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Optimization of iodide ion conductivity and nano filler effect for efficiency enhancement in polyethylene oxide (PEO) based dye sensitized solar cells



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ABSTRACT

Efficiency enhancement is achieved in dye sensitized solar cells (DSSCs) fabricated with polyethylene oxide (PEO) based gel electrolyte by optimizing the iodide ion conductivity using a binary iodide salt and TiO₂ nanofiller. The binary iodide salt system consists of K⁺ as the small cation and Pr_4N^+ as the large cation. The correlation between the efficiency variation and the short circuit current density variation with salt composition suggests that the improved iodide ion conductivity of the electrolyte plays a dominant role in enhancing the solar cell performance. The highest DSSC efficiency of 4.12% is obtained for the electrolyte with salt composition 25 wt% $Pr_4N^+1^-$: 75 wt.% KI. The incorporation of 2.5 wt% TiO₂ nano fillers into the polymer electrolyte further enhances the solar cell efficiency to 5.31%, very likely due to the increased ionic mobility caused by the increased amorphous phase content of the PEO based polymer electrolyte.

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1. Introduction

Energy resources continue to be an essential part for basically all areas of human activity. The ever increasing living standards of the society demands the increasing use of energy, which has made the human society rely on more and more energy from fossil fuels. The fossil fuel resources (oil, coal, gas etc) are not unlimited, and with the expected increase in global energy consumption in the near future, these supplies are expected to be depleted within the next 50 years or so. Therefore, the search for renewable energy that is sustainable, inexpensive and environmentally friendly, has led research community and industry to develop the solar energy technology in order to harness the solar energy. In this scenario at present commercially produced photovoltaic solar cells which are solid state p-n junction devices such as silicon based solar cells are used to concert sun light into electricity. However, these solar cells are expensive to manufacture due to various technological issues. Therefore, low cost photoelectocemical solar cells such as dye

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http://dx.doi.org/10.1016/j.electacta.2014.09.017 0013-4686/© 2014 Elsevier Ltd. All rights reserved. sensitized solar cells (DSSCs) are emerging as an alternative to expensive p-n junction photovoltaics used ar present. DSSCs use a semiconductor-liquid (or gel) electrolyte junction as opposed to the classical solid sate p-n junction [1,2]. However, liquid electrolyte based DSSCs have many draw backs like electrolyte leakage and evaporation, flammability and instability at higher temperatures and electrode deterioration. Therefore, a considerable research effort in this area is focused on developing solid or quasi-solid (gel) polymer electrolyte based DSSCs. Among such polymer hosts, polyethylene oxide (PEO) has attracted much attention because of its polar nature and chemical stability [3]. PEO also exhibits many other useful properties like ease of electrolyte fabrication, excellent complexation with many ionic salts and low glass transition temperature making it an ideal host polymer for DSSC electrolytes [4,7].

Most of the reported DSSCs comprised of electrolytes containing a single ionic salt [5-7] with either a small cation or a large cation. Both these cation types have their own advantages, when used in a DSSC as discussed later. There are only very few reported cases of DSSC electrolytes containing two dissimilar cations [8-10]. In our recent studies, we have observed that the combined effect of smaller (like K⁺) and larger (like Pr₄N⁺) cations in the electrolyte







Table 1

Weight percentages of KI, $Pr_4N^*I^-$ and I_2 used for the preparation of the polymer gel electrolytes. Bold figures corresponds to the electrolyte composition which gives the maximum solar cell efficiency.

KI wt% w.r.t. $Pr_4N^+I^-$	Sample	PEO/g	PC/g	KI/g	Pr ₄ N ⁺ I ⁻ /g	I_2/g
0	A	0.100	0.800	0.000	0.060	0.0048
25	В	0.100	0.800	0.150	0.045	0.0060
50	С	0.100	0.800	0.030	0.030	0.0070
60	D	0.100	0.800	0.036	0.024	0.0075
75	E	0.100	0.800	0.045	0.015	0.0080
90	F	0.100	0.800	0.054	0.006	0.0087
100	G	0.100	0.800	0.060	0.000	0.0092

enhances the solar cell efficiency compared to the DSSCs with a single cation electrolyte [8,9]. This efficiency enhancement can be well understood by examining the relationship between the short circuit current density and the iodide ion conductivity and also by the effect of cation adsorption by the TiO_2 electrode [8,11].

