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# Efficiency enhancement by mixed cation effect in dye-sensitized solar cells with PAN based gel polymer electrolyte

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# ABSTRACT

Dye-sensitized solar cells based on nano-porous TiO<sub>2</sub> photo-anode and quasi-solid polymer (or gel) electrolytes are emerging as low cost alternatives to conventional inorganic photovoltaic devices. Although many attempts have been made in order to improve the relatively low power conversion efficiencies of these solar cells, to our knowledge there are very few reports aimed at using a binary system of two different iodide salts toward efficiency enhancement in these cells. In this paper we report for the first time in detail, the effect of using a binary iodide salt mixture with different size cations on the efficiency enhancement in dye sensitized solar cells with polyacrylonitrile (PAN) based gel polymer electrolyte and suggest a possible mechanism for this enhancement, based on short circuit photocurrent which is directly related to the iodide ion concentration [I<sup>-</sup>]. The gel electrolyte was made of PAN, ethelene carbonate (EC), Propylene carbonate (PC), salt mixture and I<sub>2</sub>. The binary iodide salt mixture consists of potassium iodide (KI) and Tetra propyl ammonium iodide (Pr<sub>4</sub>NI). Although the gel electrolyte with 100% (w/w) KI exhibited the highest overall ionic conductivity at room temperature, it showed the lowest iodide ion  $(I^{-})$  contribution to conductivity. On the other hand, the electrolyte with 100% (w/w) Pr<sub>4</sub>NI exhibited the lowest overall ionic conductivity but had the highest iodide ion(I<sup>-</sup>) contribution. The dye-sensitized solar cells of configuration Glass/FTO/TiO2/N-719 Dye/electrolyte/Pt/FTO/glass were fabricated using the gel electrolytes of different salt ratios and with nanoporous TiO<sub>2</sub> electrode sensitized with Ruthenium dye (N719). With identical electrolyte compositions, the solar cell with 100% (w/w) KI showed an efficiency of 4.98% and the cell with 100% (w/w)  $Pr_4NI$  showed an efficiency of 4.47%. However, the cell with the mixed iodide system, 16.6% (w/w) KI+83.4% (w/w) Pr<sub>4</sub>NI showed the highest efficiency of 5.36% with maximum short circuit current density ( $J_{sc}$ ) of 13.79 mA cm<sup>-2</sup>, open circuit voltage ( $V_{oc}$ ) of 679.10 mV and a fill factor of 57.25%.

The variation of efficiency ( $\eta$ ) with iodide ion concentration [I<sup>-</sup>] follows the same trend as the  $J_{SC}$  which appears to be governed by the iodide ion conductivity of the gel electrolyte. The dependence of the short circuit photocurrent and the open circuit photovoltage on the cation type generally agrees with reported data for related systems. However, the occurrence of a maximum in the solar cell efficiency and short circuit photocurrent at 16.6% (w/w) KI+83.4% (w/w) Pr<sub>4</sub>NI salt composition is an important finding.

The efficiency enhancement of about 8% achieved by employing the binary iodide mixture in the gel electrolyte instead of a single iodide salt, could be utilized for achieving efficiency enhancement in many dye sensitized solar cell systems based on polymeric, gel or solvent electrolytes.

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# 1. Introduction

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Photoelectrochemical (PEC) solar cells based on nanostructured, dye-sensitized titanium dioxide  $(TiO_2)$  have attracted worldwide attention as a low cost alternative to conventional silicon and thin film solar cells [1–3]. A typical dye-sensitized solar cell (DSSC) consists of a semi-transparent dye-sensitized, nano-porus nano

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crystalline TiO<sub>2</sub> film, an electrolyte with a redox couple and a Pt coated counter electrode. These dye-sensitized solar cells generally employ a solvent electrolyte based on acetonitrile and a  $I^{-}/I_{3}^{-}$  redox couple and have impressive energy conversion efficiencies reaching around 11%. However, a major drawback of these solution based solar cells, originally developed by Gratzel and coworkers [1] is the lack of long-term stability due to liquid leakage, usage of volatile liquids such as acetonitrile, electrode corrosion, and photodecomposition of the dye in the solvent medium. In order to overcome these problems, many efforts have been made by replacing the liquid electrolyte by gel polymer electrolyte (or quasi-solid electrolyte) [4–10]. In particular, PAN based gel polymer electrolytes are found to be reasonably good ionic conductors and they have been used successfully in quasi solid-state DSSCs [10-15]. In these PAN based gel electrolytes, whether they are cationic or anionic conductors, it is generally accepted that the electrolytic solution formed by dissolving the ionic salt in a ethylenecarbonate/propylenecarbonate (EC/PC) co-solvent is "entrapped" in cages formed by the PAN polymer matrix yielding almost liquid like ionic conductivities [16]. For the action of a DSSC, the gel electrolyte has to be an anion conductor and in most cases these are iodide ion (I<sup>-</sup>) conductors. The iodide ion conductivity contribution to the overall ionic conductivity of the electrolyte in a DSSC is a major factor which determines the short circuit current density (J<sub>SC</sub>) and hence the efficiency of a DSSC. This is because, the iodide ion, while participating in the redox reaction, also shuttles between the photo-electrode and the counter electrode. Quaternary ammonium salts such as Pr<sub>4</sub>NI, Bu<sub>4</sub>NI and Hex<sub>4</sub>NI are therefore widely used as ionic salts in these electrolytes. Although iodide ion conductivity is an important parameter in determining the short circuit photocurrent and the efficiency of DSSCs, not much systematic research work has been reported on this aspect.

