international journal of hydrogen energy XXX (2013) 1–7



Available online at www.sciencedirect.com

# SciVerse ScienceDirect



journal homepage: www.elsevier.com/locate/he

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

A.K. Arof<sup>*a*,\*</sup>, M.F. Aziz<sup>*a*</sup>, M.M. Noor<sup>*a*,*d*</sup>, M.A. Careem<sup>*a*,*c*</sup>, L.R.A.K. Bandara<sup>*c*</sup>, C.A. Thotawatthage<sup>*b*</sup>, W.N.S. Rupasinghe<sup>*b*</sup>, M.A.K.L. Dissanayake<sup>*b*,*c*</sup>

<sup>a</sup> Centre for Ionics University of Malaya, Physics Department, University of Malaya, 50603 Kuala Lumpur, Malaysia

<sup>b</sup> Institute of Fundamental Studies, Hantana Road, Kandy, Sri Lanka

<sup>c</sup> Department of Physics, University of Peradeniya, Peradeniya, Sri Lanka

<sup>d</sup> Centre for Foundation Studies, International Islamic University Malaysia, Jalan Universiti, 45350 Petaling Jaya, Selangor, Malaysia

#### ARTICLE INFO

Article history: Received 28 November 2012 Received in revised form 26 June 2013 Accepted 10 July 2013 Available online xxx

Keywords: Dye-sensitized solar cells PVdF Mixed cation effect Gel electrolytes TiO<sub>2</sub>

#### ABSTRACT

This paper reports the effect of using a mixed iodide salt system with two dissimilar cations to enhance the efficiency of dye-sensitized solar cells made with polyvinylidenefluoride (PVdF) based gel electrolyte. Instead of a single iodide salt, a mixture of potassium iodide (KI) with a small K<sup>+</sup> cation and tetrapropylammonium iodide (Pr<sub>4</sub>NI) with a bulky Pr<sub>4</sub>N<sup>+</sup> cation were used to provide the required iodide ion conductivity. Solar cells of configuration FTO/TiO<sub>2</sub>/Dye/electrolyte/Pt/FTO were fabricated using a mesoporous TiO<sub>2</sub> electrode sensitized with a Ruthenium dye (N719). With identical electrolyte compositions, the cells with KI and Pr<sub>4</sub>NI alone gave efficiencies of 2.37% and 2.90% respectively. The cell with the mixed iodide system, KI:Pr<sub>4</sub>NI = 16.6:83.4 (% weight ratio), however, showed an enhanced efficiency of 3.92% with a short circuit current density of 9.16 mA cm<sup>-2</sup>, open circuit voltage of 674.4 mV and a fill factor of 63.4%.

Copyright © 2013, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

# 1. Introduction

Dye-sensitized solar cells (DSSCs), introduced by Gratzel in 1991 [1] have the potential to be the low cost alternatives to conventional inorganic photovoltaic devices. Considerable amount of research is going on worldwide to produce a reliable DSSC with high efficiency [2–6]. A typical DSSC consists of a photo-electrode containing a dye-sensitized mesoporous  $TiO_2$  layer coated on an ITO glass and a liquid electrolyte containing an iodide/triiodide redox mediator and a Pt metal counter electrode. Such DSSCs sensitized with ruthenium based dyes work well and show good efficiencies around 12% in the laboratory [7]. The major problem with the liquid electrolyte based DSSCs is their poor long term stability due to evaporation, leakage, flammability of the liquids, decomposition of the dye, etc. Most of these problems can be solved by using polymer based gel type electrolytes as they can have reasonable ionic conductivity and flexibility required for

<sup>\*</sup> Corresponding author. Tel.: +60 379674085; fax: +60 379674146. E-mail address: akarof@um.edu.my (A.K. Arof).

<sup>0360-3199/\$ –</sup> see front matter Copyright © 2013, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.ijhydene.2013.07.028

making good contacts between components within the solar cell. Use of various such quasi-solid polymer electrolytes in DSSCs has been reported but the conversion efficiencies obtained are relatively poor compared to those with liquid electrolytes [8–10].