It is also reported that the incorporation of inorganic nano fillers into the polymer electrolyte increases the solar cell efficiency [4,12]. The high crystallinity of PEO based polymer electrolytes leads to low ionic conductivity which directly affects the short circuit current density. It has also been shown that in the case of Li⁺ ion conducting, PEO based polymer electrolytes the incorporation of inorganic nano fillers increases the amorphous phase content of PEO which facilitates the higher ionic conductivity [13–16]. In this paper we report the efficiency enhancement due to both these effects, namely the mixed cation effect together with TiO₂ nano filler effect in DSSCs fabricated with PEO based quasi solid state polymer electrolytes. As far as we are aware, this is the first report on using both, the mixed cation effect and the nano filler effect for enhancing the efficiency of DSSCs.

2. Experimental

2.1. Electrolyte preparation

Polyethylene oxide (PEO) (Mw ~ $6 \times 10^6 \text{ g mol}^{-1}$) and tetrapropyl ammonium iodide (Pr₄N⁺I⁻) with purity > 98% were purchased from Aldrich. Propylene carbonate (PC), iodine chips (I₂) and KI with purity > 98% were purchased from Fluka. Ruthenium (N3) dye was purchased from Solaronix SA. PEO, TiO₂ (Degussa P-25), Pr₄N⁺I⁻ and KI were vacuum dried at 50 °C for 24 hrs prior to use.

For the preparation of the polymer gel electrolyte samples, the weights of PEO (0.1 g) and PC (0.8 g) were kept unchanged and the mass ratio of the two ionic salts Pr₄N⁺I⁻ and KI was varied while the total weight of two salts was maintained at 0.06 g. The weight of the I₂ was taken by keeping the salt to iodine ratio as 1: 10. First, appropriate amounts (Table 1) of the two salts were dissolved in PC using a magnetic stirrer. Upon the total dissolution of the two salts, PEO was added and the mixture was further stirred over night. Stirring was continued for another 12 hrs after the addition of I₂ chips in order to obtain a homogeneous gel electrolyte. The same procedure was carried out for preparing the electrolyte samples with different salt compositions. After measuring the conductivities of above electrolytes and the efficiencies of the solar cells comprising them, the best electrolyte composition (E) giving the maximum solar cell efficiency was identified and polymernanofiller composite electrolytes were prepared by adding appropriate amounts of TiO₂ to this composition as depicted in the Table 2.

2.2. Conductivity measurements.

Ionic conductivities of the gel polymer electrolytes were determined by AC complex impedance spectroscopy using a computer controlled Autolab (PGSTAT 128 N) impedance analyzer in the frequency range 0.1 Hz - 10 MHz. For impedance measurements, the electrolyte film was sandwiched between two polished stainless steel electrodes. The temperature of the sample was varied from 30 °C to 55 °C and the measurements were taken at 5 °C intervals after keeping the sample for about 15 min at each selected temperature for thermal stability. The conductivity values at each temperature were determined from the impedance measurements.

2.3. DC polarization measurements

DC polarization test was performed in order to estimate the ionic character of the gel polymer electrolytes and to determine the iodide (I⁻) ion contribution to the total ionic conductivity. The electronic contribution to the total ionic conductivity was determined from DC polarization curves taken by sandwiching an electrolyte sample between two polished stainless steel (SS) blocking electrodes in the configuration SS/electrolyte/SS and applying 1.0 V across the sample. Similarly, to determine the iodide ion (I⁻) contribution to the total ionic conductivity, DC polarization curves were taken by sandwiching the polymer gel electrolyte samples between two I₂ non - blocking electrodes in the configuration Pt/I₂/electrolyte/I₂/Pt and applying a voltage of 1 V. These experiment was carried out for each sample at room temperature.

