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Polymethylmethacrylate (PMMA) based quasi-solid electrolyte with binary iodide salt for efficiency enhancement in TiO₂ based dye sensitized solar cells

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1. Introduction

Dye sensitized solar cells (DSSCs) based on nanostructured titanium dioxide (TiO₂) offer a low cost alternative to conventional silicon and thin film solar cells [1–3]. However a major drawback of these DSSCs based on electrolytic solutions is the lack of long-term stability due to liquid leakage, electrode corrosion and photodecomposition of the dye in the solvent medium. In order to overcome these problems, many attempts have been made to replace the liquid electrolyte by gel polymer electrolyte (or quasi-solid electrolyte) [4-7]. Although polyacrylonitrile (PAN) based gel polymer electrolytes have been used successfully in guasi solid-state DSSCs due to their relatively high anionic conductivities, not much work has been reported on DSSCs using polymethylmethacrylate (PMMA) based gel electrolytes [8-10]. In these PAN based and PMMA 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 ethylene carbonate/propylene carbonate (EC/PC) co-solvent

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ABSTRACT

Enhancement of efficiency by using iodide mixture (Pr_4NI and KI), instead of a single iodide salt, in N719 dye-sensitized solar cells with a polymethylmethacrylate (PMMA) based gel electrolyte is investigated. The salt ratio is varied to optimize efficiency. With 100 wt.% KI and 100 wt.% (Pr_4NI) efficiencies under AM 1.5 illumination are 3.39% and 3.21%, while 22.2:77.8 wt.% ratio KI: Pr_4NI shows the highest efficiency of 3.99 %. This is an efficiency enhancement of 18%. Variation of efficiency with salt composition appears to correspond to the change in short circuit photocurrent density (J_{sc}) and the iodide ion conductivity.

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is "entrapped" in cages formed by the host polymer matrix yielding almost liquid like ionic conductivities [11,12].

PMMA is a low cost, vinyl polymer with chemical formula $[CH_2 C(CH_3)(CO_2CH_3)]_n$ that possesses many desirable properties such as light weight, high light transmittance, chemical resistance, colorlessness, resistance to weathering corrosion and good insulating properties [13]. Although several lithium ion conductors based on PMMA has been reported particularly for lithium ion secondary batteries, to our knowledge not many studies have been reported on anionically conducting PMMA based polymer electrolytes which can be used in dye sensitized solar cells [14–17].

To be used in a DSSC, the gel electrolyte has to be an anion conductor and in majority of the cases these are iodide ion (I⁻) conductors. The contribution of the iodide ion conductivity to the overall ionic conductivity of the electrolyte in a DSSC is a major factor which determines the short circuit photocurrent density (J_{SC}) and hence the efficiency of a DSSC. This is because, the iodide ions (I⁻, I₃⁻), while participating in the I⁻/I₃⁻ redox reaction, also shuttle between the photo-electrode and the counter electrode. During the solar cell action the I⁻ ions migrate from the Pt counter electrode to the dye sensitized TiO₂ photoanode while the tri-iodide ions (I₃⁻) migrate from the TiO₂ electrode to the Pt counter electrode. Although iodide ion conductivity is







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an important parameter in determining the short circuit photocurrent and the efficiency of a DSSC, not much systematic research work has been reported on this aspect.

Tetrapropylammonium iodide (Pr_4NI) with a bulky cation has been used with a PMMA host polymer and solar cell efficiencies reaching 3.21% have been reported [18]. Potassium iodide (KI) with a small alkali cation has 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 [19–21]. 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 [22–25].

There are only very few published reports on the use of binary iodide mixtures in DSSCs. According to some recent reports, electrolytes with iodide salt mixtures have shown better DSSC performance compared to using only a single iodide salt [21]. Several studies on the effect of cations on DSSC performance have shown that while bulky cations such as Pr_4N^+ and Hex_4N^+ generally enhance the iodide ion conductivity in the electrolyte through better ionic dissociation, small size cations with high charge density, such as K⁺, Li⁺ and Na⁺ contribute towards better photogeneration of electrons at the dye and faster diffusion dynamics at the dye-semiconductor interface [26-28]. Therefore, it would be interesting to explore the combined effect of using a binary mixture of two iodide salts consisting of a bulky cation and a smaller alkali cation with high charge density in order to benefit from both abovementioned mechanisms. The aim of the present work is to try to enhance the efficiency of a DSSC with a PMMA based gel electrolyte by optimizing the weight ratio of the two iodide salts Pr₄NI and KI and to establish the correlation between the iodide ion conductivity and short circuit photocurrent density (I_{sc}) .