Iodide ions are used in most polymer gel electrolyte based DSSCs as an anion conductor is needed for the operation. The iodide ion conductivity in the electrolyte is a major factor that determines the short circuit current density (Jsc) and hence the efficiency of a DSSC [11]. To increase the iodide ion contribution to the overall conductivity of iodide based electrolytes, quaternary ammonium salts containing large cations such as Pr<sub>4</sub>NI, Bu<sub>4</sub>NI and Hex<sub>4</sub>NI are widely used as ionic salts. Several host polymers have been used to prepare gel electrolytes with such iodide salts and investigated in DSSCs. PAN based gel type polymer electrolytes with tetrapropylammonium iodide (Pr<sub>4</sub>N<sup>+</sup>I<sup>-</sup>) have been found to give efficiencies reaching about 3% [12,13]. Reasonable efficiencies have also been reported with PAN/Bu<sub>4</sub>NI system [14,15]. DSSCs with PVdF or PVdF:HFP gel polymer electrolyte having various iodide salts have also shown reasonably good efficiencies [16-19]. KI is a popular salt which is used widely to provide the iodide ion conductivity in a large number of DSSC systems [20-22]. Most of these gel electrolytes are usually prepared by dissolving the salts in mixed ethylene carbonate-propylene carbonate (EC/ PC) co-solvents and adding the host polymer to form gels. It should be noted that in such gel polymer electrolytes, it is generally accepted that the electrolytic solution containing the ionic salts is trapped inside cages formed by the host polymer matrix giving rise to almost liquid like ionic conductivities [23].

The cations in the electrolyte are expected to play a dual role in determining the overall efficiency of a DSSC. They influence the charge injection mechanism at the TiO<sub>2</sub>/electrolyte interface and the  $J_{\rm sc}$  through the iodide ion conductivity [24–27]. While the bulky cations such as Pr<sub>4</sub>N<sup>+</sup> and Hex<sub>4</sub>N<sup>+</sup> are expected to reduce cationic conductivity and thereby enhance the iodide ion conductivity in the electrolyte, small cations with high charge density, such as K<sup>+</sup>, Li<sup>+</sup> or Na<sup>+</sup> are expected to contribute towards better photo-generation of electrons and their faster transfer across the dye–TiO<sub>2</sub> interface [11]. Therefore, using a mixture of two iodide salts consisting of a bulky cation and a small cation with a high charge density in the polymer gel electrolyte would be useful to enhance the efficiency of DSSSCs utilizing the above two effects produced by the cations.

The beneficial effect of using this type of binary iodide salt mixture in enhancing the efficiency of quasi-solid state DSSCs has already been observed and reported. The two binary iodide mixtures  $MgI_2 + Pr_4NI$  and  $MgI_2 + Hex_4NI$  have shown efficiency enhancement effects in PAN gel electrolyte based DSSCs [28,29]. In a more recent paper by our group, 8% efficiency enhancement has been reported in a DSSC with PAN based electrolytes containing a binary mixture of  $Pr_4NI$  and KI [11]. In the present work a similar investigation is reported with PVdF as the host polymer in the gel electrolyte instead of PAN but the binary salt mixture remains same as earlier, consisting of  $Pr_4NI$  with a bulky cation and KI with a smaller cation. The present investigation was carried out in order to confirm the general nature of the mixed cation effect in enhancing the efficiency of DSSCs independent of the host polymer system. PVdF can be a better polymer host as PVdF based gel type electrolytes in a DSSCs have given high efficiencies  $\sim 6.7\%$  [19].

# 2. Experimental

#### 2.1. Preparation of gel polymer electrolytes

The starting materials used PVdF and  $Pr_4NI$  with purity greater than 98% were purchased from Aldrich and EC, PC, iodine chips (I<sub>2</sub>) and KI with purity greater than 98% were obtained from Fluka. Ruthenium (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.

The electrolyte samples were prepared by keeping the weights of PVdF (0.05 g), EC (0.20 g) and PC (0.20 g) unchanged and changing the individual weights of KI and Pr<sub>4</sub>NI so that their total weight remained at 0.05 g. The weight of iodine was taken to be one tenth of the total mole amount of the iodide salts. Appropriately weighed quantities of EC, PC, Pr<sub>4</sub>NI and KI were mixed in a closed glass bottle by continuous stirring at room temperature for about for 12 h until the entire KI has been dissolved. PVdF was added to the above mixture and heated up to 125 °C and kept for about 15 min while stirring for PVdF to fully dissolve. The mixture was cooled down to 80 °C and left at this temperature for 5 more minutes and then allowed to cool down to room temperature. Then, I<sub>2</sub> chips were added and the mixture was continuously magnetically stirred overnight (12 h) to obtain a homogeneous gel electrolyte. This procedure was repeated for all the compositions shown in Table 1.