Tetrapropylammonium iodide ( $Pr_4N^+I^-$ ) has been used with a PAN host polymer and solar cell efficiencies reaching about 3% have been reported [13,17]. Solar cells using PAN gel polymer electrolyte incorporating tetrabutylammoniumiodide ( $Bu_4N^+I^-$ ) as the salt has also been reported to show reasonably good efficiencies [11,15]. KI has also been used widely to participate in the iodide/triiodide redox reaction and to provide the iodide ion conductivity in a large number of DSSC systems [18–20]. Several studies have revealed that cation in the electrolyte has a profound influence not only in determining the short circuit current density ( $J_{sc}$ ) but also on the electrolyte/semiconductor interface electron dynamics and hence on the efficiency of DSSCs [21–24].

There are only very few published reports on the use of a binary iodide mixture in DSSCs. According to some recent reports, electrolytes with iodide salt mixtures have shown better DSSC performance compared to using only one iodide salt [20,25]. This can be understood by studying the dual role of the cation in determining the short circuit current density through iodide ion conductivity as well as in influencing the charge injection mechanism at the semiconductor/electrolyte interface.

A study of the influence of cations on the excited-state deactivation kinetics of a dye coated  $TiO_2$  has shown that the magnitude of electron injection yields of dye varies with the charge-to-radius ratio of the cation in the electrolyte [23]. The effect of photo-generation of electrons and their diffusion in DSSCs having electrolytes containing double cationic system has also been reported [24]. In another study DSSCs containing aqueous electrolytes with various cations have shown that short circuit current density increases with the increasing charge density of the cation in the electrolyte while the fill factor, open circuit voltage and efficiency decreases [26,27]. Therefore, from these findings it is clear that while bulky cations such as  $Pr_4N^+$  and  $Hex_4N^+$  are expected to minimize the cationic conductivity and enhance the iodide ion conductivity in the electrolyte, cations with high charge density, such

as K<sup>+</sup>, Li<sup>+</sup> or Na<sup>+</sup> are expected to contribute towards better photogeneration of electrons at the dye and faster diffusion dynamics at the dye–semiconductor interface. Therefore, it would be natural to explore the combined effect of using a binary mixture of two iodide salts consisting of a bulky cation and a small alkali cation with high charge density in the electrolyte in order to benefit from both above mentioned mechanisms. With this idea in mind, we have studied the present system by choosing the quarteneryammonium salt ( $Pr_4NI$ ) as the salt with a bulky cation and KI as the salt with a small alkali cation.

The aim of the present work is to try to enhance the efficiency of a DSSC with a PAN based gel electrolyte by maximizing the short circuit photocurrent ( $J_{sc}$ ) through enhanced iodide ion conductivity by having the optimum molar ratio of a binary iodide mixture consisting of  $Pr_4N^+I^-$  with a bulky cation as one iodide salt and KI with a small alkali cation as the second iodide salt.

Our group has already observed the beneficial effect of using this type of binary iodide salt mixture on the efficiency enhancement in quasi-solid state DSSCs in a recent study where we have used the binary iodide mixtures  $MgI_2 + Pr_4NI$  in one system and  $MgI_2 + Hex_4NI$  in the other system [25,28]. As far as we are aware, this is the first report of a DSSC employing a binary iodide system incorporating an alkali salt with a small cation (K<sup>+</sup>) and a quaternary ammonium iodide with a bulky cation (Pr<sub>4</sub>N<sup>+</sup>), focusing the role of iodide ion conductivity.

# 2. Experimental

# 2.1. Electrolyte preparation

PAN and Pr<sub>4</sub>NI with purity greater than 98% purchased from Aldrich and EC, PC, iodine chips (I<sub>2</sub>) and KI with purity greater than 98% purchased from Fluka were used as starting materials. Ru (N719) dye was purchased from Solaronix SA. All the chemicals except I<sub>2</sub> and PC were vacuum dried at 60 °C for 24 h in a vacuum oven (Eyela VOS – 450D) prior to use.

For preparing the electrolyte samples, based on our previous experience, the weights of PAN (0.10 g), EC (0.40 g) and PC (0.40 g) were kept unchanged while the total weight of KI and Pr<sub>4</sub>NI was maintained at 0.06 g. The weight of iodine was taken to be one-tenth of the total mole amount of the iodide salts. Appropriately weighed quantities were mixed in a glass bottle by magnetic stirring. Initially EC, PC, PAN, Pr<sub>4</sub>NI and KI were mixed by continuous stirring at room temperature for about for 2 h until the entire KI has been dissolved. Then the mixture was stirred further keeping it at 80 °C for about 30 min until PAN was fully dissolved. Finally the mixture was allowed to cool down to room temperature and I<sub>2</sub> chips were added and again continuously magnetically stirred in a closed bottle overnight (12 h) to obtain a homogeneous gel electrolyte. This procedure was repeated for all the compositions shown in Table 1.

