INCORPORATION OF TERTIARY ALKALINE IODIDE SALTS IN POLYACRYLONITRILE (PAN) BASED GEL POLYMER ELECTROLYTES TOWARD THE EFFICIENCY ENHANCEMENT OF DYE SENSITIZED SOLAR CELLS

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ABSTRACT

Solid or gel polymer (quasi-solid) electrolytes are better alternatives for the liquid electrolytes in many devices including Dye Sensitized Solar Cells (DSSCs). However, the major disadvantage of employing them in DSSCs is the low efficiencies in the solar cells compared with them having liquid electrolytes. Numerous efforts have been focused on to overcome this problem during the past decade, such as, the use of mixture of polymers, optimizing the salt to polymer concentration ratios, incorporation of ionic liquids etc,.

In this scenario, for the first time in DSSC research history, we have shown the effect using binary iodide salts in the electrolyte towards the enhancement of the efficiencies of DSSCs. As an extension to that study, here we report the effect of using tertiary cations, namely, potassium iodide (KI), Cesium iodide (CsI) and Tetra propyl ammonium iodide ($Pr4N^+I^-$) in the electrolyte on the overall efficiency of DSSCs. The solar cells of configuration Glass/FTO/TiO_2/ Ruthenium dye (N719)/electrolyte/Pt/FTO/glass were fabricated using nanocrystalline mesoporous TiO_2 electrodes. While the DSSCs comprising with binary salts, KI+Pr_4NI (16.6% W/W) and KI+CsI (50% w/w) showed the overall efficiencies of 6.42 %, 6.76% respectively, the DSSC with optimized tertiary cationic mixture of salts having KI+CSI+Pr4NI (15% CsI mole of KI) showed an overall efficiency of 6.92%. The short circuit current density, open circuit voltage and the fill factor of optimized DSSC were 15.27 mA cm^{-2}, 761.0 mV and 60.1 % respectively. Even though the overall efficiency enhancement is not very significant, the use of tertiary iodide salts in the electrolyte for further enhancing the overall efficiencies of DSSCs is a novel research finding.

Keywords : Tri-cation, Alkaline Iodide salt, DSSCs.

1. INTRODUCTION

Dye Sensitized Solar cells based on nano structured titanium dioxide (TiO_2) are low cost alternative to conventional silicon based thin film solar cells. After the discovery of DSSC with remarkable efficiency by Gratzel and co-workers, DSSC technology has attracted vast interest and numerous research studies have been conducted during the last decade towards the efficiency enhancement of DSSCs with long-term stability [1]. According to the latest reports, efficiency of DSSC in laboratory scale already exceeded the 13%. However, this high efficiency DSSSCs suffer from several technological draw backs such as usage of liquid electrolytes in these DSSCs, which causes sealing problems, and long term stability at elevated temperature [2-3]. Therefore, many studies have been done aiming to replace these liquid electrolytes by gel polymer (quasi-solid state) electrolytes. PAN (Polyacrylonitrile) based gel polymer electrolyte had shown reasonably good ionic conductivity and has been successfully employed in quasi solid state DSSCs [4, 5]. These electrolytes generate polymer matrix for electrolyte which has ionic salt dissolved in EC and PC co-solvents entrapped in host polymer and shows liquid like conductivities.

It is well known fact that, due to their poor solubility in many solvents, RbI and CsI having larger cations than the Li ions, cannot be successfully use in electrolytes for DSSCs [6]. However, an important issue in the preparation of electrolytes for DSSC is the enhancement of the iodide ion mobility [4]. This can be achieved by either reducing the mobility of cations or trapping them with some molecules. In polymeric gel electrolyte, the situation is different from that of a liquid one, where, owing to solvation, the smallest ion is the less mobile one. Further, in polymer-gel electrolytes, the larger cations of similar electronic configuration interact more strongly with the polymer due to viscous forces, thus enhancing anionic diffusion [7]. In this context, for the first time in DSSC history we have showed that efficiency enhancement can be achieved by using binary alkaline salts, instead of single cationic salt [Slar Asia 2011]. After that many research groups around the world have confirmed this effect by using different binary alkaline iodide salts [4, 5, 8-10]. The cause for this enhancement was proved by studying the dual role of the cation in determining the short circuit current density through iodide ion conductivity as well as in influence of the charge injection mechanism at the semiconductor/electrolyte interface. As an extension to our original work with binary salts, here we report the effect of usage of tertiary alkaline cations in the electrolyte towards the efficiency enhancement of DSSCs.