We have already reported the beneficial effect of using this type of binary iodide salt mixture on the efficiency enhancement in quasisolid state DSSCs in recent studies [26–30]. As far as we are aware, this is the first report of a DSSC employing a PMMA based gel electrolyte incorporating a binary iodide salt system with a small alkali cation (K⁺) and a bulky quaternary ammonium cation (Pr_4N^+) emphasizing the role of iodide ion conductivity.

This work would enable us to establish the favorable "mixed cation effect" as a general phenomenon applicable to different types of polymer hosts used in DSSCs.

2. Experimental

All the chemicals used were of purity greater than 98%. Polymethylmethacrylate (PMMA) (M.W.120,000, Aldrich), ethylene carbonate (EC) (Fluka), propylene carbonate (PC) (Fluka), potassium iodide (KI) (99.5%, Fluka), tetrapropylammonium iodide (Pr₄NI) (98%, Aldrich), iodine (Fluka), glacial acetic acid (99%, Fisher scientific), Triton-X (Aldrich), and ethanol (BDH) were used as received. Titanium dioxide powder (TiO₂) (P-25) was purchased from Degussa AG. Fluorine-doped tin oxide glass plates (FTO) (Nippon glass of sheet resistance 10–12 Ω /square) were used as a substrate for coating TiO₂ paste. Ruthenium dye (N719) (di-tetrabutylammonium cisbis(isothiocyanato) bis(2,2'-bipyridyl-4,4' dicarboxylicacid) purchased from Solatronix was used as the sensitizer. All the chemicals except I₂ and PC were vacuum dried at 60 °C for 24 h prior to use.

2.1. Preparation of the PMMA based gel electrolyte

In order to prepare the electrolyte samples, based on few trial experiments to optimize the gel electrolyte composition, the weights of PMMA (0.20 g), EC (0.40 g) and PC (0.40 g) were selected and kept unchanged while varying the KI:Pr₄NI weight ratio and keeping the total weight of KI and Pr₄NI 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, Pr₄NI and KI were mixed by continuous stirring at room temperature for about 2 h until the entire KI has been dissolved. Then PMMA was added and the mixture was stirred further keeping it at 80 °C for about 30 min until PMMA was fully dissolved. Finally the mixture was allowed to cool down to room temperature and I₂ 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.

2.2. Conductivity measurements

The ionic conductivity of the gel polymer electrolyte samples was determined by the AC complex impedance method using a Solartron SI-1260 impedance analyzer in the frequency range of 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. For all the seven 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 for all seven samples by sandwiching each 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 by sandwiching each sample between two iodine non-blocking electrode pellets in the FTO/Pt/l₂/electrolyte/I₂/Pt/FTO configuration in order to estimate the iodide ion contribution to the total ionic conductivity.

2.4. TiO₂ electrode preparation

The TiO₂ paste was prepared by grinding 0.20 g of TiO₂ (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 then spread on a pre-cleaned, fluorine-doped conducting tin oxide (FTO) glass (Nippon glass of sheet resistance $10-12 \Omega/sq$). An active cell area of 0.25 cm² was obtained by spreading the paste using the doctor blade technique and sintering at 450 °C for 45 min. The resulting TiO₂ 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 TiO₂ film was found to be around 12 µm. Dye absorption was carried out by immersing the TiO₂ film in an ethanolic dye solution containing ruthenium dye N719 for 24 h.

Table 1

Compositions of the electrolytes prepared by varying KI to $Pr_4N^+I^-$ salt ratio. For all the compositions, the weights of PMMA, EC and PC were kept at 0.20 g, 0.40 g and 0.40 g respectively.

Electrolyte	KI (g)	$Pr_4N^+I^-(g)$	$I_{2}\left(g\right)$	Weight ratio KI/Pr4N ⁺ I ⁻ %	Mole ratio [KI]/[Pr ₄ N ⁺ I ⁻] %
А	0.000	0.060	0.0049	0:100	0:100
В	0.005	0.055	0.0052	8.3:91.7	14.6:85.5
С	0.010	0.050	0.0056	16.6:83.4	27.3:72.7
D	0.013	0.047	0.0058	22.2:77.8	35:65
E	0.020	0.040	0.0063	33.3:66.7	48.4:51.6
F	0.030	0.030	0.0070	50:50	65.4:34.6
G	0.060	0.000	0.0092	100:0	100:0

Bold data correspond to the solar cells with highest efficiency.