Table 1

Weight percentages of KI and  $Pr_4NI$  used to prepare the PAN based polymer gel electrolyte. The weights of PAN, EC and PC were kept at 0.1 g, 0.4 g and 0.4 g respectively for all the compositions.

Electrolyte	KI % (W/W)	$Pr_4N^{+}I^{-}~\%~(W/W)$	KI (g)	$Pr_4N^+I^-(g)$	$I_2(g)$
Α	0	100	0.00	0.06	0.0049
В	8.3	91.7	0.005	0.055	0.0052
С	16.6	83.4	0.01	0.05	0.0056
D	33.3	66.7	0.02	0.04	0.0063
Ε	50.0	50.0	0.03	0.03	0.0070
F	100.0	0	0.06	0.00	0.0092

Bold values correspond to the electrolyte composition which gives the maximum solar cell efficiency.

# 2.2. Conductivity measurements

The ionic conductivity of the gel polymer electrolyte samples was determined by the AC complex impedance method with a computer controlled Solatron SI–1260 impedance analyzer in the frequency range 20 Hz–10 MHz. Disc shaped thin films sandwiched between two polished stainless steel electrodes were used for impedance measurements. The temperature of the sample was varied from about 30 °C to about 60 °C at approximately 5 °C intervals. The temperature of the sample was allowed to stabilize at each measuring temperature for about 30 min. For all the six compositions studied, the ionic conductivity at each temperature was extracted from the corresponding impedance plots.

### 2.3. DC polarization measurements

In order to estimate the ionic nature of the gel electrolyte, the dc polarization test was carried out at room temperature by sandwiching the electrolyte sample between two stainless steel (SS) blocking electrodes in the SS/electrolyte/SS configuration and applying a small dc voltage of about 1 V and measuring the variation of the resulting current with time. This test was repeated for all the samples sandwiching them between two iodine non-blocking electrode pellets in the SS/I<sub>2</sub>/electrolyte/I<sub>2</sub>/SS configuration in order to estimate the iodide ion contribution to ionic conductivity.

# 2.4. TiO<sub>2</sub> electrode preparation

TiO<sub>2</sub> paste was prepared by grinding 0.20 g of TiO<sub>2</sub> (Degussa P-25) with 12 drops (about 0.15 g) of glacial acetic acid, one drop (about 0.02 g) of triton X-100 and about 2 ml of ethanol. This paste was spread on a pre-cleaned, fluorine-doped conducting tin oxide (FTO) glass (Nippon sheet glass  $10-12 \Omega/sq$ ). An active cell area of 0.25 cm<sup>2</sup> was obtained by spreading the paste using the doctor blade technique and sintering at 450 °C for 45 min. The resulting TiO<sub>2</sub> nano-porous film was allowed to cool down to room temperature. The thickness of the film on FTO glass was measured with the help of a homemade, calibrated profilometer and the average film thickness of the TiO<sub>2</sub> film was found to be around 12 µm. Dye absorption was carried out by immersing the above film in ethanolic dye solution containing Ruthenium dye N719 [RuL<sub>2</sub>(NCS)<sub>2</sub>:2TBA where, L=2,2'-bipyridyl-4,'-dicarboxylic acid; TBA = tetrabutylamonium] for 24 h.

# 2.5. Solar cell fabrication and characterization

polymer The electrolyte gel based dvesensitized cells (DSSCs) of configuration solar glass/FTO/TiO<sub>2</sub>/Dye/electrolyte/Pt/FTO/glass were fabricated by sandwiching the polymer electrolyte between the dye adsorbed TiO<sub>2</sub> electrode and a platinum (Pt) coated FTO glass. The photocurrent-voltage (I-V) characteristics of the cells were measured under the illumination of 100 mW cm<sup>-2</sup> (AM 1.5) simulated sunlight using a homemade computer controlled setup coupled to a Keithley 2000 multimeter and a potentiostat/galvonostat HA-301. A Xenon 500 lamp was used with AM 1.5 filter to obtain the simulated sunlight with above intensity.

# 3. Results and discussion

# 3.1. Characterization of the gel polymer electrolyte

Different compositions of the gel polymer electrolyte, PAN:EC:PC:  $Pr_4N^+I^- + x$  wt% KI,  $I_2$ , for x = 0%, 8.3%, 16.6%, 33.3%, 50%, 100% prepared with the binary iodide mixture  $Pr_4N^+I^-$  and KI used in this study are shown in Table 1. A photograph of the six

**Fig. 1.** The six gel polymer electrolyte samples (PAN:EC:PC:  $Pr_4N^+I^- + x \text{ wt% KI}, I_2$ ) in inverted sample bottles to show the gel nature of the electrolytes; The compositions (*x*) from left to right are (in wt% KI): 0%, 8.3%, 16.6%, 33.3%, 50%, 100%.

samples in inverted sample bottles is shown in Fig. 1 to show the "gel" nature of the electrolytes.