2.4. TiO₂ electrode preparation.

TiO₂ paste was prepared by grinding 0.2 g of TiO₂ with 12 drops (~0.15 g) of Glacial Acetic acid, 1 drop (~0.02 g) of Triton X-100 and about 2 ml of ethanol. The paste was doctor bladed on pre - cleaned Fluorine - doped conducting Tin Oxide (FTO) glass (Nippon sheet glass 10–12 Ω /sq.) keeping the active cell area of 0.25 cm². The TiO₂ plates were sintered at 450 °C for 45 min. and slowly cooled down to room temperature. They were subsequently dipped in ethanolic dye solution containing Ruthenium dye N 535 [RuL₂ (NCS)₂: 2TBA where, L=2,2' - bipyridyl - 4', dicorboxylic acid; TBA=tetrabutyl ammonium] for 24 hrs.

2.5. Solar cell fabrication and I-V characterization

DSSCs were fabricated by sandwiching the gel polymer electrolyte in the configuration $FTO/TiO_2/dye/electrolyte/Pt/FTO$. The photo current - voltage (*I-V*) characteristics of the cells were measured under the illumination of 100 mW cm⁻² (AM 1.5) simulated sunlight using a homemade computer controlled setup coupled to a Keithley 2000 multi meter and a potentiostat/galvanostat HA - 301. A Xenon 500 lamp was used with AM 1.5 filter to obtain the simulated sunlight with above intensity.

2.6. Flat band potential measurements on liquid electrolyte samples

Mott-Schottky (C-V) measurements were taken by immersing a TiO_2 electrode in an electrolyte solution containing EC, PC, KI and Pr₄NI salts, but without PEO. The salt ratio of KI to Pr₄NI in the

Table 2

Weights of TiO₂ nano filler added to the sample E for the preparation of the nano composite gel electrolytes. Bold figures correspond to the electrolyte composition which gives the maximum solar cell efficiency.

TiO ₂ wt% w.r.t. solid chemicals	Sample	PEO/g	PC/g	KI/g	$Pr_4N^+I^-/g$	TiO ₂ /g	I_2/g
0.0	Е	0.100	0.800	0.045	0.015	0.0000	0.0080
2.5	Н	0.100	0.800	0.045	0.015	0.0042	0.0080
5.0	Ι	0.100	0.800	0.045	0.015	0.0084	0.0080
7.5	J	0.100	0.800	0.045	0.015	0.0126	0.0080
10.0	К	0.100	0.800	0.045	0.015	0.0168	0.0080



Fig. 1. The seven gel polymer electrolyte samples in inverted sample bottles to show their gel nature. The compositions (PEO:PC:Pr₄N⁺I⁻ + x KI:I₂) from left to right are (in wt% KI), 0%, 25%, 50%, 60%, 75%,90%,100%.

electrolyte solution samples (in EC, PC) was identical to the salt ratios used in the PEO based gel electrolyte, used for the DSSCs. In both cases, the weights of EC and PC were kept fixed while the KI to Pr_4NI weight ratio was changed by changing the KI wt% from 0 to 100. In each solution, the TiO₂ electrode was immersed for one minute and the stabilized voltage was measured with respect to a standard calomel electrode (SCE) using Mertohm Autolab PGSTAT128 N potentiostat. The scanned frequencies were 1 kHz and 1.5 kHz.

2.7. Electrochemical impedance measurements

In order to extract the electron recombination life times (τ_r), the impedance was measured for three selected DSSCs with three KI wt. %: A (0 wt% KI), B (75 wt% KI) and C (100 wt% KI) in the frequency rage 1×10^{-2} - 1×10^{6} Hz. Impedance plots as well as plots of phase angle



Fig. 2. The ln (σ T) vs 1000/T graphs for different electrolyte compositions in the system PEO: PC: Pr₄N⁺I⁻+x wt.% KI: I₂.

vs frequency (Bode Plots) were analyzed. The recombination life time values were obtained from fitting the data to appropriate equivalent circuits.

2.8. Dark I-V characteristics

Dark I-V characteristics were measured for the three DSSCs A, B and C fabricated with the gel electrolyte with 0 wt%, 75 wt% and 100 wt% of KI. The onset voltages under reverse bias were recorded in order to estimate the suppression of electron recombination.

3. Results and discussion

3.1. 1Characterization of the gel polymer electrolyte

Polymer gel electrolyte samples with different compositions prepared according to Table 1 are shown in Fig. 1. The inverted sample bottles shows the "gel" nature of the samples. The solid nature of the gel samples have been further increased by the addition of the TiO_2 nano particles.