2.5. Solar cell fabrication and characterization

The gel polymer electrolyte based solar cells of configuration glass/ FTO/TiO₂/dye/electrolyte/Pt/FTO/glass were fabricated by sandwiching the polymer electrolyte between the dye adsorbed TiO₂ 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⁻² (AM 1.5) simulated sunlight using a homemade computer controlled setup coupled to a Keithley 2000 multimeter 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.

3. Results and discussion

3.1. Characterization of the PMMA based gel polymer electrolyte

Seven different compositions of the gel polymer electrolyte, PMMA: EC:PC: $Pr_4NI + x$ wt.% KI, I_2 , for x = 0, 8.3, 16.6, 22.2, 33.3, 50, 100 prepared with the binary iodide mixture $Pr_4NI + KI$ are shown in Table 1. A photograph of the seven samples in inverted sample bottles is shown in Fig. 1 to show the "gel" nature of the electrolytes.

The variation of conductivity (ln σ) plotted against the reciprocal temperature for different electrolyte compositions is shown in Fig. 2. The electrolyte containing only Pr₄NI as the salt (sample A) has the lowest conductivity at all measured temperatures. It has a conductivity of 2.05×10^{-3} S cm⁻¹ at 30 °C. The conductivity gradually increases with increasing amount of KI in the electrolyte and the electrolyte containing only KI (sample G) shows the highest conductivity of 4.06×10^{-3} S cm⁻¹ at 30 °C.

From the linear shapes seen in Fig. 2, 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 PMMA based gel electrolytes are formed essentially by "entrapping" the EC/PC (ethylene carbonate/propylene carbonate) co-solvent based electrolytic solution in the matrix formed by PMMA quite similar to a polyacrylonitrile (PAN) based gel electrolyte [9,10,31]. PC is a solvent with low viscosity and high dielectric constant. While the high dielectric constant favors salt dissociation, the low viscosity would lead to high ionic mobility in the electrolytic solution. Therefore, we would expect the conducting properties of the PMMA based gel electrolyte system to be determined essentially by the properties of the entrapped electrolytic solution.



Fig. 2. The variation of ln σ T plotted against the reciprocal absolute temperature for PMMA/EC/PC/KI/Pr₄NI/l₂ electrolytes containing different KI: Pr₄NI ratios.

According to Fig. 2, the activation energy values, which correspond to the gradients in linear Arrhenius plots, are almost constant for all the gel electrolyte samples studied and essentially independent of the salt concentration ratios [KI]/[Pr₄NI]. The ion transport in organic solution electrolytes appears to be governed by a single activation process which depends on the solvent family [32–34]. According to some recent reports, 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 on the type of solvent, in particular on the nature of the solvent heteroatom [33,34]. The activation process in the solvent electrolyte is very likely the dipole re-orientation which depends on the dipole relaxation rates. In a solid electrolyte, on the other hand, 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, however, 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. A similar interpretation can be used to explain the observed conductivity vs temperature variation of the present gel electrolyte system which



Fig. 1. The seven gel electrolyte samples prepared with different KI:Pr₄NI ratios expressed as KI wt.% with respect to total weight of the salt mixture in "inverted" sample bottles to show the gel nature of the electrolytes. From left to right, the KI wt.% are: 0, 8.3, 16.6, 22.2, 33.3, 50, 100.

essentially consists of an electrolytic solution "entrapped" in a PMMA matrix. 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 sample G (only with KI salt) originates from two types of ions, namely K^+ ions and I^-/I_3^- ions and all these ions contribute to the highest conductivity seen for this sample. On the other hand, the ionic conductivity of the sample with Pr_4NI only (sample A) is the lowest. This can be expected as the cation Pr_4N^+ in this electrolyte sample is bulky in comparison with K^+ ion. For this sample, the iodide ions (I^-) are expected to make the dominant contribution to the ionic conductivity. As the weight percentage of KI in the electrolyte increases from sample A to G, the dissociated K^+ and I^- ions from KI are expected to make a dominant contribution to the total ionic conductivity of the gel electrolyte because of the increased number of K^+ and I^- ions and high mobility of K^+ ions in comparison with the bulky Pr_4N^+ ions.