The variation of conductivity (on log scale) plotted against the reciprocal temperature for different electrolyte compositions are shown in Fig. 2. The conductivity of the electrolyte containing only Pr<sub>4</sub>NI as the salt (sample *A*) has the lowest conductivity at all measured temperatures. It has a conductivity of  $2.4 \times 10^{-3}$  S cm<sup>-1</sup> at 27 °C. The conductivity gradually increases with the increasing amount of KI in the electrolyte and the electrolyte containing only KI (sample *F*) shows the highest conductivity of  $4.4 \times 10^{-3}$  S cm<sup>-1</sup> at 27 °C.

As seen in the Fig. 2, from the linear shapes, the conductivity appears to follow the Arrhenius equation,

$$\sigma T = B \exp\left(-\frac{E_{\rm a}}{kT}\right)$$

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

In order to explain the observed variation of conductivity with reciprocal temperature, we make use of the fact that these PAN based gel electrolytes are formed essentially by "trapping" the EC/PC (ethylene carbonate/propylene carbonate) based electrolytic



**Fig. 2.** The variation of conductivity (on log scale) plotted against the reciprocal temperature for different electrolyte compositions in the system PAN:EC:PC:  $Pr_4N^+I^- + x$  wt% KI,  $I_2$ .



solution in the matrix formed by PAN [13]. PC is a solvent with low molecular weight and high dielectric constant. While the high dielectric constant favours salt dissociation, the low viscosity would lead to high ionic mobility in the electrolytic solution is formed by dissolving the two ionic salts in the EC/PC co-solvent. Therefore, we would expect the conducting properties of the gel electrolyte system in the present study to be determined essentially by the properties of the electrolytic solution at all concentrations.

According to Fig. 2, the activation energy values, which correspond to the Arrhenius plot, are almost constant for all six gel electrolyte samples studied and independent of the slat concentration ratios [KI]/[Pr<sub>4</sub>NI]. Although the temperature dependence of conductivity in organic polar solvent electrolytes is an important area in electrochemistry, to our surprise, there are only a handful of published literature available [29]. In order to explain this result, we would like to refer to two recent publications by Petrowsky and Frech [30,31] on temperature dependent ion transport in organic liquid electrolytes and amorphous polymer electrolytes. These authors suggest that ion transport in these electrolytes is governed by a single activation process which depends on the solvent family. For a given salt (or a salt mixture), the activation energy is largely independent of the salt concentration for low and moderate concentrations and the type of salt used but depends essentially only on the type of solvent, in particular on the nature of the solvent heteroatom. Their results show that the ion transport in these systems involves a single activated process, which depends on the solvent functional group. This activation process is very likely the dipole re-orientation which depends on the dipole relaxation rates.

In the case of a solid electrolyte, the ion transport would consist of thermally activated hopping from an occupied site to a vacant site, with an energy barrier equal to the activation energy,  $E_a$ . In the case of organic liquid electrolytes and amorphous polymer electrolytes, the immediate environment surrounding the mobile ionic species undergoes dipole rearrangement in response to the change in position of the mobile ion, and therefore, the energy of activation would involve the energy required for rearrangement of the local structure.

We can use a similar interpretation to explain the observed conductivity vs temperature variation of the present gel electrolyte system which essentially consists of an ionic salt (or a mixture of two salts) dissolved in the organic polar co-solvent EC/PC, "entrapped" in a PAN matrix. The energy of activation, is therefore, depends to a large extend, on the nature of the co-solvent and essentially unaffected by the type and the concentration of the salt(s). This is very likely the reason for the essentially similar activation energies seen for the conductivity plots depicted in Fig. 2.

The ionic conductivity of the sample *F* (only with KI salt) originates from two types of ions, namely K<sup>+</sup> ions and I<sup>-</sup> ions and both these ions contribute to the highest conductivity seen for this sample. On the other hand, the ionic conductivity of the sample with  $Pr_4N^+I^-$  only (sample *A*) is the lowest. As the cation  $Pr_4N^+$  in this electrolyte sample is bulky, the iodide ions (I<sup>-</sup>) are expected to make the dominant contribution to the ionic conductivity of this sample. As the weight percentage of KI in the electrolyte increases from sample *A* to *F*, the gradual increase in ionic conductivity is evidently due to the increase in the number of dissociated ions in the electrolytic solution formed by dissolving the iodide salt mixture in the EC/PC co-solvent which is "trapped" in the PAN polymer matrix. At any given salt concentration, the dissociated K<sup>+</sup> and I<sup>-</sup> ions from KI as well as I<sup>-</sup> ions from Pr<sub>4</sub>NI will make the dominant contribution to the ionic conductivity of the gel electrolyte.

