditives reached an impressive 8.01 %. The overall efficiency enhancement has been explained by the mixed cation effect on the basis of the shifting of the conduction energy band edge of TiO₂ due to the adsorption of cations from the two iodide salts and the adsorption of ionic species from the two co-additives by TiO₂ leading to the enhancement of photocurrent density as well as photovoltage. The ionic conductivity increase in the electrolyte due the presence of the co-additives does not appear to be directly contributing to the increase in the photocurrent in the DSSC. However, the efficiency of all TBP added solar cells could also be improved further by compensating for the decrease of iodide ion content in the electrolyte due to complex formation.

1. Introduction

During the last three decades, investigations on dye-sensitized solar cells (DSSCs) have under gone a considerable development as a result of nanoscience and nanotechnology as well as the developments of novel electrolytes and electrodes used in these devices. Photoelectrochemical structure of the DSSC is the key factor of these devices and efficiency enhancement can be achieved by the structural modification of different components. For example the efficiency enhancement in DSSCs can be achieved by techniques such as, by improving the light absorption by the nanostructurally modified photoanode, by improving the catalytic redox reactions at the counter electrode, by optimizing the redox electrolyte, or by using a combination of these techniques [1–3]. One of the most convenient ways to enhance the photovoltaic performance of a DSSC is the appropriate selection of chemical species in the electrolyte medium to fine tune the physicochemical properties of the electrolyte, the semiconductor photoanode and the electrolyte/photoanode interface [4,5]. The electrolytes in DSSC's generally comprise a solvent (aceto-nitrile) based I^-/I_3^- redox couple and have impressive energy conversion efficiencies around 11 %–14 % [1–3]. However, the major drawback of these volatile solvent based solar cells is liquid leakage, electrode corrosion and photo decomposition of the dye in the volatile solvent

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medium [4]. In order to overcome these drawbacks many efforts have been made over the past three decades [6–9]. One of the strategies is to use an electrolyte solution prepared by dissolving the ionic salt in an ethylene carbonate (EC)/propylene carbonate (PC) co-solvent without using the volatile acetonitrile [10-12]. In DSSCs the contribution of the iodide ions (I⁻) to the total conductivity of the electrolytes plays a crucial role determining the photo current density and hence the overall efficiency of the device. This is because the iodine ion also commutes between the photo electrode and counter electrode while participating in the redox reaction [2,13,14]. Therefore, ammonium salts with a bulky cation, such as tetrapropylammonium iodide (TPA⁺I- or Pr₄NI), tetrabutylammonium iodide (TBA⁺I⁻) and tetrahexylammonium iodide (THA⁺I⁻) are widely used as ionic salts in DSSC electrolytes because the large cations generally facilitate ionic dissociation producing more iodide (I⁻) ions. According to several recent reports the mixed cation effect in DSSCs with electrolytes consisting of a mixture of two iodide salts, one with a small cation and the other with a bulky cation (such as KI and Pr₄NI) have shown enhanced DSSC performance compared to an electrolyte with only one iodide electrolyte (such as KI or Pr₄NI). Our group has reported for the first time the beneficial effect of using this type of mixed cation iodide salts on the efficiency enhancement in DSSCs [15-20].

Another approach to enhance the photovoltaic performance of DSSCs is the use of additives in the electrolyte. Additives play an important role to enhance the photovoltaic parameters especially in liquid electrolyte-based DSSCs. These additives in the electrolytes are expected to be adsorbed onto the TiO_2 surface, thus shifting the conduction band (CB) of the TiO_2 which strongly influence the photocurrent and photovoltage. Therefore, incorporation of appropriate additives into the liquid electrolytes have been effective strategies to enhance the photovoltaic performances of DSCs.

The positive effect of additives such as 4-tert butylpyridine (TBP) and guanidinium thiocyanate (GuSCN) have already been reported by several research groups. The electron donating, Lewis base, heterocycle compounds like TBP and N-methyl benzimidazole (NMBI) have been used in electrolytes as a $V_{\rm OC}$ -improver to increase the open circuit voltage ($V_{\rm OC}$) while GuSCN has been used as both a $V_{\rm OC}$ -improver and a short-circuit photocurrent density ($J_{\rm SC}$) enhancer [21–23]. The operational mechanism of TBP and GuSCN in dye-sensitized TiO₂ solar cells is well known for conventional electrolytes. The combined effect of alkaline cations and organic additives on efficiency enhancement in gel polymer electrolyte based dye sensitized solar cells has also been reported [24].

TBP is the most commonly used additive to improve the V_{OC} . However, it reduces the J_{SC} . The role of this additive has been discussed in several reports [25–28]. By acting as a Lewis base, TBP deprotonate the TiO₂ surface by adsorption on dye-absent active sites at the TiO₂ surface and contribute to reduce the back electron recombination from TiO₂ conduction band to tri-iodide. According to published reports, TBP in the DSSC electrolytes causes a negative shift of the TiO₂ band-edge and, therefore, increases both the V_{OC} and the electron life time. On the other hand, addition of GuSCN to the electrolyte contributes to a positive shift of the TiO₂ band-edge by passivating on the surface of TiO₂. It leads to an increases in the photo electron injection efficiency and hence the photocurrent density [29–34]. Therefore, a simultaneous co-addition of these two additives to the DSSC electrolyte is expected to enhance the solar cell efficiency due to their synergetic effect, somewhat similar to the mixed cation effect described earlier.

In the present work, the favorable effects due to the addition of 4-tert butylpyridine (TBP) and guanidinium thiocyanate (GuSCN) as combined additives on the efficiency enhancement in DSSCs made with an optimized mixed cation iodide salt based, acetonitrile-free liquid electrolyte have been used to improve the efficiency of DSSCs. As far as we are aware this is the first report of a DSSC system using the beneficial effects of both the mixed cation effect incorporating a small alkali cation, K^+ and a bulky quaternary ammonium cation (TPA⁺), and the

Table 1

Compositions and photovoltaic parameters of DSSCs fabricated and characterized under each category. Series A represents the electrolyte compositions used to optimize the KI wt% in the mixed cation reference electrolyte containing TPAI (Pr₄NI). Series B represents the TBP wt % added to the reference electrolyte used in the best efficiency DSSC of series A. Series C represents the GuSCN wt % added to the reference electrolyte used in the best efficiency DSSC of series A. Series D represents the GuSCN wt % added to the best efficiency DSSC of series B exhibiting the best DSSC performance at TBP:GuSCN = 65:35 wt% ratio in the electrolyte D3.