#### 2.2. Ionic conductivity of the gel electrolytes

The ionic conductivity of the gel polymer electrolyte samples was determined by the electrical impedance spectroscopy with a computer controlled Solatron SI–1260 impedance analyzer in the frequency range 20 Hz–10 MHz. Thin film samples in disc form sandwiched between two polished stainless steel electrodes were used for the conductivity measurements. Temperature variation of the conductivity of each sample was obtained by taking measurements at

Table 1 – Electrolytes having different compositions of KI, $Pr_4N^+I^-$ and $I_2$ . Weights of other components are as follows: $PVdF = 0.05$ g: EC = 0.20 g: PC = 0.20 g; Salts: 0.05 g.						
Electrolyte	KI (g)	$Pr_4N^+I^-$ (g)	I <sub>2</sub> (g)			
А	0.0000	0.0500	0.0040			
В	0.0041	0.0459	0.0043			
С	0.0083	0.0417	0.0046			
D	0.0167	0.0334	0.0052			
E	0.0250	0.0250	0.0058			
F	0.0500	0.0000	0.0076			

approximately 5 °C intervals in the temperature range 30-60 °C. At each temperature, the sample was allowed to stabilize for about 30 min before the measurement was taken. The ionic conductivities of each sample at different temperatures were obtained using the corresponding impedance plots.

# 2.3. Photo-electrode preparation

A mesoporous TiO<sub>2</sub> layer was used as the base material for deposition of dye sensitizers. TiO<sub>2</sub> paste 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 was spread on a pre-cleaned, fluorinedoped conducting tin oxide (FTO) glass (Nippon sheet glass  $10-12 \Omega/sq$ ) using doctor blade method. The paste was spread so as to have an active area of 0.25 cm<sup>2</sup> for solar cell operation. The film was sintered at 450 °C for 45 min and allowed to cool down to room temperature. The thickness of the TiO<sub>2</sub> film was measured using a homemade, calibrated profilometer and the average film thickness of the TiO<sub>2</sub> film was found to be around 12 µm. For the dye adsorption, the film was immersed for 24 h in ethanolic dye solution containing Ruthenium dye N719  $[RuL_2(NCS)_2:2TBA where, L = 2,2'-bipyridyl-4,4'-dicarboxylic$ acid; TBA = tetrabutylammonium].

#### 2.4. Solar cell fabrication and characterization

The DSSCs having the configuration glass/FTO/TiO<sub>2</sub>/Dye/ electrolyte/Pt/FTO/glass were fabricated by sandwiching the gel polymer electrolyte between the dye-sensitized TiO<sub>2</sub> electrode and a platinum (Pt) coated FTO glass. The I–V characteristics of the cells were measured under the illumination of 100 mW cm<sup>-2</sup> (AM 1.5) simulated sunlight, from a Xenon 500 lamp, with a homemade computer controlled setup coupled to a Keithley 2000 multimeter and a potentiostat/ galvanostat HA-301.

# 3. Results and discussion

# 3.1. Characterization of the gel polymer electrolyte

The compositions of the PVdF based gel polymer electrolyte, containing I<sub>2</sub> and different percentages of the binary iodide mixture Pr<sub>4</sub>N<sup>+</sup>I<sup>-</sup> and KI, PVdF:EC:PC:(100–x) Pr<sub>4</sub>N<sup>+</sup>I<sup>-</sup> + x wt% KI, with x = 0%, 8.3%, 16.6%, 33.3%, 50%, 100% used in this study are shown in Table 1. The conductivity variation with temperature for different electrolyte compositions are shown in Fig. 1 in the form conductivity (on log scale) plotted against the reciprocal temperature. The electrolyte containing only Pr<sub>4</sub>N<sup>+</sup>I<sup>-</sup> as the salt (electrolyte A) has the lowest conductivity at all measured temperatures. This electrolyte has a conductivity of  $4.38 \times 10^{-3}$  S cm<sup>-1</sup> at 29.2 °C and  $5.71 \times 10^{-3}$  S cm<sup>-1</sup> at 50.7 °C. The conductivity gradually increases as the amount of KI in the electrolyte F) shows the highest conductivity of  $1.07 \times 10^{-2}$  S cm<sup>-1</sup> at 29.3 °C and  $1.47 \times 10^{-2}$  S cm<sup>-1</sup> at 50.3 °C.