Figs. 2 and 3 show the conductivity (on log scale) variation with the reciprocal of the absolute temperature for the electrolyte samples prepared according to the compositions given in Table 1(without nano filler) and Table 2(with TiO_2 nano filler).

The linear shape of the graphs suggests that the conductivity variation follows the Arrhenius equation.

$$\sigma T = B_{\exp}(\frac{E_a}{kT}) \tag{1}$$

where E_a is the activation energy, *B* is the pre-exponential factor and *k* is the Boltzmann constant.

The lowest conductivity of 3.17×10^{-3} S cm⁻¹ at 25 °C was obtained for the sample containing only Pr₄N⁺I⁻ as the iodide salt. As seen in Fig. 2, the conductivity gradually increases with increasing KI concentration. The highest conductivity of 6.01×10^{-3} S cm⁻¹ at 25 °C was obtained for the sample with 100% wt KI. However, out of the seven composition, the highest solar cell efficiency was obtained for the electrolyte sample E containing 75 wt% KI+25 wt% of Pr₄NI. Subsequently, TiO₂ nano



Fig. 3. The ln (σT) vs 1000/T for different electrolyte compositions in the system PEO: PC: Pr4N*I^++75 wt.% KI: y TiO_2: I_2.

filler was added to this electrolyte (sample E) in order to increase the conductivity of the electrolyte and the efficiency of the solar cells further. The ln (σ T) vs 1000/T variation for different electrolyte compositions in the filler added system PEO: PC: Pr₄N⁺I⁻+75 wt.% KI: y TiO₂: I₂ is shown in Fig. 3 and the corresponding conductivity isotherms are shown in Fig. 4. According to the conductivity vs temperature measurements (Figs. 3 and 4) the ionic conductivity has increased from 4.86×10^{-3} S cm⁻¹ to 5.69×10^{-3} S cm⁻¹ at 25 °C for the sample H containing 2.5% TiO₂. The conductivity has decreased with further addition of the TiO₂ nano filler.

The total ionic conductivity of the gel electrolyte samples is made up of individual conductivity contributions from K⁺, $Pr_4 N^+$, I^- and I_3^- ions. When PEO is used as the host polymer, the oxygen atoms in the polymer chain (hetero atoms) coordinates with the cations in the electrolyte. As the interaction of anions with the polymer is weaker the transport of anions (I^- and I_3^-) has to take place by ionic diffusion through the electrolyte medium facilitated by the flexibility of the polymer chain. In this study, PC (organic solvent) was used as the plasticizer in order to reduce the viscosity of the PEO polymer. According to the work reported by Sankar Bhattacharja *et a.l* [17] on a PEO based electrolyte system, the value of the cation diffusion coefficient (t_+) varied in the range 0.34 at 428 K to 0.41 at 448 K in the poly (ethylene) oxide-lithium triflate [(PEO)₈LiCF₃SO₃] polymer-salt complex. This implies that in PEO based polymer electrolytes, both cations and



Fig. 4. variation of conductivity with the TiO_2 wt.% for different temperatures.

anions contribute to the total ionic conductivity. It is also reported that the cationic transference number decreases by 46% with the addition of PC. Therefore, these PC incorporated PEO based gel polymer electrolytes evidently favour anionic conductivity [13,14,16,18]. On the other hand, as Pr_4N^+ cation is a large and bulky compared to K^+ cation and K^+ ions are expected to be much more mobile in the electrolyte medium compared to Pr_4N^+ ions. Therefore, the observed increase in the total ionic conductivity with increasing KI concentration very likely comes from the K⁺ ions.