| | Electrolyte Type | Varied Amount | V _{OC} (mV) | $J_{\rm SC}$ (mA cm ⁻²) | FF (%) | Efficiency (η %) |
|---|---------------------|---------------------------------|-------------------------|-------------------------------------|--------------|---------------------|
| | 1990 | n! | 1 | 14- (TDAT | 4 IVI) - NI- | |
| | | KI (wt%) | d cation sa | lits (TPAI and | a KIJ: NO | additives |
| | A0 | 0 | 726.2 | 10.88 | 66.5 | 5.26 |
| | A1 | 10 | 707.0 | 12.11 | 66.2 | 5.67 |
| | A2 | 20 | 699.5 | 13.60 | 67.6 | 6.43 |
| Α | A3 | 40 | 669.4 | 13.35 | 67.9 | 6.07 |
| | A4 | 50 | 667.1 | 13.23 | 65.3 | 5.77 |
| | A5 | 80 | 654.4 | 12.34 | 68.6 | 5.54 |
| | A6 | 100 | 638.2 | 13.21 | 66.3 | 5.51 |
| | | Single additi TBP (ww | ive - 01 (oı | nly TBP) | | |
| | BO (A 2 | %) 0.00 | 600 F | 12.60 | 676 | 6.49 |
| | BU/AZ P1 | 0.00 | 721.0 | 13.00 | 60.0 | 6.40 |
| | B1 B2 | 1.41 | 731.9 | 13.20 | 69.2 | 6.74 |
| | B3 | 4.23 | 750.3 | 13.09 | 68.9 | 6.76 |
| в | B4 | 5.65 | 751.6 | 12.07 | 69.6 | 6.79 |
| Ъ | B5 | 7.06 | 768.8 | 12.99 | 69.0 | 6.84 |
| | <u>B6</u> | 8.47 | 771.2 | 12.64 | 69.1 | 6.74 |
| | B7 | 9.88 | 782.8 | 12.59 | 65.6 | 6.47 |
| | B8 | 12.17 | 790.0 | 12.20 | 66.6 | 6.42 |
| | | Single additi GuSCN (ww%) | ive - 02 (or | nly GuSCN) | | |
| | C0/A2 | 0.00 | 699.5 | 13.60 | 67.6 | 6.43 |
| | C1 | 1.23 | 697.9 | 14.62 | 63.5 | 6.47 |
| | C2 | 2.47 | 699.2 | 14.48 | 64.3 | 6.51 |
| С | C3 | 3.70 | 704.1 | 14.77 | 64.3 | 6.68 |
| | <u>C4</u> | 4.94 | 716.5 | 15.07 | 62.6 | <u>6.76</u> |
| | C5 | 6.17 | 707.3 | 15.67 | 60.4 | 6.69 |
| | C6 | 7.40 | 706.5 | 15.31 | 60.3 | 6.52 |
| | | Binary addit | tive (TBP & | GuSCN) | | |
| | | TBP: GuSCN | (ww %) | | | |
| | D0/B5 | 100:00 | 768.8 | 12.88 | 69.0 | 6.84 |
| | D1 | 85:15 | 762.4 | 12.94 | 68.0 | 6.96 |
| | D2 | 74:26 | 806.4 | 13.53 | 66.6 | 7.27 |
| | D3 | 65:35 | 816.4 | 14.01 | 67.3 | 7.70 |
| D | D4 | 59:41 | 810.9 | 13.64 | 68.0 | 7.53 |
| D | D5 | 53:47 | 808.3 | 13.41 | 66.5 | 7.36 |
| | D6 | 46:54 | 766.9 | 13.58 | 67.7 | 7.21 |
| | D7 | 36:64 | 768.2 | 13.66 | 66.6 | 7.02 |
| | D8 | 22:78 | 742.4 | 13.33 | 67.7 | 6.77 |
| | D9/C4 | 00:100 | 716.5 | 15.07 | 62.6 | 6.76 |

two co-additives (TBP and GuSCN) to significantly enhance the efficiency of dye sensitized solar cells. This is also the first report dealing with the ionic conductivity enhancement of the redox electrolyte due to the ionic species of the two co-additives as well as the compensation for the decrease in the iodide ion content due to the complex formation by the TBP additive.

2. Experimental

2.1. Materials

Fluorine-doped tin oxide (SnO₂: F) coated conductive soda-lime glass (FTO, 7 Ω cm⁻², 2.2 mm thickness) and the Ru dye, Ditetrabutylammonium cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-



Fig. 1. Variation of the efficiencies (values marked along the curves) of DSSCs as a function of amounts added to the electrolyte. (a) KI wt% added to the electrolyte containing TPAI (Pr_4NI), (b) TBP wt% added to the mixed cation electrolyte of the highest efficiency (6.43 %) reference DSSC, (c) GuSCN wt% added to the mixed cation electrolyte of the highest efficiency (6.43 %) reference DSSC and (d) GuSCN wt% added to the highest efficiency (6.84 %) DSSC electrolyte optimized with TBP.

dicarboxylato) ruthenium (II) (N719) were purchased from Solaronix, Switzerland. TiO₂-P25 powder was purchased from Degussa and TiO₂-P90 powder from Evonic, Germany. Poly ethylene glycol (PEG-2000) (1900–2200 Mw, 99.8 % from BDH organics, ethylene carbonate (EC, 99 %) and propylene carbonate (PC, 99 %) from Fluka Analytical, Triton X-100, iodine (I₂, 99.8 %), tetrapropylammonium iodide (TPAI, 99 %), potassium iodide (KI, 99 %), 4-tert butylpyridine (TBP, 98 %), and guanidinium thiocyanate (GuSCN, 99 %) from Sigma-Aldrich were used as received. All the reagents used were of analytical grade and used without further purification or treatment.

2.2. Preparation of the electrolytes

Based on previous studies by our group, the acetonitrile-free basic electrolyte (A₂) containing TPAI (0.136 g) and KI (0.018 g) as the mixed cation iodide salts and iodine (I₂) were used to prepare the electrolytes. The weight of I₂ was taken to be the molar ratio of I⁻/ I₂, 10:1. The co-solvent was made of 0.4 g of ethylene carbonate (EC) and 0.4 g of propylene carbonate (PC). In this work four different types of electrolytes were prepared containing the two iodide salts, KI and TPAI (or Pr₄NI). These are (a) KI + TPAI without any additive, (b) KI + TPAI electrolyte with TBP as the additive, (c) KI + TPAI electrolyte with GuSCN as the additives. Under type (a), seven different electrolytes, A₀ to A₆ were prepared by varying the KI:TPAI composition ratio and keeping the molar ratio of I-/I₂ as 10:1 and characterized them [16,35]. Under type (b) nine different electrolytes, B₀ to B₈ were prepared by adding different amounts of TBP to the optimized electrolyte from type

(a), which is the electrolyte containing 20 % KI and 80 % TPAI. Similarly, under type (c), seven different electrolytes C_0 to C_6 were prepared by adding different amounts of GuSCN to the optimized (20 % KI + 80 % TPAI) electrolyte from type (a). Finally, under systems (d) ten different electrolytes D_0 to D_9 were prepared by adding GuSCN to the optimized, TBP added electrolyte (B5) of series (b) by varying GuSCN weight ratio as mentioned in the Table 1. For the preparation of all the electrolytes, properly weighed amounts of chemicals were mixed by continues magnetic stirring at room temperature in a tightly sealed glass bottle overnight to get a homogeneous electrolyte.

2.3. Conductivity measurements

The ionic conductivities of the electrolytes were determined from the electrical impedance spectroscopy (EIS) measurements carried out with a computer controlled Autolab Potentiostat/Galvanostat PGSTAT128 N with a FRA 32 M Frequency Response Analyzer (Metrohm) in the frequency range from 0.01 Hz to 1 MHz. Liquid electrolyte samples kept within a spacer placed between two polished stainless steel electrodes were used for the conductivity measurements. The initial conductivity measurement was carried out at the room temperature (around 27 °C) and the subsequent measurements were taken from 30° to 65 °C at 5 °C intervals. At each measuring temperature, the sample was allowed to stabilize for about 30 min. The ionic conductivity of the electrolytes was extracted from the corresponding impedance plots.

2.4. Cyclic voltammetry measurement

To study the effect of additives on the redox reactions of electrolytes, cyclic voltammetry (CV) analysis was carried out using a three electrode system. Ag/AgCl electrode was used as the reference electrode; two platinum wires were used as the counter electrode and the working electrode. The CV experiments were done for the four main types of optimized electrolytes, (a) without additives, (b) with only TBP, (c) with only GuSCN and (d) with both TBP and GuSCN added, at the scan rate of 20 mV s⁻¹. CV measurements were carried out with a computer controlled Autolab Potentiostat/Galvanostat PGSTAT128, under -1.2 V and +1.2 V of lower and upper vertex conditions respectively.