The ionic conductivity of the gel type electrolyte results mainly from movement of ions dissociated in the "trapped"



Fig. 1 – The variation of ionic conductivity vs temperature with % weight ratio [KI]/[Pr<sub>4</sub>N<sup>+</sup>I<sup>-</sup>] % for the PVdF based gel electrolyte: PVdF:EC:PC:KI +  $Pr_4N^+I^-$ :I<sub>2</sub>.

EC/PC co-solvent in the PVdF polymer matrix. Electrolyte sample F has only the KI salt with smaller cation K<sup>+</sup> which can be mobile and therefore its ionic conductivity must come from the contributions of both  $K^+$  and  $I^-$  ions resulting in the highest conductivity observed for this sample. In electrolyte sample A having  $Pr_4N^+I^-$  only, as the cation  $Pr_4N^+$  is bulky only the iodide ions (I<sup>-</sup>) are expected to make considerable contribution to the ionic conductivity and therefore this sample shows the lowest conductivity. As the KI concentration increases at the expense of Pr<sub>4</sub>N<sup>+</sup>I<sup>-</sup> concentration from electrolyte A to F, the conductivity gradually increases mostly due to the increase in the number of  $K^+$  ions. However, at a given salt concentration combination, the dissociated K<sup>+</sup> and I<sup>-</sup> ions from KI salt and I<sup>-</sup> ions from Pr₄N<sup>+</sup>I<sup>-</sup> salt will take part in the conduction process and contribute to the ionic conductivity of the gel electrolyte. As high molecular weight  $Pr_4N^+I^-$  is gradually replaced by low molecular weight KI, the number of iodide ions will also obviously increase with increasing KI content. The total conductivity originates from highly mobile K<sup>+</sup> cations, and I<sup>-</sup> anions from both salts and therefore the total conductivity naturally increases with increasing KI content as seen from Fig. 1.

All graphs in Fig. 1 show linear variations that can be explained assuming that the conductivity temperature dependence follows Arrhenius type behaviour given by the equation,

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

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

The parallel lines in Fig. 1 imply that the activation energy values are almost same for all six gel electrolyte samples studied and independent of the concentrations of KI and

Pr4N<sup>+</sup>I<sup>-</sup> salts. It can be assumed that these PVdF based gel electrolytes are formed essentially by "trapping" the EC/PC (ethylene carbonate/propylene carbonate) based electrolytic solution in the matrix formed by PVdF and the conducting properties of the electrolyte to be determined essentially by the properties of the electrolytic solution at all concentrations as explained in detail for the PAN based system reported earlier [11].

In organic liquid electrolytes ion transport is mainly governed by a single activation process which involves rearrangement of local structure of the liquid in the vicinity of the moving ion in addition to overcoming activation barrier [30,31]. The activation process in organic liquid electrolytes can be considered as ion translational motion mediated by relaxation of surrounding medium. Hence the activation energy in liquid based electrolytes will be expected to mainly governed by the nature of the solvents rather than the type of salt in them or the concentrations of the salt or salt mixture in them. The activation energy of the present gel polymer electrolyte system, in which the ionic conductivity results mainly from movement of ions dissociated in the "trapped" EC/PC cosolvent in the PVdF, is therefore, depends to a large extent, on the co-solvent involved and unaffected by the type and the concentration of the salt(s). This is most likely the reason for the almost similar activation energies observed for the conductivity variation for different compositions of electrolytes shown in Fig. 1.

## 3.2. Solar cell characterization

Six different dye-sensitized solar cells were fabricated using the six different electrolyte compositions shown in Table 1 and their performances at room temperature were investigated. Fig. 2 shows the  $J_{\rm sc}-V$  characteristics obtained for DSSCs with PVdF gel electrolytes containing 0% (w/w) KI (electrolyte A), 16.6% KI (w/w) (electrolyte C), and 100% (w/w)



Fig. 2 - J-V characteristics of the three dye sensitized solar cells with (a) 0 wt% KI (only with Pr<sub>4</sub>NI as the salt), (b) 100 wt% KI (only with KI as the salt) and (c) the salt mixture 16.6 wt% KI + 83.4 wt% Pr<sub>4</sub>NI.

Table 2 – Parameters of solar cells with electrolytes of
different KI/Pr <sub>4</sub> N <sup>+</sup> I <sup>-</sup> weight ratio.