We shall use the DC polarization data depicted in Fig. 3 to estimate the contribution from iodide ions  $(I^-)$  to the overall ionic conductivity of the electrolyte samples, although one cannot use the dc polarization data for a more accurate



**Fig. 3.** DC polarization curves taken for the gel electrolyte samples, PAN:EC:PC:  $Pr_4N^+I^- + x$  wt% Kl,  $I_2$ . Top four curves are taken with iodine non-blocking electrodes and the bottom curve was taken with blocking stainless steel electrodes for the 0.01 g KI sample (C).

quantitative analysis. These DC polarization curves, taken with iodine pellet non-blocking electrodes, for the gel electrolyte samples, PAN:EC:PC:  $Pr_4N^+I^- + x wt\% KI$ ,  $I_2$  for different x values clearly show the different iodide ion (I<sup>-</sup>) contributions to the overall ionic conductivity in each sample. The lowest curve is taken for a sample using stainless steel blocking electrodes and similar curves were obtained for all the samples studied. Accordingly, one can conclude that all the gel electrolytes samples studied in this work are predominantly ionic conductors and the electronic conductivity is negligibly small. The top curve corresponds to the sample with 0.01 g of KI (sample C), which behaves predominantly as an iodide ion conductor. Even samples A and B with 0 and 0.005 g KI contents behave similarly but these curves (not shown in the figure) showed a slight gradual increase in current with time possibly due to iodide ion diffusion into the non-blocking iodine electrodes. The samples with higher and higher KI concentrations (or lower and lower Pr<sub>4</sub>N<sup>+</sup>I<sup>-</sup> concentrations) exhibit less and less iodide ion contribution, with sample F (with the highest KI concentration, with 0.06 g KI content) showing the lowest I<sup>-</sup> ion contribution.

The observed trend shown by the dc polarization curves is interesting as it clearly gives an estimate of the contribution to ionic conductivity by I<sup>-</sup> ions in the electrolyte, which essentially determines the short circuit photocurrent density of the solar cell. The electrolyte samples with high Pr<sub>4</sub>N<sup>+</sup>I<sup>-</sup> contents show relatively higher iodide ion conductivity, evidently due to the bulky Pr<sub>4</sub>N<sup>+</sup> cation which is expected to be much less mobile. However, the net result of several competing factors, such as the number of dissociated iodide ions and their mobility, the number of K<sup>+</sup> ions and their mobility, the number of Pr<sub>4</sub>N<sup>+</sup> ions and their mobility, the number of ionic aggregates and the variation of viscosity of the electrolyte solution with salt concentration ratio appear to give rise to the maximum seen in the short circuit current density  $(I_{sc})$  of the solar cell around 16.6 wt% KI concentration (see Fig. 5). What is important to realize here is that it is the iodide ion conductivity which essentially determines the short circuit current density of the solar cell.

# 3.2. Characterization of dye-sensitized solar cells

The photocurrent–photovoltage (I-V) characteristics of six solar cells of configuration Glass/FTO/TiO<sub>2</sub>/Dye/electrolyte/Pt/FTO/glass were measured using gel electrolyte samples with six different KI/Pr<sub>4</sub>N<sup>+</sup>I<sup>-</sup> salt ratios (samples *A*–*F*). Although we have obtained I-V curves for six solar cells with all six electrolyte compositions, for



**Fig. 4.** The photocurrent–photovoltage (*I–V*) characteristics of three solar cells of configuration Glass/FTO/TiO<sub>2</sub>/Dye/electrolyte/Pt/FTO/glass where the gel electrolyte consisted of three different (w/w) iodide salt concentrations: (A) 0% KI (only Pr<sub>4</sub>NI), (C) 16.6% KI + 83.4% Pr<sub>4</sub>NI and (F) 100% (only KI).



**Fig. 5.** The variation of (a) the efficiency ( $\eta$ ) and (b) the short circuit current density ( $J_{sc}$ ) of all six solar cells as a function of the net molar iodide ion concentration [I<sup>-</sup>] in the PAN:EC:PC gel electrolyte with KI and Pr<sub>4</sub>NI.

the purpose of clarity only the curves for solar cells with three compositions are shown in Fig. 4. These three cells were fabricated with the gel electrolyte with 0% (w/w) KI (Sample A), 16.6% (w/w) (Sample C), and 100% (w/w) of KI (sample F). Solar cell parameters such as the open circuit voltage ( $V_{oc}$ ) and the short circuit current density ( $I_{sc}$ ) were measured and the fill factor (FF, %) and efficiency ( $\eta$ , %) were calculated for all the cells studied. The results are tabulated in Table 2(a).

Upon a suggestion by a reviewer, for the purpose of comparison, we have also tested three DSSCs made with three selected compositions of the "PAN free" solvent electrolyte which corresponds to the two end members (0 wt% and 100% wt KI) and the maximum of  $J_{sc}$  (16.6 wt% KI) and the results are shown in Table 2(b). As expected, the  $J_{sc}$  value for the best solar cell is slightly higher than the corresponding value for the best PAN based gel electrolyte cell. However, the efficiency is somewhat less for the best liquid electrolyte based cell. This appears to be due to the lower  $V_{oc}$  and fill factor values, which, to a large extend, depends on the nature of the dye sensitized TiO<sub>2</sub> plate.