As seen in Fig. 5, the highest conductivity among the nano titania filler added composite polymer electrolytes was obtained for the sample H (PEO: PC: 25 wt% $Pr_4N^+I^-$ + 75 wt.% KI) containing 2.5 wt% TiO₂ (with respect to the toal weight of the filler free electrolyte sample). It is well known that the addition of nano fillers decreases the crystallinity of PEO and increase the amorphous phase content [4,15]. This will favour the ionic mobility and in turn enhance the ionic conductivity. A further conductivity enhancement may operate due to the creation of transient hopping sites and additional conducting pathways through Lewis acid base type interactions by cationic species with TiO₂ nano particles similar to the case of PEO based Li⁺ ion systems [14–16,19]. This could also increase the ionic mobility and cationic conductivity. However, the increase in anionic conductivity, in this case the iodide ion conductivity, can only be due to the increase in the PEO amorphous phase because the iodide ions are expected to migrate in the electrolyte medium by ionic diffusion which is facilitated by the amorphous nature of the electrolyte medium. According to the work reported by Zhipeng Huo et al. [19], the apparent diffusion coefficient of I_3^- increases with the addition of TiO₂ nano particles because of the reduction of the normal gel hindrance in charge transport. The reduction of the ionic conductivity at higher TiO₂ concentrations is very likely due to the blocking effect caused by the closeness of the nano titania particles and their aggregates [15,16].

DC polarization curves taken for the gel electrolyte samples PEO: PC: Pr₄N⁺I⁻ + x wt.% KI: I₂ are shown in Fig. 5. Top six curves were obtained using I₂ non - blocking electrodes and the top most curve was taken for sample H containing 2.5% wt TiO₂. These DC polarization test results clearly show the variation of the anionic transference number for different electrolyte compositions.

In Fig. 5, the bottom dc polarization curve was obtained for the sample E (75% wt. KI, and maximum solar cell efficiency) with



Fig. 5. DC polarization curves taken for the gel electrolyte samples PEO: PC: $Pr_4N^{\dagger} + x$ wt.% KI: l_2 . Top six curves were obtained using l_2 non-blocking electrodes. The top most curve was obtained for sample H incorporating 2.5% TiO₂. The bottom curve (continuous line) was taken with stainless steel blocking electrodes for sample E.



Fig. 6. The variation of short current density (J_{sc}) of the DSSCs and the iodide ion transference number of the electrolyte with wt% KI.

stainless steel blocking electrodes. Similar curves with SS electrodes (not shown) were obtained for the other samples as well. For all these cases, the rapid decay of current with time finally approaching below 5% in 300 minutes implies the predominantly ionic nature and the negligible electronic conductivity in the samples. Other curves shown in Fig. 5 for electrolyte samples with different compositions taken with I2 non-blocking electrodes exhibit clearly the composition dependence of the iodide ion transference number. Out of the filler free electrolytes, sample E with 75 wt% KI exhibits the highest iodide ion transference number of 0.49. Addition of 2.5 wt% of nano TiO₂ filler to this sample (resulting sample H) clearly shows an enhancement in the iodide ion transference number reaching a value of 0.60. It is interesting to note that the variation of iodide ion transference number with salt weight ratio follows the same trend as the variation of the short circuit photo current density (J_{sc}) of the corresponding DSSC as seen in Fig. 6. Therefore, the increase in short circuit current density can be attributed to the increase in iodide ion conductivity in the electrolyte samples. The maxima of both, Isc of the DSSCs and the iodide ion transference number in the electrolyte, occur at 75wt% KI electrolyte composition.



Fig. 7. Photocurrent - photovoltage (*I-V*) characteristic curves for solar cells with configuration FTO/TiO₂/Dye/electrolyte/Pt/FTO fabricated with four selected electrolyte samples.

Table 3

Parameters of the solar cells with PEO: PC: $Pr_4N^+I^- + x$ KI: I_2 and PEO: PC: $Pr_4N^+I^- + x$ KI: TiO₂ I_2 gel electrolyte samples as a function of KI wt.%. Bold values correspond to the electrolyte composition which gives the highest solar cell efficiency. Sample labeling refers to compositions given in Table 2.

Sample	KI wt.%	Amount of TiO ₂ wt.%	$J_{sc}/mA \ cm^{-2}$	V _{oc} /mV	FF %	η %
А	0	-	6.47	763.1	63.3	3.12
В	25	-	7.03	756.6	60.8	3.24
С	50	-	8.60	691.2	59.7	3.55
D	60	-	9.64	681.0	57.4	3.77
E	75	-	10.83	672.3	56.6	4.12
F	90	-	9.36	682.1	62.2	3.97
G	100	-	9.23	618.2	55	3.92
Н	75	2.5	13.03	704.5	57.8	5.31
I	75	5	12.69	681.7	58.7	5.08
J	75	7.5	12.17	693.1	59.1	4.99
К	75	10	9.56	687.0	59.0	3.88
L	75	15	9.01	669.0	57.0	3.43