		0				
KI wt%	0%	8.30%	16.60%	33.30%	50%	100%
V <sub>oc</sub> (mV)	680.5	665.6	674.4	731	717.2	751
I <sub>sc</sub> (mA)	1.537	1.787	2.29	1.493	1.211	1.153
$J_{\rm sc}$ (mA cm <sup>-2</sup> )	6.148	7.148	9.16	5.972	4.844	4.612
Fill factor (%)	69.28	69.8	63.43	69.72	68.33	68.51
Efficiency (%)	2.90	3.32	3.92	3.05	2.38	2.37

of KI (electrolyte F). For the purpose of clarity the curves for the DSSCs with other compositions are not shown in this figure.

Solar cell parameters, under the irradiation of 1000 W m<sup>-2</sup>, such as the open circuit voltage (V<sub>oc</sub>) and the short circuit current density ( $J_{sc}$ ) were measured and the fill factor (FF, %) and efficiency ( $\eta$ , %) were calculated for all the cells studied. The results obtained are shown in Table 2. The fill factor was calculated using

$$FF = \frac{J_{\text{opt}} \ V_{\text{opt}}}{J_{\text{sc}} \ V_{\text{oc}}}$$

where  $J_{opt}$  and  $V_{opt}$  are the current density and voltage at maximum power output. The  $\eta$  was calculated using

$$\eta = \frac{J_{\rm sc} \ V_{\rm oc} \ FF}{\rm Total \ incident \ power \ density}$$

Table 2 shows that the performance parameters of the solar cells are sensitive to the cations present in the gel electrolyte.  $V_{oc}$  is somewhat small and  $J_{sc}$  is large for larger cation  $Pr_4N^+$ . But for the smaller cation  $K^+$ ,  $V_{oc}$  is large and  $J_{sc}$  is small. On mixing the two cations  $V_{oc}$  drops a little and increases again as the amount of smaller cation increases. The observed drop resulting in a  $V_{oc}$  of 677.4 mV for the highest efficiency cell is due to the effect of both types of cations. The  $J_{sc}$  changes most with cation concentration ratio. The fill factor remains nearly same for all KI/Pr<sub>4</sub>N<sup>+</sup>I<sup>-</sup> concentration ratio but drops a little for the highest efficiency cell. Therefore,  $J_{sc}$ , which is mostly determined by the relative amount of iodide ion concentration



Fig. 3 – Variation of (a) Efficiency and (b) Short circuit current density of dye sensitized solar cells with % wt ratio of KI/Pr<sub>4</sub>NI. The maximum solar cell efficiency and the maximum  $J_{sc}$  occur at the optimum salt ratio 16.6 wt% KI + 83.4 wt% Pr<sub>4</sub>NI.

Table 3 – The characteristics of PAN and PVdF polymers.					
	PAN	PVdF			
Formula M. wt. of monomer Amorphous density	C <sub>3</sub> H <sub>3</sub> N 53.06 g/mol 1.184 g/cm <sup>3</sup>	C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> 64.03 g/mol 1.749 g/cm <sup>3</sup>			

in the gel electrolyte, contributes significantly to the solar cell efficiency.

The efficiency ( $\eta$ , %) and the short circuit current density ( $J_{sc}$ ) of all six solar cells as a function of the KI weight percentage are shown in Fig. 3.

The efficiency variation follows essentially the same variation as  $J_{sc}$ . The salient feature is that the solar cell fabricated with the binary iodide mixture with 16.6% (w/w) KI concentration shows the highest energy conversion efficiency of 3.92% whereas the solar cells fabricated with the electrolyte having 100% KI and with 100% Pr<sub>4</sub>NI show efficiencies of 2.90% and 2.37% respectively. The binary iodide mixture having the 16.6 w/w% KI in the gel electrolyte has clearly enhanced the solar cell efficiency by 35%. It is interesting to note that the maximum efficiency is obtained with an electrolyte having a lower total ionic conductivity than with the electrolyte having the highest total conductivity.