2.5. TiO_2 photoanode preparation

For the preparation of the TiO_2 photoanode, 0.25 g of P90 TiO_2 powder and 1 mL of 0.1 M HNO3 were well ground in an agate mortar for about 15-20 minutes to obtain a homogeneous dispersion. A well cleaned fluorine-doped tin oxide (FTO) glass substrate was then coated with above dispersion by using a spin coater at 3000 rpm for 60 s to obtain a compact layer of P90 TiO₂. This P90 coated FTO glasses were sintered at 450 °C for 45 min and cooled down to room temperature. Then in order to get the photoactive layer of the DSSSC, another paste of TiO₂ was prepared as follows. Initially, 0.25 g of commercial P25 TiO₂ powder and 1 mL of 0.1 M HNO₃ were ground-well by mortar and pestle. 0.02 g of Triton X-100 and 0.05 g of PEG 2000 were used as the binder and the mixture was ground well until it became a uniform creamy paste. This P25 paste was then doctor bladed on the top of the substrates with the first P90 layer, and the bi-layered electrodes were then sintered at 450 °C for 45 min to obtain porous TiO2 electrodes each having an area of 0.25 cm². After cooling down to 80 °C above electrodes were dipped in to the solution of Ru N719 dye dissolved in 0.3 mM ethanol and kept 15 h in order to obtain dye sensitized bi-layer photoanodes.

2.6. DSSC fabrication and characterization

After the dye adsorption each TiO₂ photoanode was rinsed with absolute ethanol and air-dried to remove any moisture. In order to fabricate a DSSC of configuration FTO/TiO₂/Dye/electrolyte/Pt, an appropriate amount of the above electrolyte was sandwiched between the photoanode and the Pt counter electrode. The cell assembly was held together using steel clips under gentle pressure. The photocurrent density vs voltage (*J*–*V*) characteristics were measured under the illumination of 100 mW cm⁻² (AM 1.5) simulated sunlight with a 100 W Ozone Free Xenon Lamp and a Oriel LCS-100 solar simulator using a Metrohm Autolab Potentiostat/Galvanostat PGSTAT 128.

2.7. Electrochemical impedance spectroscopy (EIS) measurements

Electrochemical impedance spectroscopy is an important and necessary measurement to characterize the electrochemical performance of each component and interfaces of a DSSC. From EIS measurements the recombination resistance, carrier transport resistance, series resistance and the electron life can be obtained by fitting the EIS data with a suitable equivalent circuit of the DSSC. Impedance spectrum of each DSSC was obtained by using Autolab Potentiostat/ Galvanostat PGSTAT128 N with a FRA 32 M Frequency Response

Analyzer (Metrohm) under the illumination of 100 $\rm mWcm^{-2}$ (Solar simulator with AM 1.5 spectral filter) in the frequency range from 0.01 Hz to 1 MHz.



Fig. 2. *J-V* characteristics of the highest efficiency DSSCs fabricated with electrolytes containing two mixed cation iodide salts (KI and TPAI) and incorporating the additives TBP and GuSCN. Corresponding photovoltaic parameters are shown in the inset.

3. Results and discussion

3.1. Optimization of chemical compositions of electrolytes and photovoltaic performance of DSSCs

Fig. 1 shows the efficiency vs composition variations of DSSCs fabricated with different electrolytes as mentioned in the experimental section. Corresponding photovoltaic parameters were obtained from the current voltage characteristic curves of each DSSC under the illumination of 100 mW cm⁻². Table 1 gives the compositions and photovoltaic parameters of DSSCs fabricated and characterized under each category corresponding to Fig. 1. All optimizations of electrolytes were done by the *J*–*V* characterization of DSSCs. At least five different solar cells were characterized for each electrolyte composition under each type and the average values of the photocurrent density (J_{SC}) open circuit photovoltage, (V_{OC}) and the energy conversion efficiency (η) were selected for presenting in the *J*–*V* graphical format and as Tables.

Table 1 shows the compositions and photovoltaic parameters of DSSCs fabricated and characterized under each category and shown in Fig. 1.

Fig. 2 shows the *J*–*V* characteristics of the DSSCs made with the four types of electrolytes A,B,C and D exhibiting the highest efficiency.

Table 2 shows the summary of chemical compositions of the four best electrolytes, (a) A_2 optimized for KI + TPAI only, (b) B_5 optimized with TBP additive only, (c) C_4 optimized with GuSCN additive only and (d) D_3 optimized with co-additive TBP + GuSCN as determined by *J*–*V* measurements of corresponding DSSCs exhibiting the highest efficiencies.

3.1.1. Mixed cation effect on the efficiency enhancement of DSSCs

Fig. 1 (a) shows the efficiency variation of DSSCs with the different amounts of KI added to the electrolyte prepared initially with only TPAI. It can be observed that the performance of DSSCs made with mixed cation electrolyte, EC:PC:TPAI:KI, I₂ is influenced by the size and the charge density of the cation of iodide salt. This can be explained as due to the increase in the electron injection efficiency caused by the positive shift of the flat band potential (V_{FB}) or Fermi level of TiO₂ (Ec_{TiO2}) which is shifted by the KI in to more negative values due to the adsorption K⁺ ions by TiO₂ surface resulting an effective negative shift [15]. Also, the diffusion of I^-/I_3^- redox couple is facilitated by the presence of more mobile and small size cations (K⁺) than the bulky TPA⁺ ions [38]. Hence, the dye regeneration process can also be accelerated by the small cations. These results are generally in agreement with reported results for similar mixed cation electrolyte based DSSCs [15–18,36,37]. As a

Chemical compositions of electrolytes optimized using J-V measurements of DSSCs.

| Composition | Electrolyte | TBP (ww%) | GuSCN (ww%) | EC (g) | PC(g) | I ₂ (g) | TPAI (g) | KI (g) |
|-------------|----------------|-----------|-------------|--------|-------|--------------------|----------|--------|
| KI + TPAI | A ₂ | - | - | 0.4 | 0.4 | 0.0138 | 0.136 | 0.018 |
| Only TBP | B ₅ | 7.06% | _ | 0.4 | 0.4 | 0.0138 | 0.136 | 0.018 |
| Only GuSCN | C ₄ | - | 4.94 % | 0.4 | 0.4 | 0.0138 | 0.136 | 0.018 |
| TBP + GuSCN | D_3 | 65% | 35 % | 0.4 | 0.4 | 0.0138 | 0.136 | 0.018 |

result, the DSSC made with the electrolyte with 20 wt % of KI and 80 wt % TPAI (sample A_2) without any additive exhibits an efficiency of 6.43 %, with a $V_{\rm OC}$ of 699.5 mV, $J_{\rm SC}$ of 13.60 mA cm⁻² and a FF of 67.6 %. This efficiency increase due to the mixed cation effect is about 22 %.

3.1.2. Effect of TBP additive on DSSC performance

The efficiency variation vs amount of TBP (ww % of total weight) is shown in Fig. 1 (b) and Table 1. The maximum power conversion efficiency is exhibited by the cell with electrolyte sample B₅. The solar cell fabricated with this optimized electrolyte shows an increased efficiency of 6.84 % with an increased $V_{\rm oc}$ of 768.8 mV but reduced $J_{\rm sc}$ of 12.88 mA cm^{-2} . As seen from Table 1, the V_{OC} of cells made with this electrolyte has increased with the amount of TBP added and at the same time the J_{SC} has gradually decreased exhibiting the highest DSSC efficiency at the intermediate electrolyte composition B5. The electron donating nitrogen-based heterocycle organic compound, TBP, has shown a negative shift of TiO₂ band edge evidently by the chemisorption onto the dye-absent active sites at the surface of the TiO₂ [25,27,39]. This has caused a significant improvement in V_{OC} at the expense of the J_{SC} due to the decrease in the driving force for the electron injection from exited dye to the TiO₂ conduction band. TBP evidently has acted as a V_{OC} improver. The addition of 7.06 wt% TBP has increased the open circuit photovoltage by 69.3 mV. This could be attributed partly to the shift of the TiO_2 conduction band edge (V_{fb}) towards negative potentials and partly to an increase of the electron lifetime as described later. The probable mechanisms due to TBP can be summarized as (i) TBP adsorption on TiO₂ surface would shift the TiO₂ conduction band edge towards negative potentials thus increasing the open circuit photovoltage (V_{OC}) [22,27,31], (ii) according to Nazeeruddin et al. [56] and Bella et al. [57], TBP affects the surface charge of TiO₂ by decreasing the amount of adsorbed K + ions thus reducing the photoelectron generation and thereby lowering the short circuit photocurrent (J_{SC}) and (iii) TBP decreases the recombination of electrons in TiO₂ with tri-iodide in the electrolyte by preventing tri-iodide access to the TiO₂ surface and/or by complexation with iodine in the electrolyte (to be discussed later) [21,22,25,27,57]. However, higher concentrations of TBP above the optimized composition have caused lower efficiencies evidently due to the excessive reduction of the J_{SC} . The net result is that due to the incorporation of the optimized amount of TBP to the optimized mixed cation electrolyte, the DSSC efficiency has increased from 6.43 % to 6.84 %.