Comparable values of the efficiency and  $J_{sc}$  for the gel based cells and liquid based cells have been reported earlier for a PAN gel based cell and an acetonitrile electrolyte based cell made with corresponding composition [13]. A more interesting work has been reported by Grätzel et al. [32] where they have observed that the efficiencies of the solution electrolyte is comparable with the efficiency of the cells with "gelled" electrolyte. In this work, a 3-methoxypropionitrile (MPN)-based liquid electrolyte has been incorporated within a polymer matrix formed by a photochemically stable fluorine polymer, poly(vinylidenefluorideco-hexafluoropropylene (PVDF-HFP), to obtain a quasi-solid-state gel electrolyte. Authors have demonstrated that PVDF-HFP polymer can gel the MPN-based liquid electrolyte without hampering charge transport of the triiodide/iodide couple inside the polymer network. Consequently, there was no essential difference in the conversion efficiencies of dye-sensitized solar cells with liguid and polymer gel electrolytes even at AM 1.5 sunlight. This shows that the triiodide/iodide redox couple can diffuse freely in the liquid domains "entrapped" by the three-dimensional network of the PVDF-HFP polymer, despite the semi-solid nature of the electrolyte.

The results depicted in Tables 2 (a) and (b) for DSSCs incorporating the PAN based gel electrolyte and the corresponding PAN free electrolyte are in general agreement with the above observations by Gratzel et al. However, our results further shows that at an intermediate composition, in this case at 16.6 wt% KI composition, the PAN free liquid electrolyte based cell exhibits the highest efficiency and  $J_{sc}$  values, very similar to the trend exhibited by the DSSCs with the gel electrolytes.

The efficiency ( $\eta$ ) and the short circuit current density ( $J_{sc}$ ) of all six solar cells as a function of the net iodide ion concentration [I<sup>-</sup>] from both salts are shown in Fig. 5. It is interesting to see that the efficiency variation follows essentially the same variation as  $J_{sc}$ . What is most important to note is that the solar cell fabricated with the binary iodide mixture with 16.6% (w/w) KI concentration which corresponds to the relative molar iodide ion concentration [I<sup>-</sup>] of 2.08 has shown the highest energy conversion efficiency of 5.36% whereas the solar cells fabricated with the electrolyte with only KI (at [I<sup>-</sup>] = 1.81) and with only Pr<sub>4</sub>NI (at [I<sup>-</sup>] = 3.36) have shown efficiencies of 4.98% and 4.47% respectively. The use of the binary iodide mixture has clearly enhanced the solar cell efficiency by a

Table 2a

Parameters of solar cells with PAN:EC:PC: Pr<sub>4</sub>N<sup>+</sup>I<sup>-</sup> + x wt% KI, I<sub>2</sub> gel electrolyte samples of six different KI/Pr<sub>4</sub>NI molar ratios as a function of the relative [I<sup>-</sup>] iodide ion molar concentration from both salts.

Electrolyte	KI % (W/W)	Relative [I-] molar percentage (from both salts)	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (mV)	FF %	η %
Α	0	1.81	9.84	724.3	62.68	4.47
В	8.3	1.95	11.97	728.2	57.18	4.98
С	16.6	2.08	13.79	679.1	57.25	5.36
D	33.3	2.34	13.39	649.7	58.23	5.07
Ε	50.0	2.6	12.95	647.2	59.38	4.98
F	100.0	3.36	13.05	639.4	59.66	4.98

Bold values correspond to the electrolyte composition which gives the maximum solar cell efficiency.

# Table 2b

Parameters of three solar cells with three "PAN Free" liquid electrolytes EC:PC:  $Pr_4N^+I^- + x wt\%$  KI,  $I_2$  for x = 0, 16.6 and 100 wt\% of KI as a function of the relative  $[I^-]$  iodide ion molar concentration from both salts.

Electrolyte	KI % (W/W)	Relative [I <sup>-</sup> ] molar percentage	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (mV)	FF %	$\eta$ %
AA	0	2.21	9.93	703.3	57.9	4.04
СС	16.6	2.53	13.84	659.1	54.1	4.94
FF	100	4.08	11.49	605.5	58.4	4.07

Bold values correspond to the electrolyte composition which gives the maximum solar cell efficiency.

factor of about 8%. It is also important to note that from Table 2(a), although the relative molar iodide ion concentration in the six gel electrolyte samples increases from 1.81 to 3.36, the maximum value of the  $J_{sc}$  occurs at  $[I^-] = 2.08$ .

The power conversion efficiency ( $\eta$ , %) of a solar cell is given by the following equation:

$$\eta = \frac{J_{SC} V_{OC} FF}{\text{total incident power density}}$$

where the symbols have their usual meanings. According to Table 2(a),  $V_{oc}$  of the solar cells has gradually decreased with increasing KI/Pr<sub>4</sub>NI concentration ratio and the fill factor has first decreased and then increased exhibiting a minimum around 20% KI concentration. Therefore, the dominant contribution to the solar cell efficiency has evidently come from the  $J_{sc}$  and is determined essentially by the relative amount of iodide ion concentration in the gel electrolyte.