The J<sub>sc</sub> reaches a maximum value for a particular combination of the K<sup>+</sup> and Pr<sub>4</sub>N<sup>+</sup> cations as shown in Fig. 3. Similar results have been observed for PAN based systems as well [11]. One explanation for the occurrence of the maxima in the efficiency and J<sub>sc</sub> at 16.60 wt% KI concentration is as follows: As the KI percentage increases the net iodide ion concentration [I<sup>-</sup>] in the gel electrolyte increases giving rise to the initial increase in  $J_{sc}$ . At low KI concentrations one can expect that most of the available iodide ions (I<sup>-</sup>) to be free and contribute to the  $J_{sc}$  and efficiency. The maximum efficiency and the maximum Jsc occur at 16.6 wt% KI sample. The subsequent drop in J<sub>sc</sub> with increasing KI percentage is mostly due to the reduction of the number of free I<sup>-</sup> ions due to ion association leading to the formation of ion pairs, triplets and higher ionic aggregates which may not contribute to the  $J_{sc}$ . Even though the overall ionic conductivity has increased with KI content, and also the iodide ion concentration has increased with KI content, the iodide ion conductivity has gone through a maximum which corresponds to the J<sub>sc</sub> maximum. Therefore, the conductivity increase beyond the maximum efficiency composition (16.6 wt% KI), is evidently due to increase in the number of highly mobile K<sup>+</sup> ions. The remaining excess iodide ions, (beyond the maximum efficiency composition) remain in the medium as higher ionic clusters without contributing to the conductivity. The increase in viscosity of the electrolyte due to increase in KI percentage may also decrease the iodide ion mobility and reduce the J<sub>sc</sub> as well. Also at high percentage of KI, some KI salt may not dissociate and thereby not contribute to ionic conduction. The levelling off of the  $J_{sc}$ beyond about 40 wt% of KI indicates that the decreasing tendency of the current is compensated by increase in current which may arise due to formation triple ions with higher charge at high percentage of KI. The efficiency is thus related, not to the iodide ion concentration  $[I^-/I_3^-]$ , but to the iodide ion contribution to the overall ionic conductivity and the maximum efficiency in this example corresponds to the highest iodide ion conductivity. This has been established by laborious iodide ion transference number measurements for a couple of other systems [11].

The present PVdF based DSSC shows a lower efficiency compared to that of a similar PAN based DSSC reported in Ref. [11]. The difference in efficiencies obtained for the two systems can be qualitatively explained as follows: While the weight ratio in the electrolyte for the PAN:EC:PC:Salt mixture = 1:4:4:0.6, for the PVdF:EC:PC:Salt mixture it is = 1:4:4:1. Through convincing experimental evidence on PAN:EC:PC based and PVdF:EC:PC based lithium ion electrolytes developed for rechargeable lithium batteries, it has been rather well established that in both these systems, an electrolyte solution (salt dissolved in EC/PC co-solvent) is "entrapped" within a matrix formed by the polymer. The nature of the net polymer host structure and its physical properties, however, would affect the ionic conductivity (through viscosity and mobility).

As seen from Table 3 below, PVdF has a higher molecular weight per repeat unit and a higher amorphous density compared to PAN. Therefore, in the resulting "gel", the ionic mobility of iodide ions is expected to be higher in the PAN based material compared to the PVdF based material resulting a higher  $J_{\rm sc}$  and hence a higher efficiency for the DSSC based on the PAN system.

# 4. Conclusions

The dye-sensitized solar cells operated with PVdF based polymer electrolytes with a binary iodide system consisting of a small alkali cation ( $K^+$ ) and a bulky cation ( $Pr_4N^+$ ) show efficiency enhancement which can be attributed to the mixed cation effect. When the relative percentage of KI is changed in the electrolyte, the resulting efficiency variation follows that of the short circuit current density  $(J_{sc})$ . With identical polymer-EC/PC-salt compositions, the solar cell with KI alone gave an efficiency of 2.37% with  $J_{sc} = 6.15$  mA cm<sup>-2</sup> and the cell with Pr<sub>4</sub>NI alone gave an efficiency of 2.90% with  $J_{\rm sc} = 4.16$  mA cm<sup>-2</sup>. The cell with the mixed iodide system, KI:  $Pr_4NI = 16.6:83.4$  (% weight ratio) however, showed an enhanced efficiency of 3.92% with  $J_{sc} = 9.16$  mA cm<sup>-2</sup>, open circuit voltage (Voc) of 674.4 mV and a fill factor of 63.4%. We believe that the efficiency enhancement by about 35% and the occurrence of the maxima in the solar cell efficiency and in the short circuit photocurrent is an important finding that supports similar previous results.

It should be noted that current and efficiency of gel polymer electrolytes based DSSC is not determined by the total ionic conductivity of the electrolyte but by many factors including the iodide ion conductivity. In fact the net result of several competing factors in the electrolyte determine the net short circuit current density and hence the efficiency such as the number of free I<sup>-</sup> ions and their mobility, the number of free K<sup>+</sup> ions and their mobility, the number of the electrolyte solution [11]. The combination of all these effects give rise to the maximum efficiency with the electrolyte having 16.6 wt% KI.