3.1.3. Effect of GuSCN additive on DSSC performance

Fig. 1(c) and Table 1 show the optimization of the A2 electrolyte by the addition of guanidinium thiocyanate (GuSCN) additive with respect to the DSSC photovoltaic parameters. The optimized electrolyte with addition of 4.94 wt% of GuSCN shows the highest $V_{\rm OC}$ of 716.5 mV, increased (but not the highest) $J_{\rm SC}$ of 15.07 mA cm⁻² and the highest efficiency of 6.76 % compared to the DSSC of efficiency 6.43 % made with the reference electrolyte A2.

The increase of the J_{SC} due to the addition of GuSCN could be attributed to the positive shift of the flat band potential due to the adsorption of guanidinium cations (Gu+) by the TiO₂ electrode which can enhance the photoelectron injection yield. The results from electrochemical impedance spectroscopy (EIS) to be described later shows that the electron lifetime has also increased indicating that Gu⁺ cations are chemisorbed on to the TiO₂ surface, passivating the electron

recombination sites at the surface and improving the V_{OC} . Thus, GuSCN appears to act as an enhancer of both J_{SC} as well as V_{OC} . Similar observations have been reported by Kopidakis et al., Zhang et al. and Stergiopoulos et al [29–31].

3.1.4. Effect of TBP and GuSCN co-additives on DSSC performance

Based on the results shown in Fig. 1(a), (b) and (c) and Table 1, corresponding to the optimized performances of the DSSCs due to the mixed cation effect and the incorporation individual additives, TBP and GuSCN, the optimization of the electrolyte towards the efficiency enhancement in the DSSCS due to the incorporation of both these coadditives was performed and the results are shown in Fig. 1(d) and Table 1. This was carried out by varying the weight ratio of GuSCN to the TBP added, optimized electrolyte B5 which corresponds to DSSC efficiency of 6.84 %. From the synergistic effects of TBP and GuSCN both, the V_{OC} and J_{SC} values have been optimized at 65:35 ww% ratio of TBP: GuSCN and the highest DSSC efficiency (η) of 7.70 % was achieved corresponding to the optimized V_{OC} and J_{SC} values of 816.4 mV and 14.01 mA cm⁻² respectively. Accordingly, as a result of the combined effect of the mixed cation iodide electrolyte and co-additives, the best solar cell exhibits a remarkable overall increase in efficiency by about 46 % compared to the efficiency of 5.26 % for the cell with only one iodide salt TPAI and no additives. The efficiency increase due to the mixed cation effect alone is about 22 % while the additional increase due to coadditives, TBP and GuSCN is about 20 %.

3.2. Mechanism of co-additives on photovoltaic performance of DSSCs

Several research groups have discussed the mechanism of the coadditives TBP and GuSCN on DSSC performance. Kopidakis et al. have investigated the effect of guanidinium cations on the photoinduced charge density at the open circuit of dye-sensitized solar cells and found that guanidinium cations could control the surface properties of the TiO₂ electrode, resulting in the positive shift in $V_{\rm fb}$ of the TiO₂ electrode [29]. From impedance spectra of the solar cells, authors have concluded that the addition of GuSCN in the electrolyte has decreased the interfacial recombination reaction on the TiO₂ electrode. It is indicated that the guanidinium cation could suppress the surface recombination and shift the conduction band to positive potentials. According to Zhang et al., GuSCN influences the electron injection yield due to the shifting of TiO₂ flat band potential ($V_{\rm FB}$) leading to an increase of $J_{\rm SC}$ and the efficiency of DSSCs [30]. Stergiopoulos et al. have also confirmed that GuCNS species accumulate their positive charge on the semiconductor surface, inducing a positive shift of the VFB, thus increasing the electron injection efficiency and simultaneously slowing down recombination at open-circuit conditions while TBP has the effect of deprotonating the TiO₂ surface by adsorption and thus shifting the conduction band edge $(V_{\rm FB})$ of TiO₂ toward negative potentials while passivating the surface active recombination sites [31]. Boschloo et al. [28] have used charge extraction and electron lifetime measurements, to show that enhanced photovoltaic performance of DSSCs due to TBP could be attributed to a shift of the TiO₂ band edge towards negative potentials (responsible for 60 % of the voltage increase) and to an increase of the electron lifetime (40 %). Therefore, as mentioned previously, our observations on the working mechanisms of TBP and GuSCN are generally in agreement with those reported by other workers with regard to the enhancement of photovoltaic performance.

Ionic conductivity vs temperature values of electrolytes with binary iodide (KI + TPAI), single additives (TBP or GuSCN) and co-additive added electrolytes optimized using DSSC characteristics.

| | Conductivity (σ) mS cm ⁻¹ | | | | | | |
|------------------|---|----------------------------|------------------------------|---|--|--|--|
| Temperature (°C) | A ₂ only KI + TPAI | B ₅ only TBP | C ₄ only GuSCN | $\begin{array}{l} D_{3} \\ TBP + GuSCN \end{array}$ | | | |
| 27 | 9.1 | 8.0 | 10.3 | 9.3 | | | |
| 30 | 9.1 | 8.4 | 10.7 | 9.4 | | | |
| 35 | 9.6 | 9.6 | 11.8 | 10.6 | | | |
| 40 | 11.2 | 10.6 | 12.7 | 11.9 | | | |
| 50 | 12.9 | 12.8 | 15.8 | 13.7 | | | |
| 55 | 13.9 | 13.8 | 17.8 | 14.5 | | | |
| 60 | 14.8 | 14.8 | 18.1 | 15.4 | | | |
| 65 | 16.6 | 16.3 | 21.1 | 17.0 | | | |



Fig. 3. The variation of $\ln(\sigma T)$ plotted against the reciprocal temperature for different types electrolytes containing additives shown in the legends.

In the case of GuSCN, it is interesting to note that the V_{oc} of the DSSCs made with electrolyte containing this additive does not drop with the downward shift of E_c . This is due to the adsorption of large organic, guanidinium cations $[Gu^+ \text{ or } CH_6N_3^+ \text{ or } C(NH_2)_3^+$; ionic radius =0.21 nm] which blocks the charge transfer channel at the TiO₂/electronlyte interface. Therefore, the suppression of electron recombination appears to be more than sufficient to offset the V_{oc} loss from the downward shift of E_c . It is important to note that this phenomenon is different to the adsorption of other types of small cations such as Li⁺ and K⁺ in DSSC electrolytes where the J_{SC} is enhanced at the expense of the V_{oc} [15–18]. The net result is that due to the addition of GuSCN to the electrolyte, both the V_{oc} as well as J_{SC} of the DSSCs have been enhanced.

However, we are reporting for the first time, the favourable effects of the two co-additives, TBP and GuSCN on the enhancement of photovoltaic performance of the DSSCs made with acetonitrile-free redox electrolyte containing two mixed cation iodide salts, KI and TPAI, one with a smaller cation (K^+) and the other with a bulky cation (TPA⁺). All previously reported studies on co-additives have been on electrolytes with single cation iodide salts. In this work we observe that the efficiency enhancement obtained due to the mixed cation effect can be further increased by the use of the two co-additives TBP and GuSCN [15–20].