3.2. 1Characterization of dye-sensitized solar cells

Characterization of solar cells fabricated using the electrolytes with different compositions described above including those with TiO₂ filler (Tables 1 and 2) were done using the cell configuration FTO/TiO₂/Dye/electrolyte/Pt/FTO. Although we have obtained photocurrent - photovoltage (*I-V*) characteristic curves for DSSCs with all the seven electrolyte samples, for the purpose of clarity only the curves for solar cells made with four selected compositions are shown in Fig. 7. These are: 0 wt% KI(sample A), 75 wt% KI (sample E), 100 wt% KI (sample G) and 75 wt% KI + 2.5 wt% TiO₂ (sample H). The fill factor (FF) and the efficiency (η) were calculated using the open circuit voltage (*V*_{oc}) and short circuit current density (*J*_{sc}). The observed results are tabulated in Table 3. The fill factor was calculated using,

$$ff = \frac{J_{\text{opt}} V_{\text{opt}}}{J_{\text{sc}} V_{\text{oc}}} \tag{2}$$

where, are the current density and voltage at maximum power output. The efficiency was calculated using

$$\eta = \frac{\int_{sc} V_{oc} FF}{\text{Totalincidentpowerdensity}}$$
(3)

The effect of mixed cation iodide salts in enhancing the efficiency of dye sensitized solar cells have been reported by others and by us for several DSSC systems [5,8–10]. Here we report the effects f both the mixed cations and TiO₂ nano filler on enhancement of solar cell efficiency. An earlier report by Agarwala et al. on a DSSC with a PEO based polymer electrolyte with LiI and KI mixed iodide system has shown a maximum efficiency of 4.5% for 14.5 wt% of KI composition [5]. Authors have attributed this efficiency enhancement to the reduction of PEO crystallinity caused by attraction of K⁺ ion to the oxygen atoms in PEO matrix.

The effect of various cation charge densities on solar cell performance have been reported by Shi et al. [20]. Their study on Li⁺, Na⁺, K⁺ and dimethylimidazolium (DMI⁺) has shown a higher short circuit current density and a smaller open circuit voltage for small cations and vise versa. When the end members of the present system (samples A and G) are considered, the short circuit current density has changed from 6.468 mA cm⁻² (for 100 wt% Pr₄N⁺I⁻) to 9.232 mA cm⁻² (for 100 wt% KI) and the corresponding open circuit voltage has changed from 763.1 mV to 618.2 mV. Fig. 8 shows the variation of the short circuit current density and the efficiency of the solar cells with respect to the amount of KI% in the electrolyte. As can be clearly seen from this figure, the variation as the J_{sc} of the cells. The increase of the J_{sc} with increase in KI concentration in the electrolyte could be explained in terms of the enhancement of

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Electron recombination life times	τ_r) ex	tracted f	from the	impe	dance si	pectra b	v fitting	app	ropriate	equivalent	circuits.
							,				

Composition KI W/W	Solar Cell	Efficiency	Frequency (Hz)	τ_r (ms)	V _{oc} (mV)
0%	А	3.12	8.7	18.3	763
75%	В	4.12	9.2	17.3	672
100%	С	3.92	12.4	12.8	618

the iodide ion conductivity (or the iodide ion transference number) of the mixed salt electrolyte and the intercalation of cations into the TiO₂ electrode. It is generally known that the velocity of the random walk of electrons through the nanoporous TiO₂ layer in the photoanode is mainly reduced by the traps in the layer. Small cations like K⁺ and Li⁺ can intercalate into these traps causing a positive shift in the conduction band leading to an increase in the *I*_{sc} by increasing the charge injection rate while decreasing the open circuit voltage of the cell (Table 3). This positive shift caused by the intercalation of cations varies according to the type and the size of the cation used. It is greater for small cations and vise versa. On the other hand, for an iodide salt with a bulky cation such as Pr₄NI, the positive conduction band shift is smaller for the cations, but the ionic dissociation is greater generating more iodide (I⁻) ions while the cations are expected to be essentially immobile compared to the anions. Therefore, the existence of the two iodide salts with dissimilar cations gives rise to the enhancement in iodide ion conductivity of the electrolyte at some optimum composition (sample E with 75 wt% KI), it also increases the charge injection rate and hence the enhancement in the short circuit current density and the efficiency of the solar cell.