DC polarization data depicted in Fig. 3 can be used to estimate the contribution of iodide ions (I^{-}) to the overall ionic conductivity of the electrolyte samples, although one cannot use these data for a more accurate quantitative analysis. The lowest polarization curve is for sample A taken with stainless steel blocking electrodes and similar curves (not shown) were obtained for all the samples studied. Accordingly, one can conclude that all the gel electrolyte samples studied in this work are predominantly ionic conductors and the electronic conductivity is negligible. The DC polarization curves at steady state, taken with iodine pellet non-blocking electrodes, for the gel electrolyte samples, PMMA: EC:PC: $Pr_4NI + x$ wt.% KI, I_2 for different x values clearly show the different iodide ion (I⁻) contributions to the overall ionic conductivity in each sample. The height of each of these polarization curves (at steady state) measured from the x-axis gives a measure of the relative iodide ion conductivity contribution which is proportional to the iodide ion transference number. Accordingly, the top polarization curve which corresponds to the sample with 22.2 wt.% KI (sample D), corresponds to the the highest iodide ion conductivity and the highest iodide ion transference number. From all the seven DC polarization curves taken with iodine electrodes, it can be seen that the iodide ion conductivity and the iodide ion transference number initially increase with increasing KI wt.% and then decrease, exhibiting a maximum at 22.2 wt.% KI. Later we shall try to correlate this result with the variation of the short circuit photocurrent density, J_{sc} and the efficiency of the seven DSSCs.

The observed trend shown by the DC polarization curves is interesting as it clearly gives an estimate of the contribution to ionic



Fig. 3. Current/initial current vs time plots for all the seven electrolyte samples obtained by DC polarization test with I_2 non-blocking electrodes. DC polarization curve taken with stainless steel (SS) blocking electrodes for sample (A) is also included for comparison.

conductivity by I^- ions in the electrolyte, which essentially determines the short circuit photocurrent density of the solar cell.

These polarization experiments using iodine pellet non-blocking electrodes are difficult to perform due to the reactive and hygroscopic nature of iodine (pellets). Therefore, the experiments have been performed inside a glove box. We expect both types of iodide (I⁻) and triiodides (I_3^-) ions to migrate by diffusion under the applied DC voltage and gradually polarize the electrolyte resulting a gradual drop in current. As ionic dissociation is more favorable in the tetrapropylammonium iodide salt due to the large size cation (compared to the dissociation in an iodide salt with a smaller cation (eg. Lil or KI), under an applied DC field, two competing mechanisms, ionic polarization and ionic dissociation, can be expected to occur. As ionic dissociation would tend to increase the DC current, ionic polarization would tend to decrease the current and we believe that this process can yield a stepwise variation of current with time as seen in Pr₄NI containing systems. We have not seen this behavior in gel electrolyte systems containing other iodide salts like LiI and KI which contain smaller cations and have much less ionic dissociation, when tested under the same conditions using the same type of measuring system.

3.2. Characterization of dye-sensitized solar cells

The photocurrent–photovoltage (*I–V*) characteristics of seven solar cells of configuration glass/FTO/TiO₂/dye/electrolyte/Pt/FTO/glass were measured using gel electrolyte samples with seven different KI/ $Pr_4N^+I^-$ salt ratios (samples A to G). Although we have obtained *I–V* curves for solar cells with all seven electrolyte compositions, only the curves for solar cells with three compositions are shown in Fig. 4 as representative examples. These three cells were fabricated with the gel electrolyte compositions: 0 wt.% KI (sample A), 22.2 wt.% (sample D), and 100 wt.% of KI (sample G). Solar cell parameters such as the open circuit voltage (V_{oc}) and the short circuit current density (J_{sc}) were measured and the fill factor (FF %) and efficiency (η %) were calculated for all the cells studied. The results are tabulated in Table 2.