2. MATERIAL AND METHODS

Polyacrylonitrile (PAN - Mw 150,000), cesium iodide (CsI), tetrapropylammonium iodide (Pr_4NI), potassium iodide (KI), ethylene carbonate (EC), propylene carbonate (PC) and iodine chips (I_2) with purity greater than 98 % purchased from Sigma Aldrich were used as starting materials. Ruthenium dye (N719) was purchased from Solaronix SA Switzerland. All the chemicals except I_2 and PC were vacuum dried at 60 ^{o}C for 24 hours in a vacuum oven (Eyela VOS - 450D) prior to use.

2.1 Properties of polymer electrolyte

In the preparation of electrolyte samples, weights of PAN (0.1 g) EC (0.4 g), PC (0.4 g) and Pr_4NI (0.05 g) were kept unchanged while the total mole of KI and CsI was maintain at 6.024 x 10^{-5} mol. The weight of iodine was taken to be one tenth of the total mole of iodide salt. Appropriately amounts were mixed in a glass bottle by magnetic stirring. Initially EC, PC, PAN, Pr_4NI, CsI and KI were mixed by continuous stirring at room temperature for about 2 hours until the entire CsI and KI was dissolved. Then the mixture was stirred further keeping it at 80 ^{o}C for about 30 min until PAN was fully dissolved. Finally, the mixture was allowed to cool down to room temperature and I_2 chips were added and again continuously magnetically stirred in a closed bottle for 12 hours to obtain a homogeneous gel electrolyte. This procedure was repeated for all the compositions as shown in table 1. Five different compositions of the gel electrolyte, with PAN:EC:PC:Pr_4NI: [100-x]% KI + [x]% CsI:I_2, for x = 0, 5, 15, 25, 40 were prepared by changing the mole ratio of KI and CsI.

Table 1: Composition of tri iodide salt electrolyte.

Electrolyte	CsI [x]%	CsI (g)	KI (g)
A	0	0	0.0100
B	5	0.009	0.0095
C	15	0.0024	0.0085
D	25	0.0045	0.0075
E	40	0.0060	0.0060

For comparison, another series of electrolytes which contain KI and CsI were prepared with the compositions as listed in table 2 while keeping PAN (0.1 g) EC (0.4 g) and PC (0.4 g) weights constant using the same procedure as before.

Table 2: Composition of KI, CsI gel polymer double salt electrolyte.

Electrolyte	KI % (w/w)	KI (g)	CsI (g)	I_2 (g)
V	0	0.00	0.06	0.0059
W	33.3	0.02	0.04	0.0070
X	50.0	0.03	0.03	0.0076
Y	66.0	0.04	0.02	0.0081
Z	100	0.06	0.00	0.0092

2.2 TiO_2 electrode preparation

TiO_2 photoanodes consist of two layers. First layer was prepared by grinding 0.025 g of TiO_2 (Aroxide-P90) until get a creamy paste and then spin coated on a pre-cleaned, fluorine-doped conducting tin oxide (FTO) glass (Solaronix glass 7 Ω/sq) at 3000 rpm for 60 sec. Second layer was prepared by grinding 0.25 g of TiO_2 (Degussa P-25) with 1 ml of 0.1M HNO_3 acid (pH 1.0), one drop (about 0.02 g) of triton X-100 and 0.05 g of PEG-1000 (Polyethylene glycol). This paste was spread on above mention P90 TiO_2 layer. An active cell area of 0.25 cm^2 was obtained by spreading the paste using the doctor blade technique. Films were then sintered at 450 ^oC for 45 min. The resulting TiO_2 photoanodes were allowed to cool down to room temperature. Dye absorption was carried out by immersing the above film in ethanolic dye solution containing Ruthenium dye N719 [RuL2(NCS)2:2TBA where, L = 2,2-bipyridyl-4, -dicarboxylic acid; TBA = tetrabutylamonium] for 24 h.

2. 3 Solar cell fabrication and characterization

The gel polymer electrolyte based dye-sensitized solar cells (DSSCs) of configuration Glass/FTO/TiO_2/Dye/electrolyte/Pt/FTO/glass were fabricated by sandwiching the polymer electrolyte between the dye adsorbed TiO_2 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/galvonostat HA-301. A Xenon 500 lamp was used with AM 1.5 filter to obtain the simulated sunlight with above intensity.