3.3. Effect of co-additives on ionic conductivity of the DSSC electrolytes

The ionic conductivity (σ) of the optimized electrolyte samples, A2,

B5, C4 and D3 exhibiting the best solar cells performances at different temperatures from 27 °C to 65 °C are shown in the Table 3. The variation of ln (σ *T*) vs 1/*T* for these electrolytes is shown in Fig. 3.

According to the ionic conductivity values shown in Table 3 and Fig. 3, the conductivity of the electrolyte B_5 containing only TBP as an additive is the lowest at almost all measured temperatures. It has a conductivity of 8.0×10^{-3} S cm⁻¹ at 27 °C. The conductivity gradually increases with increasing of temperature from room temperature (27 °C) to 65 °C and the highest conductivity values at all measured temperatures are shown by the electrolyte C₄ with only GuSCN as the additive. It has the conductivity of 10.3×10^{-3} S cm⁻¹ at 27 °C. As shown in the Fig. 3, from the linear graphs, the conductivity appears to follow the Arrhenius Eqs. (1) and (2),

$$\sigma T = B \, e^{\frac{E_a}{kT}} \tag{1}$$

$$\ln\sigma T = -\frac{E_a}{k} \frac{1}{T} + \ln B \tag{2}$$

Where, E_a is the Activation energy, B is the pre-exponential factor and k is the Boltzmann constant.

The ionic conductivity of the electrolyte samples is determined by the number of dissociated free cations and anions available in the electrolyte as well as their ionic mobilities. The ionic conductivity of all mixed cation electrolyte samples (series A) used in this work prior to the addition of the two co-additives, originates from two types of ions, namely, potassium (K⁺) and tetrapropyl ammonium (TPA⁺) cations and iodide and tri-iodide (I⁻ /I₃⁻) anions and all these ions contribute to the observed total conductivity. However, from the two iodide salts KI and TPAI, the contribution to overall ionic conductivity from smaller size K⁺ ions are expected to be higher than conductivity from bulky TPA⁺ cations due to their lower ionic mobility [16,40].

Kalaignan et al. and Klaboe et al. have confirmed by Raman analysis, when the salt and the iodine were mixed in the electrolyte with 10:1 mol ratio, all added I₂ has completely converted to the I₃⁻⁻ ions with no trace free iodine. The conversion of free iodine I₂ to tri-iodide ions I₃⁻⁻ by the reaction I₂ + I- \rightarrow I₃- makes a significant contribution to the iodide ion conductivity of the electrolyte [35,41]. The ionic conductivity of electrolyte sample series B, which contains only TBP as the additive, has the lowest values at all measured temperatures. According to Aronson et al. and Reid et al. [43] the pyridine and the iodine will form Py⁺I- complexes thereby reducing the number of I- and I₃- ions available for conduction. However, small portion of Py⁺I- complexes can converts to the I₃- with Py₂I- finally leaving only a smaller number of I- and I₃- ions available for iodide ion conductivity [27,42,43]. These authors have suggested the following four reactions between pyridine derivatives and iodine and iodide:

$$[1]Py + I_2 \Rightarrow PyI_2(complex)$$

$$[2]PyI_2 \Rightarrow Py^+ + I^-$$

$$[3]Py^+I^- \Rightarrow Py^+ + I^-$$

$$[4]2Py^+I^- \Rightarrow Py_2I^- + I_{3^-}$$

This complex formation (reaction, 1) being the dominating reaction compared to reactions 2,3 and 4, would lead to a drop in the number of iodide ions (I⁻) and the iodide ion conductivity and hence a drop in J_{sc} in the corresponding DSSC.

On the other hand, it is interesting to see that the ionic conductivity of only GuSCN added electrolyte (series C), shows the highest ionic conductivity at all measured temperatures. With increasing the number of charge carriers, the ionic conductivity will increase as expected. As per the CRC handbook of Chemistry and Physics (Ed.W.M Haynes), most of the anions and cations in sample C₄ are mobile significantly contributing to the total conductivity [40]. Diffusion coefficients of the cations and anions of sample C₄, TPA⁺, K⁺, I⁻, and SCN⁻ in aqueous solutions are reported as 0.623, 1.957, 2.04 and 1.758 (in 10^{-5} cm² s⁻¹) respectively [44]. Here it shows that the diffusion coefficient of thiocyanide ion (SCN⁻) also has a comparable value with other two major ions, K⁺, I⁻ contributing to conductivity. This explains the reason for the highest conductivity of the series C electrolytes at all temperatures.

There are no reports available in the literature on the effect of GuSCN addition on ionic conductivity of electrolytes. However, there are many reports as already cited in this paper on the effect of GuSCN on the improved performance of DSSCs by enhancing the short circuit photo current density. As discussed earlier, this has been attributed to the positive shift of the conduction band of TiO2 photoanode, which enhances the generation of photoelectrons. In this work, according to the results of ionic conductivity measurements (Fig. 3 and Table 3), the conductivity of the electrolyte has increased significantly due to the addition of GuSCN. This conductivity increase is evidently due to the increased carrier concentration of the electrolyte due to dissociated free guanidinium cations (Gd⁺) and thiocyanate anions (SCN⁻) in the GuSCN added electrolyte. These ions, therefore, do not contribute directly to the iodide ion conductivity enhancement in the electrolyte. The ionic radii of different ionic species in the GuSCN added electrolyte are Gd^+ ion (guanidinium cation, $[CH_6N_3]^+$): 0.190 nm, SCN- ion: 0.220 nm [45], K⁺ ion: 0.138 nm, TPA⁺ ion: 0.460 nm [46] and iodide ion: 0.201 nm.

As explained earlier, GuSCN exhibits strong ionic dissociation compared to the TBP providing more mobile ionic species in the electrolyte medium. Typically, in an electrolyte medium, higher ionic conductivity is generally associated with higher concentration of mobile ions and their ionic mobility. Pyridinium refers to the cation [C₅H₅NH]⁺ is the conjugate acid of pyridine. The molar mass of Pyridine, C5H6N is 80.110 g·mol⁻¹ while that of Guanidine (CH₅N₃) is 59.072 g·mol⁻¹. Therefore, both, the pyridinium cation, Py^+ (or $[C_5H_5NH]^+$) as well as its complex with iodine, Py₂I⁻ ion in the iodine containing solution is expected to be bulkier and heavier than the Guanidinium cation, [CH₆N₃]⁺. The ionic mobility of the Py⁺ cations and Py₂I- anions in the electrolyte solution of PC and EC co-solvent are therefore expected to be lower in the TBP added electrolytes (series B) compared to the GuSCN added electrolytes (series C). This would explain the observed higher conductivity of the GuSCN added electrolyte compared to the TBP added electrolyte.

Mason et al. [33] have used neutron diffraction experiments and molecular dynamics simulations to study the structure of aqueous solutions of two electrolytes guanidinium sulfate (a mild protein conformation stabilizer) and guanidinium thiocyanate (a powerful denaturant). These neutron diffraction studies, have predicted very strong ion pairing in solutions of Gdm₂SO₄ but ionic dissociation to free Gu⁺ and SCN⁻ ions in solutions of GuSCN. Shahan et al. [47] have reported that in phthaloyl chitosan (PhCh)-based gel polymer electrolytes (GPEs) containing GuSCN as an additive the maximum ionic conductivity of 12.69×10^{-3} S cm⁻¹ was achieved by the electrolyte containing 3 wt% GuSCN. Ionic conductivity of aqueous solutions containing different guanidinium salts (chloride, thiocyanate, sulphate, and carbonate) has been studied by Hunger et al. [34] and authors reported that for aqueous solutions of GuSCN, the ion association is negligible.