The efficiency (η) and the short circuit current density (J_{sc}) of all seven solar cells as a function of wt.% KI are shown in Fig. 5. It is interesting to see that the efficiency variation follows a similar trend as the J_{sc} . It is important to realize that the solar cell fabricated with the binary iodide mixture with 22.2 wt.% KI + 77.8 wt.% Pr₄NI shows the highest



Fig. 4. The photocurrent–photovoltage (*I–V*) characteristics of three solar cells of configuration glass/FTO/TiO₂/dye/electrolyte/Pt/FTO/glass where the gel electrolyte consisted of three different (w/w) iodide salt concentrations: (A) 0 wt.% KI (only Pr₄NI), (D) 22.2 wt.% KI + 77.8 wt.% Pr₄NI and (G) 100% KI. (100 mW cm⁻², A.M. 1.5, active area 0.25 cm⁻²).

Table 2

Parameters of solar cells with PMMA:EC:PC: $Pr_4NI + x wt.\% KI$, I_2 gel electrolyte samples of seven different KI/Pr_4NI molar ratios as a function of the relative $[I^-]$ iodide ion molar concentration from both salts.

Electrolyte	Weight ratio KI/Pr ₄ N ⁺ I ⁻ %	Relative I ⁻ mole percentage	$J_{\rm sc}$ (mA cm ⁻²)	$V_{\rm oc}~({\rm mV})$	Fill factor (FF) %	Efficiency (η) %
А	0:100	1.80	7.42	714.8	60.50	3.21
В	8.3:91.7	1.93	7.47	734.6	59.50	3.27
С	16.6:83.4	2.06	8.72	705.8	57.90	3.57
D	22.2:77.8	2.14	10.70	657.1	56.80	3.99
E	33.3:66.7	2.32	9.73	665.6	55.60	3.60
F	50:50	2.57	8.90	644.1	58.90	3.38
G	100:0	3.33	7.55	700.1	64.10	3.39

Bold data correspond to the solar cells with highest efficiency.

energy conversion efficiency of 3.99% and has the highest short circuit photo current density of 10.70 mA cm⁻². Another important observation is that the two end member solar cells fabricated with the electrolyte with only KI and with only Pr_4NI have shown efficiencies of 3.39% and 3.21% respectively. The use of the binary iodide mixture has clearly enhanced the solar cell efficiency by a factor of about 18% compared to the higher efficiency end member. It is also important to note that from Table 2, although the relative molar iodide ion concentration in the seven gel electrolyte samples increases gradually from 1.80 to 3.33 as the wt.% KI increases, the maximum value of the J_{sc} occurs at $[I^-] = 2.14$. The remaining iodide ions at higher $[I^-]$ concentrations evidently do not contribute to J_{sc} and solar cell action and very likely remain as higher ionic or neutral aggregates.

The power conversion efficiency (η %) of a solar cell is given by the following equation:

$$\eta = \frac{J_{\rm SC}V_{\rm OC}FF}{\rm Total\,incident\,power\,density}$$

where the symbols have their usual meanings. According to Table 2, the V_{oc} value and the fill factor (FF) of the highest efficiency solar cell are lower compared to the V_{oc} and FF values of the two end members. Therefore, the dominant contribution to the solar cell efficiency clearly comes from the J_{sc} and is determined essentially by the relative amount of iodide ion conductivity in the gel electrolyte.

3.3. Cation influenced charge transfer dynamics in DSSCs

Cations play an important role in the performance of DSSCs. The cation/ TiO_2 interactions cause two effects in a DSSC: (i) a positive shift

of the flat band potential of the semiconductor and (ii) the creation of deeper electron-trapping states, which play an important role in electron transport through TiO_2 to the current collector [37]. Cations in the electrolyte can efficiently screen the photo-injected electrons on the TiO_2 film, ensuring that electro-neutrality is maintained throughout the TiO_2 network. Ionic migration in an electrolyte is therefore strongly correlated with electron transport in the TiO_2 film [24,38].

The dependence of J_{sc} and V_{oc} on the type and the nature of the cation takes place due to interfacial kinetics of the dyed TiO₂ film. Upon light illumination of the dyed nanoporous TiO₂ film, the injected electrons from the excited dve molecules are accumulated at the conduction band of TiO₂, and the cations in the electrolyte become adsorbed into the TiO₂ film for charge compensation. The V_{oc} is determined by the relative positions of the flat band potential and the redox potential of the electrolyte ($V_{oc} = |V_{fb} - V_{red}|$). The flat band potential of TiO₂ is moved positively due to the cation adsorption and it is associated in the drop in photovoltage of the DSSC. The associated drop in photovoltage depends upon the size and charge density of the cations. As compared to the bulky cations, small sized cations could easily be adsorbed onto the TiO₂ grain surface resulting to a larger potential drop. However, due to this positive shift of the TiO₂ flat band potential, the driving force for the charge injection from the excited dye molecules to TiO₂ increases, resulting to a large injection efficiency and thus a higher photocurrent.