2.4 EIS measurements

In order to see the effects of CsI on the electron life time and the interfacial charge-transfer resistance, R_{ct2}, electrochemical Impedance Spectroscopy (EIS) measurements were performed on the DSSCs using a Metrohm Autolab Potentiostat/Galvanostat PGSTAT 128 N with a FRA 32 M Frequency Response Analyzer (FRA) covering the 1 MHz - 0.01 Hz frequency range. These measurements were carried out under the illumination of 100 mW cm^{-2} using the same solar simulator that was used for I-V measurements.

3. RESULTS AND DISCUSSION

The variation of efficiency of DSSCs versus salt composition of the electrolytes which contain KI and CsI is shown in Fig.1 and the solar cell parameters extracted from the current - voltage curves are tabulated in table 3. The DSSC " X " fabricated with the gel electrolyte containing the binary iodide mixture of 50 wt% KI and 50 wt% CsI ($KI_{(0.03)}$:$CsI_{(0.03)}$) showed the highest energy conversion efficiency of 6.85 % and the highest short circuit photo current density of 17.61 mA cm^{-2}. The solar cells fabricated using the electrolyte containing only CsI (sample Z) and with only KI (sample V) as the iodide salt in the gel electrolyte showed the efficiencies of 6.42 and 5.72 %, respectively. Therefore, significant enhancement in the efficiency can be seen with the use of the binary iodide mixtures in all the six DSSCs and for the best DSSC the efficiency is increased by a factor of about 7 % compared to the higher efficiency end member. It can be noted that that from Table 3, the efficiency (%) and the short circuit current density (J_{sc}) of all six solar cells follows a same pattern. Open circuit voltage (V_{oc}), increase and become stable when adding CsI to the system. Similar pattern was observed in PAN based LiI + CsI double iodide salt system by Bandara et al too [8].

Table 3: J-V characteristics of KI+CsI double salt system

Electrolyte	KI % (w/w)	J_{sc} (mA cm^{-2})	V_{oc} (v)	FF (%)	Eff (%)
V	0.0	13.04	733.2	59.8	5.72
W	33.3	16.68	688.6	57.8	6.64
X	50.0	17.61	666.9	58.4	6.85
Y	66.6	16.11	669.3	60.9	6.56
Z	100.0	15.29	668.6	62.8	6.42

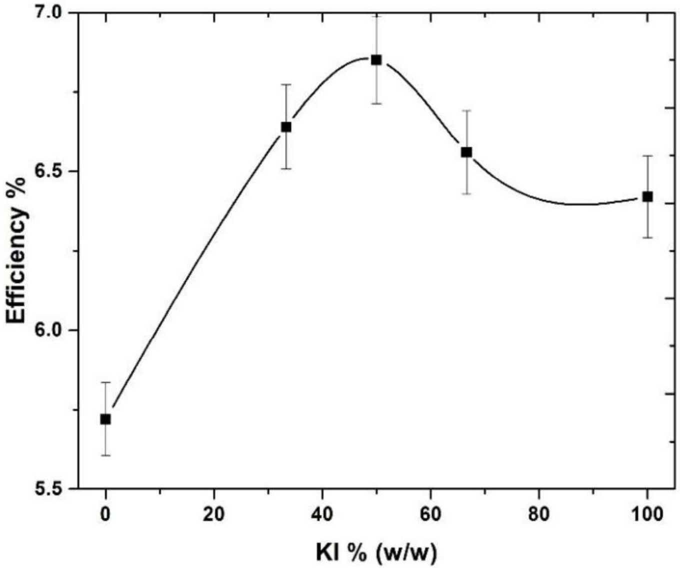

Fig.1. Efficiency variation with KI% (w/w) of KI+CsI system.

In addition to above double salt system, we have investigated the effect of another binary salt system, KI+Pr_4NI in the electrolyte towards the efficiency enhancement of of DSSCs [4]. Though the preparation of photoanode is slightly different than the method we used to prepare the photoanodes in this study, we have used the optimized salt ratios and amounts for further investigations under this study. Therefore, the electrolyte composition of 0.1 g of PAN, 0.04 g of EC, 0.04 g of PC, 0.01 g of KI, 0.05 g of Pr4NI and 0.0056 g of I_2) was selected. The variation of efficiency of DSSCs versus salt composition of the electrolyte which contain KI, CsI and Pr_4NI is shown in Fig.2. As can be seen from the figure DSSCs fabricated with 15% amount of CsI in the KI+ Pr4N system showed the highest efficiency.