# Acknowledgements

A.K. Arof thanks the University of Malaya for the sabbatical leave to the University of Peradeniya, Sri Lanka and for the support to attend ISPE 13. A.K. Arof also thanks the International Programme in the Physical Sciences (IPPS), Sweden for financial support during his stay in Sri Lanka.

#### REFERENCES

- Regan BO, Gratzel M. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO<sub>2</sub> films. Nature 1991;353(6346):737.
- [2] Tennakone K, Senadeera GKR, Perera VPS, Kottegoda IRM, De Silva LAA. Dye-sensitized photoelectrochemical cells based on porous SnO<sub>2</sub>/ZnO composite and TiO<sub>2</sub> films with a polymer electrolyte. Chemistry of Materials 1999;11(9):2474–7.
- [3] Gratzel M. Conversion of sunlight to electric power by nanocrystalline dye-sensitized solar cells. Journal of Photochemistry and Photobiology A: Chemistry 2004;164(1-3):3-14.
- [4] Bandara TMWJ, Dissanayake MAKL, Mellander B-E. Dye sensitized solar cells with poly(acrylonitrile) based plasticized electrolyte containing MgI<sub>2</sub>. Electrochimica Acta 2010;55:2044–7.
- [5] Grätzel M. Photoelectrochemical cells. Nature 2001;414(6861):338–44.
- [6] Wu J, Lan Z, Hao S, Li P, Lin J, Huang M, Fang L, Huang Y. Progress on the electrolytes for dye-sensitized solar cells. Pure and Applied Chemistry 2008;80(11):2241–58.
- [7] Yella Aswani, Lee Hsuan-Wei, Tsao Hoi Nok, Yi Chenyi, Chandiran Aravind Kumar, Nazeeruddin Md Khaja, et al. Porphyrin-sensitized solar cells with cobalt (II/III)-based redox electrolyte exceed 12 percent efficiency. Science 2011;334:629–34.
- [8] Xia J, Li F, Huang C, Zhai J, Jiang L. Improved stability quasisolid-state dye-sensitized solar cell based on polyether framework gel electrolytes. Solar Energy Materials and Solar Cells 2006;90(7–8):944–52.
- [9] Lan Zhang, Wu Jihuai, Lin Jianming, Huang Miaoliang. Quasisolid-state dye-sensitized solar cell based on a polymer gel electrolyte with in situ synthesized ionic conductors. Comptes Rendus Chimie 2010;13:1401–5.
- [10] Lai Yi-Hsuan, Chiu Chih-Wei, Chen Jian-Ging, Wang Chun-Chieh, Lin Jiang-Jen, Lin King-Fu, et al. Enhancing the performance of dye-sensitized solar cells by incorporating nanosilicate platelets in gel electrolyte. Solar Energy Materials and Solar Cells 2009;93(10):1860–4.
- [11] Dissanayake MAKL, Thotawatthage CA, Senadeera GKR, Bandara TMWJ, Jayasundera WJMJSR, Mellander B-E. Efficiency enhancement by mixed cation effect in dyesensitized solar cells with PAN based gel polymer electrolyte. Journal of Photochemistry and Photobiology A: Chemistry 2012;246:29–35.
- [12] Ileperuma OA, Dissanayake MAKL, Somasunderam S. Dyesensitised photoelectrochemical solar cells with polyacrylonitrile based solid polymer electrolytes. Electrochimica Acta 2002;47(17):2801–7.
- [13] Dissanayake MAKL, Bandara LRAK, Bokalawala RSP, Jayathilaka PARD, Ileperuma OA, Somasunderam S. A novel gel polymer electrolyte based on polyacrylonitrile (PAN) and its application in a solar cell. Materials Research Bulletin 2002;37(5):867–74.