The activation energy values calculated from the slopes of the Arrhenius plots in Fig. 3, for the four electrolytes, A_2 , B_5 , C_4 and D_3 are 0.0170 \pm 001, 0.025 \pm 0.001, 0.021 \pm 0.001 and 0.015 \pm 0.001 eV respectively. Petrowsky et al. have shown that the temperature dependence of the ionic conductivity of organic liquid electrolytes and amorphous polymer electrolytes is governed by a single activated process for a given type of organic solvents [48]. The above activation energies in a narrow range of values between 0.015 – 0.025 eV obtained for the four electrolytes based on EC/PC co-solvent used in the present work appears to be generally in agreement with this idea. The observed differences in activation energy values can be very likely due to the different ionic radii and ionic mobilities of different ionic species involved.



Fig. 4. CV plots at a scan rate of 20 mV $\rm s^{-1}$ for optimized four different electrolytes.

consists of the EC + PC co-solvent. Therefore, any difference in the activation energy depends on the size and the mobility of the dissociated ionic species. According to the above activation energy values, relatively high activation energy of 0.025 \pm 0.001 eV can be observed for the electrolyte with binary iodide salts and only with TBP as the additive (B₅). As explained above, the migrating ionic species in this electrolyte are the cations and iodide ions from the mixed cation binary iodide salts and small number of Py₂I⁻ and I₃- ions originating from the reaction of TBP with I₂ as described earlier. The presence of the undissociated complex Py.I₂ in the medium is expected to increase the viscosity of the medium and hence the activation energy, while only a small fraction of Py₂I⁻ and I₃- ions would contribute to the ionic conductivity. The formation of the complex Py.I2 will also reduce the expected number of I3ions originating from I₂ in the medium. The overall effect is therefore an increase in activation energy and a decrease in ionic conductivity of the TBP added electrolytes as seen in Fig. 3.

The electrolyte D3 has the binary mixed cations and iodide ions along with ions from the two co-additives TBP and GuSCN and exhibits the lowest activation energy and moderately higher conductivity in the series. This could be related to the presence of the two small size ions Gu^+ (or Gd^+) and SCN^- having higher mobilities from well dissociated GuSCN additive. The electrolyte with only GuSCN as the additive has the highest ionic conductivity and activation energy similar to the TBP added electrolyte. The highest conductivity evidently results from the availability of the two small size ions Gd^+ and SCN- and the availability of sufficient I⁻ and I₃- ions originating from I₂, as there is no possibility of the formation of the complex Py.I₂.

From the analysis of the electrolyte conductivity data, it is clear that the two co-additives do not directly contribute to the increase in the number of iodide ions and hence the iodide ion conductivity in the electrolyte which essentially determines the short circuit photocurrent density of the corresponding DSSCs. This clearly suggests that the increase of J_{SC} and V_{OC} of corresponding DSSCs results solely from the shifting of the conduction band edge of the TiO₂ by the two co-additives. As already mentioned, this situation is different to the case of J_{SC} and efficiency enhancement in DSSCs fabricated with mixed cation iodide salts where there is a direct correlation between the iodide ion conductivity of the electrolyte and the J_{SC} and efficiency of the corresponding DSSC [15–18].

3.4. Effect of co-additives on the electrolytes by cyclic voltammetry (CV)

The CV experiments were conducted on the four optimized electrolytes namely, (a) without additives, (b) with only TBP, (c) with only GuSCN and (d) with both TBP and GuSCN added system at the scan rate

Oxidation and reduction potentials, cathodic peak current (I_{pc}) and anodic peak current (I_{pa}) data obtained from the CV graph.

| Electrolyte | E _{ox} | E _{red} | $\Delta E_{\rm red-ox}$ (V) | I _{pc} (red) | I _{pa} (ox) | I _{pc} / |
|-------------|-----------------|------------------|-----------------------------|-----------------------|----------------------|-------------------|
| Additive | (V) | (V) | | (mA) | (mA) | I _{pa} |
| No additive | 0.91 | -0.38 | 1.29 | -5.75 | 15.15 | 0.38 |
| Only TBP | 0.99 | -0.35 | 1.34 | -6.40 | 15.10 | 0.42 |
| Only GuSCN | 0.65 | -0.33 | 0.98 | -7.17 | 13.20 | 0.54 |
| TBP + GuSCN | 0.67 | -0.39 | 1.01 | -5.08 | 11.06 | 0.46 |

of 20 mV s⁻¹ and results of voltammograms are shown in Fig. 4. According to the Fig. 4, the cyclic voltammograms showed an oxidation (anodic) peak current (I_{pa}) and a redox (cathodic) peak current (I_{pc}) for all four types of electrolytes. It is observed that the peak positions and values were slightly changed due to the introduction of additives to the electrolyte medium. The first peak that appeared in positive side is related to the oxidation of the $3I^-$ to I_3^- . In the reverse direction, the cathodic peak appearing at negative side of the curve is due to reversible reduction reaction of I_3^- to $3I^-$. All the information obtained from the cyclic voltammograms are tabulated in Table 4.

According to the Fig. 4 and Table 4, the positive shift of the anodic peak (oxidation) after adding TBP to the electrolyte medium can be clearly seen. This peak shift towards the positive voltage is attributed to the positive shift of redox potential of the electrolyte due to the addition of TBP. This can be correlated with the improvement in the $V_{\rm OC}$ as shown in Table 1. Similar observations based on CV measurements have been reported by Abdulkarim et al. as in their study with urea as an additive to the electrolyte [52].

However, in the reduction reaction, a higher cathodic peak current (I_{pc}) represents a faster redox reaction rate in the electrolyte [53]. According to the Fig. 4, a higher cathodic peak current was observed for the GuSCN added electrolyte system. This enhancement in peak current is correlated with the enhanced photocurrent density (J_{SC}) of the DSSC fabricated with the GuSCN as the only additive in the electrolyte.

As can be seen from the Table 4, redox potential difference (ΔE_{red-ox}) is the lowest for the electrolyte with GuSCN as the only additive. These observations consistent with similar observations reported by Prima et al., where the dye regeneration in the electrolyte with only GuSCN as an additive appears better [54] and it was also reflected from the corresponding enhancement in the J_{SC} of the device (inset of Fig. 1).

The I_{pc}/I_{pa} ratio represents the electrochemical reversibility over the reduction and oxidation reaction. According to Wang et al. [22], the electrochemical reversibility of the electrolyte occurs when the I_{pc}/I_{pa} ratio is nearly equal to 1. As can be seen from the Table 4, the electrolyte with only GuSCN shows the I_{pc}/I_{pa} value much closer to 1 compared to other electrolytes. Hence, the electrochemical reversibility is highest in

the electrolyte with only GuSCN and the lowest in the electrolyte with no additives. The electrochemical reversibility of the electrolyte with co-additive showed the second best among other electrolytes. Moreover, as reported by Prima et al. [54], the high electrochemical reversibility can be correlated with higher conductivity of electrolyte, which is consistence with our conductivity results. This means that the electrolyte with only GuSCN as the additive shows the highest conductivity value and the electrolyte with co-additive TBP + GuSCN shows the second best conductivity value (Table 3).

3.5. Impedance and kinetics analysis of DSSCs

Electrochemical Impedance Spectroscopy (EIS) provides an effective technique for investigating the kinetics of the interfacial photochemical process in a DSSC. The EIS measurements of solar cells fabricated with above four different electrolytes under the illumination of 100 mW cm^{-2} (1.5 AM spectral filter) were done in the frequency range of 0.01 Hz to 1 MHz at the V_{OC} . Fig. 5(a) shows the Nyquist plots which were fitted with the equivalent circuit shown in the inset. Each Nyquist plot exhibits two semicircles, a larger semicircle at low frequencies and a smaller semicircle at high frequencies. Each fitted circuit consists of series resistance (R_s), charge transfer resistance (R_1) at the interface of redox electrolyte and Pt counter electrode, the back electron transfer resistance (R_2) at TiO₂ photo anode/ redox electrolyte interface. RQ_1 and RQ_2 are constant phase elements of the capacitance corresponding to R_1 and R_2 , respectively [49,50]. The electron back reaction from photoanode to electrolyte, i.e. charge recombination resistant (R_2) is a key factor that determines the overall solar cell performance [21]. As shown in Table 4 and Fig. 5 (a), the R_2 value has increased with the addition of TPB additive to the electrolyte. This suggests that the electron recombination rate is reduced by forming a partial blocking layer at the interface of TiO₂/redox electrolyte [27,51]. Therefore, the overall solar cell performance would be enhanced by the enriched electron transfer kinetics and the Fill factor.