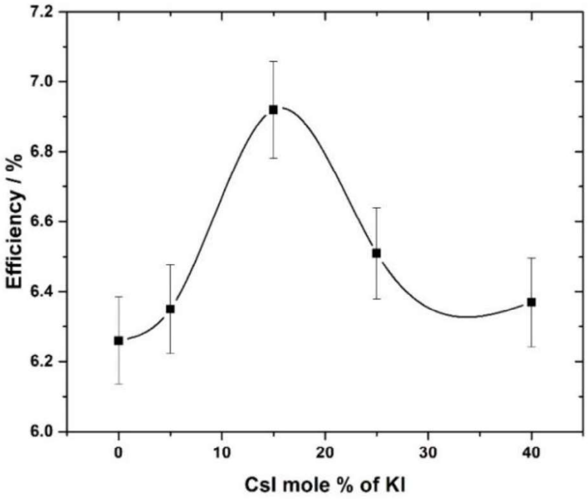

Fig.2. Efficiency variation with CsI mole % of KI for KI+CsI+Pr_4NI system.

The average solar cell parameters obtained from the I-V curves are tabulated in the table 4. The solar cell C fabricated with the gel electrolyte containing the tri iodide mixture with 15% CsI mole of KI ($KI_{(0.0024)}$:$CsI_{(0.0085)}$:$Pr_4NI_{(0.05)}$) has showed the highest energy conversion efficiency of 6.92. The solar cells fabricated using the electrolyte with 0% CsI of KI (sample A-$KI_{(0.01)}$:$Pr_4NI_{(0.05)}$) showed an efficiency of 6.26%. Therefore, it confirmed that replacement of some amount of KI with CsI in the KI+ Pr_4NI system, enhanced the solar cell efficiency and obtained the highest efficient at 15% CsI. This enhancement is about 6% when compared with the efficiency of the DSSC with no Csi in the KI+CsI+Pr4NI electrolytic combination.

Table 4: J-V characteristics of KI+CsI+Pr4NI tri iodide system.

Electrolyte	CsI [x]%	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)	Eff (%)
A	0	14.60	724.2	59.2	6.26
B	5	15.49	750.8	54.6	6.35
C	**15**	**15.27**	**761.0**	**60.1**	**6.92**
D	25	13.70	730.3	65.1	6.51
E	40	14.50	725.1	60.6	6.37

Fig.3 shows the Nyquist plots of the electrochemical impedance spectra of DSSCs with electrolyte A, C and X in the frequency range of $1x10^{-2}$ - $1x\ 10^{6}$ Hz. Each Nyquist plot shows two semicircles. The larger semicircle in the low-frequency range is related to the charge transport/accumulation at dye-attached TiO_2/electrolyte interface resistance (R_{ct2}), and the smaller semicircle in high-frequency region is attributed to the charge-transfer resistance of the Pt counter electrode/electrolyte interface (R_{ct1}) [11, 12]. The impedance parameters were extracted using the equivalent circuit model (inset of Fig.3), and the fitted lines are shown as solid lines in the Nyquist plots. The calculated values of the series resistance (R_s), charge-transfer resistance of the Pt/electrolyte interface (R_{ct1}) and charge-transfer resistance of the TiO_2/electrolyte interface (R_{ct2}) based on the equivalent circuits for the three types of DSSCs are tabulated in Table 5.

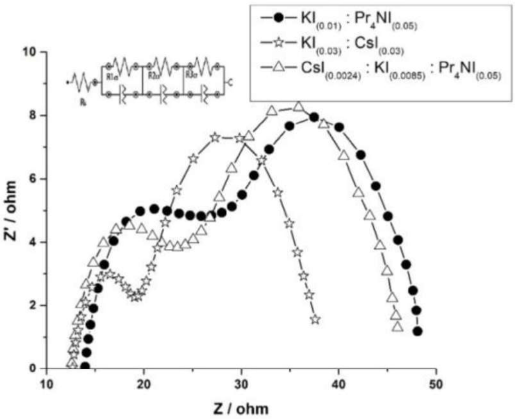

Fig.3 . Impedance plots taken for the three different DSSCs with electrolyte A, C and X in the frequency range of $1x10^{-2}$ - $1x\ 10^{6}$ Hz.