In the literature we have come across 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 [21]. The influence of different single iodide salts on the performance of dye sensitized solar cells containing phosphazene-based non-volatile electrolytes has been reported [35]. The photovoltage was highest in the



Fig. 5. The variation of (a) the efficiency (η) and (b) the short circuit current density (J_{sc}) of all seven solar cells as a function of the wt.% KI in the PMMA:EC:PC gel electrolyte containing KI and Pr₄NI.

1-methyl-3-propylimidazolium (PMII) system and decreased in the order PMII > NH₄I > Nal > Lil. The Lil salt has produced the lowest V_{oc}. The effect of cations on the open circuit photo-voltage and charge injection efficiency of dye has been reported for Li⁺ and 1,2-dimethyl-3-hexylimidazolium ion [36]. The electrolyte containing Li⁺ has produced a lower V_{oc} compared to the cell with larger imidazolium ion.

The influence of cation charge density on the photovoltaic performance of DSSCs has been studied for Li⁺, Na⁺, K⁺ and dimethylimidazolium (DMI⁺) ions by Yushuai Shi et al. [28]. The results show that, from DMI⁺ to Li⁺ 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 obtained for the two end members in the present binary system where the J_{sc} values are 7.42 mA cm⁻² for the 100 wt.% Pr₄NI system and 7.55 mA cm⁻² for the 100 wt.% KI system. The drop in V_{oc} is higher for the Li⁺ ions due to a larger downward shift of the conduction band edge induced by the adsorption of Li⁺ cations on the surface of nano-titania grains. It is interesting to note that, with the two end members in our binary iodide system we see this behavior, where the V_{oc} values are 714.8 mV for the 100 wt.% Pr₄NI system and 700.1 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⁺ and K⁺ can intercalate into the lattice of nano-TiO₂ 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} .

In the present system the adsorption of cations, K^+ 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 $V_{\rm oc}$ values. This effect is expected to be more pronounced for smaller K⁺ ions (ionic radius, 0.138 nm) than for bulky Pr_4N^+ ions (ionic radius, 0.460 nm) as the number of adsorbed K⁺ 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, the drop in $V_{\rm oc}$ due to this effect should be greater for the solar cell with electrolyte with 100 wt.% KI concentration (sample G) compared to the drop in $V_{\rm oc}$ for the cell with 100 wt.% Pr₄NI electrolyte (sample A). It is interesting to see that in our binary system, the J_{sc} has increased at the expense of $V_{\rm oc}$ from cell A to cell D. Again, the $J_{\rm sc}$ has increased at the expense of $V_{\rm oc}$ from cell G to cell D. The mixed cation effect works unfavorably for the V_{oc} (Table 2).

The occurrence of the maxima in the efficiency and I_{sc} at 22.2 wt.% KI concentration or at $[I^-] = 2.14\%$ molar iodide ion concentration can be explained as follows. The net iodide ion concentration [I⁻] 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 22.2 wt.% KI sample, giving rise to an initial steeper increase in I_{sc} (Fig. 5). At these low iodide ion concentrations one can expect that all the available iodide ions (I^{-}) to be free and to contribute to the I_{sc} and efficiency. The maximum efficiency and the maximum I_{sc} occur at the relative iodide ion concentration of 2.14% which corresponds to sample D with 22.2 wt.% KI sample. The subsequent drop in Isc with increasing iodide ion concentration [I⁻] is largely due to the reduction of the number of free I⁻ ions due to the formation of ion pairs, triplets and higher ionic and neutral aggregates which do not contribute to the J_{sc} . Some contribution to this drop in J_{sc} 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 dominate the salt concentration at high wt.% KI.

From the DC polarization curves depicted in Fig. 3, one can obtain an estimate of the iodide ion transference number for each electrolyte composition, as this is equal to the height of the dc polarization curve at 300 min measured relative to the curve taken with stainless steel electrodes. A plot of the transference number with electrolyte composition is shown in Fig. 6. It is interesting to see again the correlation between the transference number variation and the variation of J_{sc} providing further evidence that the iodide ion conductivity of the gel electrolyte essentially determines the short circuit photo current and the cell efficiency.