As shown in Fig. 5 (b), the Bode phase plots exhibit the frequency peaks of the charge transfer process of four different DSSCs fabricated

Table 5

Fitted EIS parameters (Series Resistance R_S , charge transfer resistance of interfaces R_1 and R_2 and electron life time τ_0 of DSSC's using the equivalent circuit shown in the inset of Fig. 5(a).

| Electrolyte | $R_{\rm S}\left(\Omega ight)$ | $R_1(\Omega)$ | $R_2\left(\Omega\right)$ | $\tau_{\rm e}$ (ms) |
|-------------|-------------------------------|---------------|--------------------------|---------------------|
| No additive | 10.5 | 3.0 | 21.0 | 9.27 |
| Only TBP | 10.8 | 3.6 | 25.3 | 13.60 |
| Only GuSCN | 13.4 | 12.0 | 19.3 | 7.85 |
| TBP + GuSCN | 7.1 | 6.4 | 20.0 | 10.96 |



Fig. 5. (a) EIS spectra (Nyquist plots) of four DSSCs fabricated with four different electrolytes shown in the inset. (b) Bode phase plots extracted from the EIS spectra.

| Variation of ionic conductivity of the 7 | BP added liquid electrolyte, | EC: PC: Pr ₄ NI: KI, I ₂ , | + TBP with $I_2:I^-$ | molar ratio. |
|--|------------------------------|--|----------------------|--------------|
|--|------------------------------|--|----------------------|--------------|

| Electrolyte | $I_2 \neq g$ | Mole ratio $I_2:I^-$ | EC /g | PC /g | KI / g | Pr ₄ NI /g | TBP /µl | Conductivity (mS cm^{-1}) |
|----------------|--------------|----------------------|-------|-------|--------|-----------------------|---------|------------------------------|
| E1 | 0.0124 | 0.90:10 | 0.40 | 0.40 | 0.018 | 0.0136 | 75.52 | 7.82 |
| E ₂ | 0.0138 | 1.00:10 | 0.40 | 0.40 | 0.018 | 0.0136 | 75.52 | 8.67 |
| E ₃ | 0.0166 | 1.20:10 | 0.40 | 0.40 | 0.018 | 0.0136 | 75.52 | 9.06 |
| E ₄ | 0.0179 | 1.30:10 | 0.40 | 0.40 | 0.018 | 0.0136 | 75.52 | 8.68 |
| E ₅ | 0.0210 | 1.50:10 | 0.40 | 0.40 | 0.018 | 0.0136 | 75.52 | 8.46 |
| E ₆ | 0.0241 | 1.75:10 | 0.40 | 0.40 | 0.018 | 0.0136 | 75.52 | 6.47 |

with the four different electrolytes. Table 5 shows the calculated electron life time (e) from the characteristic frequency peak (f_{max}), using the Eq. (3).

$$\tau = \frac{1}{2\pi f_{\text{max}}} \tag{3}$$

As shown in Table 4, the electron life time has increased due to the addition of TBP and the DSSC fabricated with only TBP added electrolyte shows a high τ_e value. It may due to the photoinjected electrons diffusing slowly through the TiO₂ network for a longer time. Because of the poor ionic conductivity of TBP containing redox electrolyte (Fig. 2 and Table 3) and the negative shift of the CB of the TiO₂ film causing a low $J_{\rm sc}$, due to the slow dye regeneration process. In addition, the negative shift of the TiO₂ conduction band-edge due to the TBP would slow down the electron injection from the excited dye molecules to CB of $\mathrm{TiO}_2,$ and also the recombination process would be slowed down by the presence of the pyridine blocking layer. As a result, the photo injected electrons will diffuse through the TiO₂ network slowly. On the other hand, the electrolyte with GuSCN as the only additive shows higher ionic conductivity and the excited dye molecules will return to their ground state quickly by the fast response of the redox electrolyte. The positive shift of the TiO₂ conduction band-edge would enhance the photo injecting process from the excited dye molecule to the CB of TiO₂. This would reduce the electron life time inside the TiO₂ photo anode. The cumulative effect due to the presence of both additives, TBP and GuSCN has led to an intermediate life time of 10.96 ms and enhanced the performance of solar cells by increasing the photocurrent and reducing the recombination of injected electrons on the TiO2 conduction band with redox pair in the electrolyte [5].

3.5.1. Effect of co-additives on DSSC performance: A comparison with literature

It would be interesting to compare our results with results reported by other workers in respect of the effect of addition of the TBP and GuSCN additives to DSSCs. Nakada et al. [21] have studied the DSSC system with the electrolyte consisting of different cations such as Li⁺, tetra-*n*-butylammonium (TBA⁺), or 1,2-dimethyl-3-propylimidazolium (DMPIm⁺) in various concentrations, with and without 4-tert-butylpyridine (TBP). The increase of $V_{\rm oc}$ by the addition of TBP into the electrolyte containing Li^+ and the I^-/I_3^- redox couple was mainly attributed to the shift of the TiO₂ conduction band back to the negative potential by reducing the amount of adsorbed Li cations. Wang et al. [22] have reported the experimental and theoretical aspects of the influence of 4-tert-butylpyridine/guanidinium thiocyanate co-additives on band edge shift and recombination of dye-sensitized solar cells. The results have shown that the frontier orbitals between TBP and TiO₂ are sufficiently overlapped to induce the negative shift of Fermi energy, increasing the open-circuit voltage. The Gu + cations appears to be tightly adsorbed on to TiO2 surface to by electrostatic attraction to form a passivated layer due to the Coulomb attraction, depressing the recombination rate and improving the short-circuit photocurrent. The overall photovoltaic performance improves as a result of a synergistic effect of the two co-additives. DSSC based on the optimal molar ratio (9:1) of TBP and GuSCN in their work has resulted a short-circuit current density of 13.74 mA cm⁻², open-circuit voltage of 0.74 V, fill factor of



Fig. 6. Variation of ionic conductivity of the TBP added liquid electrolyte, EC: PC: Pr4NI: KI, I2, + TBP with I2:I- molar ratio.

0.70 and overall efficiency of 7.12 %.

Lee et al. [23] have studied the effects of deoxycholic acid (DCA) in a dye solution as a co-adsorbate and guanidinium thiocyanate (GuSCN) in an electrolyte as an additive, on the photovoltaic performance of dye-sensitized solar cells (DSSCs). The addition of GuSCN into the electrolyte has enhanced the photovoltage of DSSCs which has been explained as due to the adsorption of guanidinium cations following the dye adsorption that facilitates the self-assembly of dye molecules so as to either reduce the dark current or positively shift the conduction band edge of the TiO₂. The value of τ_e has increased as a result of GuSCN addition.

Boschloo et al. [27] have studied the quantification of the Effect of 4-tert-butylpyridine addition to I^-/I_3^- redox electrolytes in dye-sensitized nanostructured TiO2 solar cells. They have observed that, in an electrolyte containing 0.7 M LiI and 0.05 M I2 in 3-methoxypropionitrile, the addition of 0.5 M TBP gave an increase of the open-circuit potential of 260 mV. Using charge extraction and electron lifetime measurements, this increase has been attributed to a shift of the TiO₂ band edge toward negative potentials (responsible for 60 % of the voltage increase) and to an increase of the electron lifetime (40 %). At a lower TBP concentration the shift of the band edge was similar, but the effect on the electron lifetime was less pronounced. The working mechanism of TBP has been summarized as follows: according to Nazeeruddin et al. and Bella et al, (1) TBP affects the surface charge of TiO_2 by decreasing the amount of adsorbed protons and/or K⁺ ions [55, 56]. Also, as several studies suggesting, (2) It decreases the recombination of electrons in TiO2 with tri-iodide in the electrolyte by preventing triiodide access to the TiO₂ surface and/or by complexation with iodine in the electrolyte [21,22,25,27,56].