- [14] Ileperuma OA, Kumara GRA, Murakami K. Quasi-solid polymer electrolytes based on polyacrylonitrile and plasticizers for indoline dye sensitized solar cells of efficiency 5.3%. Chemistry Letters 2008;37(1):36–7.
- [15] Ileperuma OA, Kumara GRA, Yang H-S, Murakami K. Quasisolid electrolyte based on polyacrylonitrile for dye-sensitized solar cells. Journal of Photochemistry Photobiology A: Chemistry 2011;217(2–3):308–12.
- [16] Cai N, Li Y, Zhao Y, Ji W, Zhang X, Xiong S. Study of PVDF based quasi-solid state dye-sensitized solar cells. Acta Energiae Solaris Sinica 2010;31(3):302–5.
- [17] Noor MM, Buraidah MH, Yusuf SNF, Careem MA, Majid SR, Arof AK. Performance of dye-sensitized solar cells with (PVDF-HFP)-KI-EC-PC electrolyte and different dye materials. International Journal of Photoenergy 2011;2011:5. Article number 960487.
- [18] Ahn SK, Ban T, Sakthivel P, Lee JW, Gal Y-S, Lee J-K, et al. Development of dye-sensitized solar cells composed of liquid crystal embedded, electrospun poly(vinylidene fluoride-co-hexafluoropropylene) nanofibers as polymer gel electrolytes. ACS Applied Materials and Interfaces 2012;4(4):2096–100.
- [19] Leea Kun-Mu, Suryanarayanan Vembu, Hoc Kuo-Chuan. High efficiency quasi-solid-state dye-sensitized solar cell based on polyvinyidene fluoride-co-hexafluoro propylene containing propylene carbonate and acetonitrile as plasticizers. Journal of Photochemistry and Photobiology A: Chemistry 2009;207:224–30.
- [20] Chen J, Peng T, Fan K, Xia J. Iodine-free quasi solid-state dyesensitized solar cells based on ionic liquid and alkali salt. Journal of Materials Chemistry 2011;21(41):16448–52.
- [21] Li P, Wu J, Hao S, Lan Z, Li Q, Huang Y. Quasi-solid state dyesensitized solar cells based on the cross-linked poly(ethylene glycol) electrolyte with tetraethoxysilane. Journal of Applied Polymer Science 2011;120(3):1752–7.
- [22] Agarwala S, Thummalakunta LNSA, Cook CA, Peh CKN, Wong ASW, Ke L, et al. Co-existence of LiI and KI in fillerfree, quasi-solid-state electrolyte for efficient and stable dyesensitized solar cell. Journal of Power Sources 2011;196(3):1651–6.
- [23] Jayathilaka PARD, Dissanayake MAKL, Albinsson I, Mellander B-E. Dielectric relaxation, ionic conductivity and thermal studies of the gel polymer electrolyte system PAN/EC/PC/LiTFSI. Solid State Ionics 2003;156(1–2):179–95.
- [24] Shen X, Xu W, Xu J, Liang G, Yang H, Yao M. Quasi-solid-state dye-sensitized solar cells based on gel electrolytes containing different alkali metal iodide salts. Solid State Ionics 2008;179(35–36):2027–30.
- [25] Watson DF, Meyer GJ. Cation effects in nanocrystalline solar cells. Coordination Chemistry Reviews 2004;248(13–14):1391–406.
- [26] Kelly CA, Farzad F, Thompson DW, Stipkala JM, Meyer GJ. Cation-controlled interfacial charge injection in sensitized nanocrystalline TiO<sub>2</sub>. Langmuir 1999;15(20):7047–54.
- [27] Kambe S, Nakade S, Kitamura T, Wada K, Yanagida S. Influence of the electrolytes on electron transport in mesoporous  $TiO_2$ -electrolyte systems. Journal of Physical Chemistry B 2002;106(11):2967–72.
- [28] Thotawatthage CA, Senadeera GKR, Bandara TMWJ, Dissanayake MAKL. Mixed cation effect in enhancing the efficiency of dye sensitized solar cells based on polyacrylonitrile (PAN) and nano-porous TiO<sub>2</sub>. In: Dissanayake MAKL, et al, editors. Proceedings of the International Conference on Solar Energy Materials, Solar Cells and Solar Energy Applications (Solar Asia – 2011). Kandy, Sri Lanka: Institute of Fundamental Studies; 2011. p. 175–205.

# INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2013) 1–7

- [29] Bandara TMWJ, Dissanayake MAKL, Jayasundara WJMJSR, Albinsson I, Mellander B-E. Efficiency enhancement in dye sensitized solar cells using gel polymer electrolytes based on a tetrahexylammonium iodide and MgI<sub>2</sub> binary iodide system. Physical Chemistry Chemical Physics 2012;14(24):8620-7.
- [30] Petrowsky M, Frech R. Temperature dependence of ion transport: the compensated Arrhenius equation. Journal of Physical Chemistry B 2009;113(16):5996–6000.
- [31] Petrowsky M, Frech R. Salt concentration dependence of the compensated Arrhenius equation for alcohol-based electrolytes. Electrochimica Acta 2010;55(4):1285-8.