4. Conclusions

In dye sensitized solar cells, made with PMMA based gel polymer electrolyte incorporating a binary iodide salt system consisting of a small alkali cation (K⁺) and a bulky cation (Pr_4N^+), the variation of efficiency with wt.% KI follows a similar variation as the J_{sc} which appears to be governed by the iodide ion conductivity in the electrolyte. This is further supported by the iodide ion transference number estimated from dc polarization data taken with iodine non-blocking electrodes. The dependence of the short circuit photocurrent and the open circuit photovoltage on the cation type of the two end member compositions generally agrees with reported data for related systems. The maximum efficiency and the maximum in J_{sc} occur at 22.2 wt.% KI concentration, which corresponds to a relative molar iodide ion



Fig. 6. The variation of (a) the short circuit current density (J_{sc}) and (b) the iodide ion transference number estimated from DC polarization curves of Fig. 3 for all seven solar cells as a function of the wt% KI in the PMMA:EC:PC gel electrolyte containing KI and Pr₄NI.

concentration of 2.14%. With identical electrolyte compositions, the solar cell with 100 wt.% KI showed an efficiency of 3.39% and the cell with 100 wt.% Pr₄NI showed an efficiency of 3.21%. However, the cell with the mixed iodide system with 22.2 wt.% KI + 77.8 wt.% Pr₄NI showed the highest efficiency of 3.99% which corresponds to the maximum in J_{sc} of 10.70 mA cm⁻².

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References

- [1] B.O. Regan, M. Gratzel, Nature 353 (1991) 737-739.
- [2] M. Gratzel, J. Photochem. Photobiol. A 164 (2004) 3-14.
- [3] M.K. Nazeerddin, A. Kay, I. Rodicio, R. Humphrey-Baker, E. Muller, P. Liska, N. Vlachopolous, M. Gratzel, J. Am. Chem. Soc. 115 (1993) 6382–6390.
- [4] H. Yang, M. Huang, J. Wu, Z. Lan, S. Hao, Mater. Chem. Phys. 110 (2008) 38–42.
 [5] W. Kubo, S. Kambe, S. Nakade, T. Kitamura, K. Hanabusa, S. Yanagida, J. Phys. Chem.
- B 107 (2003) 4374-4381. G TMWL Bandar, MAKL Dissanaurko B E Mollander, Electrochim Acto 55
- [6] T.M.W.J. Bandara, M.A.K.L. Dissanayake, B.-E. Mellander, Electrochim. Acta 55 (2010) 2044–2047.
- [7] O.A. Ileperuma, M.A.K.L. Dissanayake, S. Somasunderam, L.R.A.K. Bandara, Sol. Energy Mater. Sol. Cells 84 (2004) 117–124.
- [8] T.M.W.J. Bandara, M.A.K.L. Dissanayake, I. Albinsson, B.-E. Mellander, J. Power Sources 195 (2010) 3730–3734.
- [9] O.A. Ileperuma, M.A.K.L. Dissanayake, S. Somasunderam, Electrochim. Acta 47 (2002) 2801–2807.
- [10] M.A.K.L. Dissanayake, L.R.A.K. Bandara, R.S.P. Bokalawala, P.A.R.D. Jayathilaka, O.A. Ileperuma, S. Somasunderam, Mater. Res. Bull. 37 (2002) 867–874.
- [11] A.M. Stephan, Eur. Polym. J. 42 (2006) 21-42.
- [12] P.A.R.D. Jayathilaka, M.A.K.L. Dissanayake, I. Albinsson, B.-E. Mellander, Solid State Ionics 156 (2003) 179–195.
- [13] K. Yuichi, K. Krishna, N. Koichi, J. Appl. Polym. Sci. 63 (3) (1997) 363-368.
- [14] J.Y. Song, Y.Y. Wang, C.C. Wan, J. Power Sources 77 (1999) 183–187.