3.6. Optimization of I_2 content in the TBP added electrolytes

As already discussed in Sections 3.1.2 and 3.3 in detail, the addition of TBP has the effect of decreasing the number of iodide ions (I⁻) in the



Fig. 7. Dependence of I-V characteristics of the DSSCs fabricated with TBP added liquid electrolytes made with different I₂: I- molar ratios.

 Table 7

 Dependence of photovoltaic parameters of the DSSCs fabricated with TBP added electrolyte EC: PC: Pr₄NI: KI, I₂, + TBP on I₂: I⁻ molar ratio.

| Electrolyte | Mole ratio I ₂ : I ⁻ | Conductivity (mS cm ⁻¹) | V _{OC} (mV) | J _{SC} (mA∕ cm ^{−2}) | FF % | Eff % |
|----------------|--|--|-------------------------|---|-------------|-------------|
| E ₁ | 0.9:10 | 7.82 | 768.4 | 12.72 | 69.7 | 6.81 |
| E ₂ | 1.0:10 | 8.67 | 766.9 | 12.98 | 68.9 | 6.85 |
| E ₃ | 1.2:10 | 9.06 | 763.2 | 13.40 | 68.8 | 7.04 |
| E ₄ | 1.3:10 | 8.68 | 764.8 | 12.90 | 69.8 | 6.89 |
| E ₅ | 1.5:10 | 8.46 | 764.1 | 12.67 | 70.4 | 6.82 |
| E ₆ | 1.75:10 | 6.47 | 766.9 | 12.33 | 70.4 | 6.66 |



Fig. 8. Variation of (a) the ionic conductivity of the TBP added electrolyte, (b) the short circuit photocurrent J_{sc} and (c) the DSSC efficiency as a function of the added iodide content exhibiting the maxima at I_2 : I^- molar ratios of 1.2:10.

electrolyte due to complexation with iodine to form the complex PyI_2 , thereby reducing the short circuit photocurrent and hence the efficiency of the DSSCs. We have succeeded in compensating for this effect by studying the variation of electrolyte conductivity with I_2 :I- (iodine:iodide ion) molar ratio from 0.9:10 to 1.75:10 for the TBP added EC: PC:



Fig. 9. Comparison of I-V characteristics of DSSCs made with four different types of electrolytes after compensating for the reduction of I_2 in the two (*) TBP added electrolytes.

| Table 9 | | | | | | | | | | |
|----------------|------------|----|-------|---------|-----|-------|--------------|----|-----|-------|
| Photovoltaic | parameters | of | DSSCs | (*after | the | I_2 | optimization | in | TBP | added |
| electrolytes). | | | | | | | | | | |

| Electrolyte | V _{OC} | $J_{ m SC}$ | FF | Efficiency % |
|-------------------------------------|-----------------|-------------|------|--------------|
| No additives | 699.5 | 13.60 | 67.6 | 6.43 |
| only TBP* | 763.2 | 13.40 | 68.8 | 7.04 |
| only GuSCN | 716.5 | 15.07 | 62.6 | 6.76 |
| $\text{TBP} + \text{GuSCN}^{\star}$ | 793.7 | 14.73 | 68.5 | 8.01 |

Pr₄NI: KI, I₂ electrolyte. Results are shown in Table 6 and Fig. 6.

It can be seen from Table 6 and Fig. 6 that the electrolyte conductivity increases first with increasing the I_2 content in the electrolyte and reaches the maximum value at I_2 :I⁻ molar ratio of 1.2 :10. This is evidently due to the creation of more iodide (I-) ions in the electrolyte in order to compensate for the decrease of iodide ions due to the complex formation by TBP as explained earlier in Section 3.3. This increased I_2 content will increase the photocurrent density in the solar cells fabricated with this optimized TBP added electrolytes. Further addition of iodine however would form ionic aggregates and ion pairs and reduce the iodide ion conductivity and hence the photocurrent density of the DSSCs.

Photovoltaic parameters of the DSSCs fabricated with TBP added and iodine compensated electrolyte EC: PC: Pr₄NI: KI, I₂, + TBP are shown in Fig. 7 and Table 7. It can be seen that the highest DSSC efficiency of 7.04 % correspond to the highest photocurrent density of 13.40 mA/cm⁻². Dependence of photovoltaic parameters of the DSSCs fabricated with TBP added electrolyte EC: PC: Pr₄NI: KI, I₂, + TBP on I₂: I- molar ratio is shown in Table 7.

It is interesting to see the variation of (a) the ionic conductivity of the TBP added electrolyte, with optimized I_2 : I^- molar ratio of 1.2:10 ratios, (b) the short circuit photocurrent density and (c) efficiency of DSSCs as a function of the added iodine (I_2) content as depicted in Fig. 8. These variations clearly suggests that for the DSSCs fabricated with TBP added electrolyte, the short circuit photocurrent density and the efficiency are

Table 8

Chemical compositions of the four electrolytes including the two optimized TBP added electrolytes (B₅ and D₃) after the I₂ compensation.

| Composition | Electrolyte | TBP (ww%) | GuSCN (ww %) | EC (g) | PC (g) | I2 (g) | TPAI (g) | KI (g) |
|--------------|----------------|-----------|--------------|--------|--------|--------|----------|--------|
| KI + TPAI | A ₂ | _ | - | 0.4 | 0.4 | 0.0138 | 0.136 | 0.018 |
| only TBP* | B ₅ | 6.81 % | _ | 0.4 | 0.4 | 0.0166 | 0.136 | 0.018 |
| only GuSCN | C ₄ | - | 4.94 % | 0.4 | 0.4 | 0.0138 | 0.136 | 0.018 |
| TBP* + GuSCN | D_3 | 65 % | 35 % | 0.4 | 0.4 | 0.0166 | 0.136 | 0.018 |

essentially determined by the iodide ion conductivity part in the electrolyte, as demonstrated by several DSSC systems with mixed cation electrolytes reported in the literature [15–18].

The *I*–*V* characteristics and photovoltaic parameters of the best DSSCs fabricated with optimized, I_2 compensated electrolyte compositions given in Table 8 are shown in Fig. 9 and Table 9 respectively.

Table 9 clearly shows the best photovoltaic parameters of the DSSCs made with electrolytes with (a) mixed cations only, (b) mixed cations with TBP only as an additive, (c) mixed cations with GuSCN only, and (d) mixed cations with two co-additives TBP and GuSCN. In these DSSCs made with both TBP added electrolytes have been compensated to obtain the optimized iodide ion conductivity by incorporating extra iodine (I₂) to maintain the I₂: I⁻ molar ratios of 1.2:10.

4. Conclusions

In this work we have studied for the first time, the effect of the electrolyte additives TBP and GuSCN on the photovoltaic performance of DSSCs fabricated with an acetonitrile-free liquid electrolyte consisting of two mixed cation iodide salts, KI and TPAI in non-volatile EC and PC co-solvent. It was observed that the optimized single additive TBP increases the V_{0c} but reduces the J_{sc} thereby increasing the DSSC efficiency from 6.43 % to 6.84 %. The addition of GuSCN to the electrolyte on the other hand, boosted both the $V_{\rm oc}$ and $J_{\rm sc}$ values and increased the efficiency from 6.43 % to 6.76 %. The addition of both additives, TBP and CuSCN, in the optimized ratio of 65:35 increased the DSSC efficiency to 7.70 %. This co-additive added electrolyte was further optimized by compensating for the reduction of iodide ion concentration due to Py.I₂ complex formation and the resulting DSSC exhibited the highest cell efficiency of 8.01 %. This impressive 26.6 % increase in efficiency due to the optimized synergetic effect is among the highest reported so far for co-additive incorporated DSSCs.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

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