The Bode phase plots of EIS spectra, as shown in Fig.4, display the frequency peaks of the charge-transfer process at the TiO_2/electrolyte interface of the three DSSCs. The characteristic low-frequency peak f_{max} is located at 21.25 Hz for the $KI_{(0.03)}$:$CsI_{(0.03)}$ electrolyte cell, at 18.60 Hz for the $KI_{(0.01)}$:$Pr_4NI_{(0.05)}$ electrolyte cell, and at 13.70 Hz for the $KI_{(0.0024)}$:$CsI_{(0.0085)}$:$Pr_4NI_{(0.05)}$ cell. The electron lifetime (τr) in the DSSCs can be determined from the value of f_{max}. Table 5 shows the relationship between V_{oc}, J_{sc}, and τr for the three types of DSSCs.

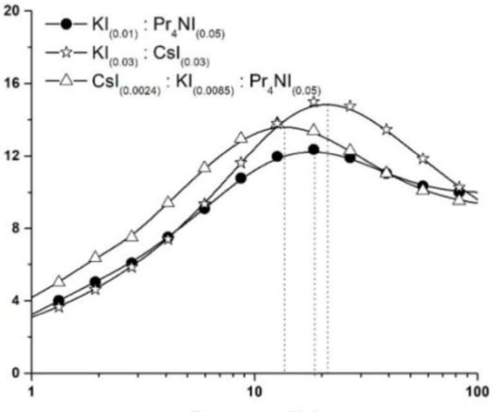

Fig.4. Complex impedance data plotted as phase angle vs frequency (Bode Plots) for the three DSSCs with electrolyte A, C and X in the frequency range of $1x10^{-2}$ - $1x\ 10^{6}$ Hz.

Table 5: J-V characteristics and the charge transfer resistance values of the DSSC with different electrolytes.

Electrolyte	J_{sc}	V_{oc}	FF	Eff	τ bode (ms)	R_s/Ω	$R_{ct1/}\ \Omega$	R_{ct2}/Ω	R_{ct3}/Ω
A	14.6	724.2	59.2	6.26	8.55	14.1	5.58	8.13	20.6
X	17.61	666.9	58.4	6.85	7.42	12.8	5.98	14.1	5.71
C	15.27	761.0	60.1	6.92	11.55	12.7	4.45	7.94	21.2

From Table 5, it can be seen that the electron life time τr is highest for cell C which contain three iodide salt, and the V_{oc} of this cell is also the highest. τr values of cell A and cell X are significantly lower, and their V_{oc} values are also lower compared to the cell C. Shorter electron life time means faster recombination [13]. Therefore, replacing larger cationic alkaline salt like CsI with KI will reduce non-radiative recombination either with dye cations or with I^-_3 redox species. While comparing the electrolyte A and C which is in the same electrolyte system, less recombination leading to increased number of electrons arriving at the collecting electrode then increase J_{sc}. The enhancement in V_{oc} and J_{sc} by replacing KI with CsI, so that the overall result has been the enhancement in efficiency.

When comparing the resistant values extracted from equivalent circuits for nyquist plots, the electrolyte A and C which is in the same electrolyte system, the call C has comparable low resistant values for R_s, R_{ct1} and R_{ct2} than the cell A. Therefore, it is clear that J_{sc} is increased because of low interfacial resistant.

4. CONCLUSION

This paper reports for the first time, the effect of a tri iodide system consisting of two alkali cation (K^+ and Cs^+) and quaternary ammonium cation (Pr_4N^+) in DSSCs with PAN based electrolytes on the solar cell efficiency. The maximum efficiency enhancement can be obtained by incorporating 15 % CSI in the KI + Pr4NI binary salt system. About 6% efficiency enhancement can be achieved by replacing binary cationic electrolyte with tertiary cationic electrolyte in DSSCs. The tertiary cationic system studied in this study with DSScs showed 6.92% efficiency with 15.27 mA cm^{-2} short ciricuit current density and these values are significantly higher when compared with the values obtained in the quasi -solid state DSSC s.

5. ACKNOWLEDGMENTS

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