- [15] O. Bohnke, G. Frand, M. Rezrazi, C. Rousselot, C. Truche, Solid State Ionics 66 (1–2) (1993) 105–112.
- [16] K.M. Abraham, M. Alamgir, J. Electrochem. Soc. 137 (1990) 1657-1658.
- [17] Peng Wang, Shaik M. Zakeeruddin, Jacques E. Moser, Mohammad K. Nazeeruddin, Nat. Mater. 2 (2003) 402–407.
- [18] H. Iqbal, K. Perera, V.A. Seneviratn, W.N.S. Rupasinghe, C.A. Thotawattage, G.K.R. Senadeera, M.A.K.L. Dissanayake, Proceedings of Solar Asia 2011 Int. Conf, Institute of Fundamental Studies, Kandy, Sri Lanka, 2011, pp. 163–165.
- [19] Junnian Chen, Tianyou Peng, Ke Fan, Jiangbin Xia, J. Mater. Chem. 21 (2011) 16448–16452.
- [20] Pinjiang Li, Wu, Jihuai, Sancun Hao, Zhang Lan, Qinghua Li, Yunfang Huang, J. Appl. Polym. Sci. 120 (3) (2011) 1752–1757.
- [21] S. Agarwala, L.N.S.A. Thummalakunta, C.A. Cook, C.K.N. Peh, A.S.W. Wong, L. Ke, G.W. Ho, J. Power Sources 196 (2011) 1651–1656.
- [22] X. Shen, W. Xu, J. Xu, G. Liang, H. Yang, M. Yao, Solid State Ionics 179 (2008) 2027–2030.
- [23] D.F. Watson, G.J. Meyer, Coord. Chem. Rev. 248 (2004) 1391-1406.
- [24] C.A. Kelly, F. Farzad, D.W. Thompson, J.M. Stipkala, G.J. Meyer, Langmuir 15 (1999) 7047–7054.
- [25] S. Kambe, S. Nakade, T. Kitamura, K. Wada, S. Yanagida, J. Phys. Chem. B 106 (2002) 2967–2972.
- [26] C.A. Thotawatthage, G.K.R. Senadeera, T.M.W.J. Bandara, M.A.K.L. Dissanayake, Proceedings of Solar Asia 2011 Int. Conf. Institute of Fundamental Studies, Kandy, Sri Lanka, 2011, pp. 175–177.
- [27] M. Graetzel, Inorg. Chem. 44 (20) (2005) 6841-6851.
- [28] Y. Shi, Y. Wang, M. Zhang, X. Dong, Phys. Chem. Chem. Phys. 13 (2011) 14590–14597.
- [29] T.M.W.J. Bandara, M.A.K.L. Dissanayake, W.J.M.J.S.R. Jayasundara, I. Albinsson, B.-E. Mellander, Phys. Chem. Chem. Phys. 14 (2012) 8620–8627.
- [30] M.A.K.L. Dissanayake, C.A. Thotawatthage, G.K.R. Senadeera, T.M.W.J. Bandara, W.J. M.J.S.R. Jayasundera, B.-E. Mellander, J. Photochem. Photobiol. A 246 (2012) 29–35.
- [31] Zhang Lan, Wu, Jihuai, Jianming Lin, Miaoliang Huang, Polym. Adv. Technol. 22 (12) (2011) 1812–1815.
- [32] R.M. Fuoss, C.A. Kraus, J. Am. Chem. Soc. A 55 (1933) 2387–2399.
- [33] Matt Petrowsky, Roger Frech, J. Phys. Chem. B 113 (2009) 5596-5606.
- [34] Matt Petrowsky, Roger Frech, Electrochim. Acta 55 (2010) 1285–1288.
- [35] S.-H.A. Lee, A.-M.S. Jackson, A. Hess, S.-H. Fei, S.M. Pursel, J. Basham, C.A. Grimes, M.
- W. Horn, H.R. Allcock, T.E. Mallouk, J. Phys. Chem. C 114 (2010) 15234–15242. [36] N.-G. Park, S.-H. Chang, J. van de Lagemaat, K.-J. Kim, A.J. Frank, Bull. Korean Chem.
- Soc. 21 (10) (2000) 985–988. [37] K. Kalyanasundaram (Ed.), Dye-sensitized solar cells, Taylor & Francis, New York,
- 2010, p. 57. [38] K. Hara, T. Horiguchi, T. Kinoshita, K. Sayama, H. Arakawa, Sol. Energy Mater. Sol.
- [38] K. Hara, I. Horiguchi, I. Kinoshita, K. Sayama, H. Arakawa, Sol. Energy Mater. Sol Cells 70 (2001) 151.