The variation of the efficiency  $\eta$ ,  $J_{sc}$  and  $V_{oc}$  with iodide ion concentration in the electrolyte can be explained not only by focusing on the relative iodide ion concentration [I<sup>-</sup>], but also by considering the role played by the cations in the electrolyte. As seen from Fig. 5, up to the maximum efficiency electrolyte composition of 16.6% (w/w) KI (sample *C*), the efficiency has increased along with  $J_{sc}$  despite the drop in  $V_{oc}$ , suggesting that the iodide ion concentration dominates the solar cell action. Beyond this KI concentration, the efficiency and the  $J_{sc}$  both gradually decrease with increasing [I<sup>-</sup>] concentration. However, the  $V_{oc}$  continues to decrease gradually as the KI salt concentration increases from 0 wt% KI (samples *A* and *B*) to 100 wt% KI (sample *F*) suggesting that the variation of the  $V_{oc}$  is determined essentially by the concentration of the small radius alkali ions (K<sup>+</sup>) in the gel electrolyte.

There are only very few studies reported on the use of binary iodide mixtures and different iodide salts emphasizing on the effect of cations on solar cell parameters in DSSCs. For the binary iodide system LI+KI in a PEO based gel electrolyte, the maximum solar cell efficiency of 4.5% has been achieved at 14.5 wt% of KI [20]. This has been attributed to a decrease in crystallization of the PEO based electrolyte caused by K<sup>+</sup> ions which are attracted to ether oxygens in the polymer matrix, making the polymer more amorphous. In this system, the short-circuit photocurrent density ( $J_{sc}$ ) has also reached a maximum at 14.5 wt% KI concentration. This behavior is, therefore, similar to the behavior seen for the present system. However, these authors have not attempted to correlate the solar cell efficiency directly with iodide ion conductivity in the electrolyte.

The influence of different single iodide salts on the performance of dye sensitized solar cells containing phosphozene-based non-volatile electrolytes has also been reported [33]. The anionic conductivities were highest in the 1-methyl-3-propylimidazolium (PMII) system and decreased in the order PMII>NH<sub>4</sub>I>NaI>LiI. The photovoltage has followed the same order. In other words, both the  $J_{sc}$  and  $V_{oc}$  showed the highest values for the PMII salt. The LiI salt has produced the lowest  $V_{oc}$ . In our binary system, we observe a similar decreasing trend for  $J_{sc}$  and  $V_{oc}$  from Sample C (with 83.4 (w/w) Pr<sub>4</sub>NI) to Sample *F* (100% w/w KI) with the 100 wt% KI containing system producing the lowest  $V_{\rm oc}$  of 639.4 mV.

The effect of cations on the open circuit photo-voltage and charge injection efficiency of dye has been reported for Li<sup>+</sup> and 1,2-dimethyl-3-hexylimidazolium ion [34]. The electrolyte containing Li<sup>+</sup> has produced a lower  $V_{oc}$  compared to the cell with imidazolium ion. However, the  $J_{sc}$  and the efficiency of solar cells containing Li<sup>+</sup> ions were relatively higher. Results for the solar cells with the two end members in our binary system generally agrees with these findings as well.

The influence of cation charge density on the photovoltaic performance of DSSCs has been studied for Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup> and dimethyeimidazolium (DMI<sup>+</sup>) ions by Shi et al. [35]. The results show that, from DMI<sup>+</sup> to Li<sup>+</sup> the short circuit current density ( $J_{sc}$ ) increases due to the increase in electron injection rates with increase in cation charge density. This again is consistent with the results for the two end members in the present binary system where the  $J_{sc}$  values are  $9.84 \text{ mA cm}^{-2}$  for the 100 wt% Pr<sub>4</sub>NI system and 13.05 mA cm<sup>-2</sup> for the 100 wt% KI system. The drop in  $V_{oc}$  is higher for the Li<sup>+</sup> ions due to a larger downward shift of the conduction band edge induced by the adsorption of Li<sup>+</sup> cations on the surface of nano titania grains. It is interesting to note that, with the two end members in our binary iodide system also we see this behavior, where the  $V_{oc}$  values are 724.3 mV for the 100 wt% Pr<sub>4</sub>NI system and 639.4 mV for the 100 wt% KI system.

From the above findings reported on different DSSC systems, it is clear that in liquid electrolytes and in some polymer and gel electrolytes, different cations can have different effects on  $V_{oc}$ . Small radius cations such as Li<sup>+</sup> and K<sup>+</sup> can intercalate into the lattice of nano TiO<sub>2</sub> causing a positive shift of the conduction band edge potential. This increases the driving force for charge injection and typically leads to a higher  $J_{sc}$  at the expense of  $V_{oc}$ . Results of the end members of the present system, as well as the systems discussed earlier [34,35] agrees very well with this interpretation.

According to our results (Table 2(a)), the open circuit voltage of the DSSCs has decreased gradually from 724.3 mV for electrolyte A (0% KI) to 639.4 mV for electrolyte F(100% KI).