Incorporation of TiO₂ nano particles into the electrolyte improved the J_{sc} , V_{oc} and the fill factor of the DSSCs enhancing the overall solar cell efficiency by 28.9%. The best efficiency was obtained for sample H with 2.5 wt.% of TiO₂ (Table 3). These results are somewhat similar to the results reported by Z. Huo et al. for the DSSC system fabricated with (P(VDF-HFP)) based nano composite gel electrolyte containing TiO₂ nano particles [19]. The reduction of the crystalinity (or enhancement of the amorphous phase content) of the PEO electrolyte with the addition of the TiO₂ nano filler facilitates the anion migration. In the DSSC with optimized filler added electrolyte (sample H) this would lead to an increases in the short circuit photo current density of the solar cell. At the same time it reduces the rate of recombination of electrons at the dyed TiO₂ photoanode/electrolyte interface leading to a reduction of the dark current resulting a higher photo voltage, V_{oc} as seen in



Fig. 8. Variation of efficiency and short circuit current density, J_{sc} with respect to the KI wt.% in the electrolyte.

Table 3. The efficiency of the solar cells decreases with further addition of the nano filler. As stated previously, this is very likely due to the reduction of anion mobility caused by the blocking effect [11]. Therefore the combined effect of three processes, namely (a) the enhancement of the current density due to the increased iodide ion conductivity resulting from the mixed cation effect in the electrolyte, (b) the positive shift of the conduction band position of the TiO₂ due to the K⁺ cation adsorption, and (c) the conductivity enhancement of the electrolyte due to the increased amorphous phase content of the PEO based electrolyte caused by the addition of nano TiO₂ filler eventually enhances the overall efficiency of the solar cell comprising the optimized electrolyte H.

3.3. Salt concentration dependence of open circuit voltage (V_{oc}) - Alternative experimental evidence

In order to confirm the dependence of $V_{\rm oc}$ with wt% KI observed in I-V measurements of DSSCs, we have performed three alternative experiments: Flat band potential of the TIO₂ electrode, electrochemical impedance and dark I-V characteristics. Results of these experiments are briefly described below.

Results of the Flat Band Potential measurements taken on the TiO_2 electrode immersed in an electrolyte solution having the same composition as the gel electrolyte but without the PEO polymer are shown in Fig. 9. This figure clearly shows the movement of the flat band potential V_{fb} of the TiO₂ electrode in contact with the electrolyte solution as the KI salt concentration is gradually increased. The gradually decreasing trend of the V_{fb} follows essentially the decreasing trend in V_{oc} with increasing wt% of KI.

However, our attempts to do the Flat Band Potential measurements using the PEO based "gel electrolyte" was not successful due to practical difficulties of using a "gel" electrolyte. We believe that even in the presence of PEO, which is acting like a host matrix, the movement of the flat band with salt concentration would essentially be similar.

Impedance plots taken for the three selected DSSCs with three KI wt. %: A (0 wt% KI), B (75 wt% KI) and C (100 wt% KI) in the frequency rage 1×10^{-2} - 1×10^{6} Hz are shown in Fig. 10. In an



Fig. 9. Variation of the Flat Band Potential of the TiO_2 electrode immersed in an electrolyte solution having the same composition as the gel electrolyte but without the PEO polymer.



Fig. 10. Impedance plots taken for the three selected DSSCs with three KI wt. %: A (0 wt% KI), B (75 wt% KI) and C (100 wt% KI) in the frequency rage 1×10^{-2} - 1×10^{6} Hz.

ideal impedance spectrum, three semicircles could be seen which corresponds to the charge transference resistance of Pt counter electrode/electrolyte interface (R_{1CT}), TiO₂ electrode/electrolyte interface (R_{2CT}) and ion diffusion of the electrolyte respectively (R_{3CT}) [21,22]. However, in the present study only the first two arcs appeared in the impedance spectrum. The third arc which corresponds to the ion diffusion could not be obtained since the low frequencies needed to obtain this arc are out of the instrument's frequency range. Electron recombination life times (τ_r) extracted from the impedance spectra by fitting appropriate equivalent circuits are shown in Table 4. A higher electron recombination lifetime implies that the photogenerated electrons get sufficient time to go through the TiO_2 layer [21,22]. As seen in the Fig. 10, out of the three solar cells, the cell A assembled using the electrolyte with 0 wt% KI (or 100 wt% Pr4NI) shows the highest charge transfer resistance. In dark, solar cell works as a leaky capacitor. Therefore, under forward bias conditions, photogenerated electrons are transported through TiO₂ layer and participate in the reduction of I_3^- to I^- .