The adsorption of cations, in this case K<sup>+</sup> and  $Pr_4N^+$  ions, on the surface of nano titania grains would cause the conduction band edge to move to the positive side (downward shift) independent of the cation charge density, thereby decreasing the  $V_{oc}$  values. This effect is expected to be more pronounced for smaller K<sup>+</sup> ions (ionic radius, 0.138 nm) than for bulky  $Pr_4N^+$  ions (ionic radius, 0.46 nm) as the number of adsorbed K<sup>+</sup> cations per unit area of nano titania grain surface would be much greater than the number of  $Pr_4N^+$  ions adsorbed, due the difference in their sizes. Therefore, a gradual drop in  $V_{oc}$  due to this effect should be expected with increase in KI concentration, and the greatest drop should be for the electrolyte sample with 100% KI concentration (sample F) as this sample has the highest number of K<sup>+</sup> ions. The observed drop in  $V_{oc}$  values shown in Table 2(a) is in agreement with this interpretation.

We have shown that the behavior of the two end member electrolytes in the present system with regard to the  $J_{sc}$  and  $V_{oc}$  values generally agrees well with the observations made for similar systems reported in the literature. The occurrence of the maxima in the efficiency and  $J_{sc}$  at 16.6% (w/w) KI concentration or at [I<sup>-</sup>] = 2.08%

molar iodide ion concentration needs further explanation. The net iodide ion concentration [I<sup>-</sup>] in the gel electrolyte results from the dissociation of both ionic salts. From our calculations, it can be seen that the net iodide ion concentration resulting from ionic dissociation of both salts increases from the 0 wt% KI end to the 100 wt% KI end giving rise to a steeper increase in  $J_{sc}$ . At these low iodide ion concentrations, the conductivity due to free iodide ions and the resulting to the maximum efficiency and maximum J<sub>sc</sub> increases with increasing [I<sup>-</sup>]. The maximum efficiency and the maximum Isc occur at the relative iodide ion concentration of 2.08%. The subsequent drop in  $J_{sc}$  is largely due to the reduction of the number of free I<sup>-</sup> ions due to the formation of ion pairs and higher ionic aggregates which do not contribute to the *I*<sub>sc</sub>. Some contribution to this drop in Isc may also come from the decrease in the ionic mobility caused by the increase in viscosity of the electrolyte medium at higher wt% KI due to the presence of non-dissociated KI solutes, which dominates the salt concentration at high wt% KI.

It has been observed earlier also that for smaller cations, ion paring is significant even at relatively low salt concentrations [33]. Neutral ion pairs and higher ionic aggregates that form at these concentrations do not contribute to ionic conductivity. In addition, at higher salt concentrations, electrostatic cross linking of the polymer chains and also the increased viscosity of the gel medium substantially reduces the mobility of iodide ions and contributes to the drop in conductivity. From these mechanisms the existence of the efficiency maximum and the  $J_{sc}$  maximum at an intermediate iodide ion concentration can be understood clearly.

As seen from Fig. 5, after about 2.5 molar % of I<sup>-</sup> ion concentration, the J<sub>sc</sub> starts to level off. This could be due to a modest increase in iodide ion conductivity due to the formation of triple ions as suggested by Fouss and Kraus in 1933 for electrolytic solutions [31] and also due to ionic re-dissociation which increase the fraction of free iodide ions.

# 4. Conclusions

This paper reports for the first time, the effect of a binary iodide system consisting of a small alkali cation (K<sup>+</sup>) and a bulky cation (Pr<sub>4</sub>N<sup>+</sup>) in DSSCs with PAN based electrolytes on the solar cell efficiency. The variation of efficiency follows exactly the variation of J<sub>sc</sub> which appears to be governed by the iodide ion conductivity in the electrolyte. The dependence of the short circuit photocurrent and the open circuit photovoltage on the cation type generally agrees with reported data for related systems. The maximum efficiency and the maximum in J<sub>sc</sub> occurs at 16.6 wt% KI concentration, correspond to a relative molar iodide ion concentration of 2.08%. With identical electrolyte compositions, the solar cell with 100% (w/w) KI showed an efficiency of 4.98% and the cell with 100% (w/w) Pr<sub>4</sub>NI showed an efficiency of 4.47%. However, the cell with the mixed iodide system, 16.6% (w/w) KI+83.4%(w/w) Pr<sub>4</sub>NI showed the highest efficiency of 5.36% which corresponds to the maximum in  $J_{sc}$  of 13.79 mA cm<sup>-2</sup>. We believe that the occurrence of the maxima in the solar cell efficiency and short circuit photocurrent is an important finding.

The efficiency enhancement caused by this mixed cationic effect could be utilized in all the dye sensitized solar cell systems studied so far (and to be studied hence forth) using polymeric, gel or solution electrolytes to increase the efficiency by about 8–10% which we believe is quite significant in DSSC research. The values obtained for the efficiency, 5.36%, and the short circuit current density, 13.79 mA cm<sup>-2</sup>, is reasonably high for a quasi-solid state DSSC compared to many systems reported by others.

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