When the impedance data are represented as a plot of phase angle vs frequency (Fig. 11, Bode Plots), the maximum frequencies correspond to the three DSSCs with three different KI concentrations (A, B, C). The recombination life time values obtained from fitting the data to appropriate equivalent circuits is shown in Table 5.

Table 5

Onset of the reverse breaking voltage of the tree DSSCs with three different KI wt %.

Composition Wt.% KI	DSSC	Reverse Breaking down voltage (onset)
0%	A	-320 mV
75%	В	-270 mV
100%	С	-250 mV

Higher value of the recombination life times (τ_r) of cell A implies greater suppression of recombination losses leading to a higher open circuit voltage while the opposite is true for the cell C with the smallest value of τ_r .

Dark I-V characteristics of the three DSSCs A, B and C fabricated with the gel electrolyte with 0 wt%, 75 wt% and 100 wt% of KI are shown in Fig. 12. The onset under reverse bias occurs at three different voltages as shown in Table 5. Results show that the recombination is better suppressed in the cell A, compared to cell B and in the cell B compared to cell C in agreement with the results obtained from impedance data.

Dark current is supposed to occur at the TiO₂/electrolyte interface where the photosensitizers are not adsorbed. To suppress dark current, pyridine derivatives such as *tert*-butylpyridine (TBP) have been employed as co-adsorbates on the TiO₂ surface, resulting in the improvement of photovoltage [23]. TBP is considered to adsorb on the uncovered TiO₂ surface. Similarly, Pr₄N⁺ cations in the present system, can be expected to get adsorbed in to the TiO2 surface and contribute towards suppression of the dark current, and improve the V_{oc} . Clearly, this effect is greatest for the DSSC with the 100 wt. % Pr₄NI electrolyte (or 0 wt.% KI electrolyte) and decreases gradually as the amount of Pr4NI is decreased (or the amount of KI is increased). This is reflected as a gradual drop in $V_{\rm oc}$ as expected. A corresponding decrease in short circuit photocurrent density, J_{sc} is observed up to the maximum efficiency composition of 75 wt.% KI evidently resulting from the negative shift of the conduction band level of TiO_2 caused by the adsorption of Pr_4N^+ by TiO_2 surface. The drop in J_{sc} after the maximum efficiency composition is very likely due to the "electrolyte effect" where the decrease in iodide ion concentration due to (a) reduced Pr₄NI salt content, (b) increased KI salt concentration leading to the formation of higher ionic aggregates and (c) increased viscosity in the medium.



Fig. 11. Impedance data plotted as phase angle vs frequency (Bode Plots), for the three DSSCs with three KI wt. %: A (0 wt% KI), B (75 wt% KI) and C (100 wt% KI) in the frequency rage 1×10^{-2} - 1×10^{6} Hz.



Fig. 12. Dark I-V characteristics of the three DSSCs A, B and C fabricated with the gel electrolyte with 0 wt%, 75 wt% and 100 wt% of KI.

5. Conclusions

Efficiency enhancement has been achieved in dye sensitized solar cells (DSSCs) fabricated with polymer gel electrolytes PEO: PC: $Pr_4N^+I^-+x$ KI: I_2 containing two iodide salts with two dissimilar size cations. The mixed cation effect enhances the short circuit photo-current density through enhanced iodide ion conductivity and improved electron dynamics at the TiO₂ electrode/electrolyte interface. The nano-filler effect due to the incorporation TiO₂ nano fillers into the polymer electrolyte further enhances the solar cell efficiency evidently due to the increased ionic mobility caused by the increased amorphous phase content of the PEO based polymer electrolyte.

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