MIXED CATION EFFECT IN GEL POLYMER ELECTROLYTES INTENDED FOR SOLAR CELLS

I. ALBINSSON[1*], M.A.K.L. DISSANAYAKE[2], T.M.W.J. BANDARA[1,3,4] AND B.-E. MELLANDER[4]

[1]*Department of Physics, University of Gothenburg, Gothenburg, Sweden*

[2]*Institute of Fundamental Studies, Kandy, Sri Lanka*

[3]*Department of Physical Sciences, Rajarata University of Sri Lanka, Mihintale, Sri Lanka*
[4]*Department of Physics, Chalmers University of Technology, Gothenburg, Sweden*

Corresponding Author, email: *ialbin@physics.gu.se*

ABSTRACT

Recently, quasi-solid-state dye-sensitized solar cells (DSSCs) attracted attention due to their improved physical and chemical stability and therefore they offer a better long term cell performance compared to that of cells based on liquid electrolytes although their efficiency is relatively poor. In 2011 we presented a way to improve the DSSC performance by capturing the mixed cation effect for quasi-solid-state DSSCs. In that work a gel polymer electrolyte, based on polyacrylonitrile (PAN) host polymers and the salts tetrahexylammonium iodide (Hex_4NI) and MgI_2 were blended to enhance the DSSC performance. The work highlighted the influence of mixed cations on the performance of quasi solid state DSSCs. Interestingly the net ionic conductivity is decreased with amalgamation of small amounts of MgI_2 but still an improved cell performance was observed. The addition of 20% MgI_2 with respect to the Hex_4NI amount into the electrolyte resulted in a 22 % decrease of the net ionic conductivity (from 2.51 to 1.96 mS cm^{-1}) and conversely a cell efficiency improvement by 13%.

Subsequently, the mixed cation effect for quasi-solid-state DSSCs was thoroughly investigated by studying another binary iodide salt mixture of KI and tetrapropylammonium iodide (Pr_4NI). In that work a conductivity drop was also observed but with an increasing amount of Pr_4NI and a decreasing amount of KI in the electrolyte. As a matter of fact, the cell with an electrolyte containing 16.6 % KI and 83.4% Pr_4NI showed the highest DSSC efficiency, 20% higher compared to that of the cell with the highest conducting electrolyte containing only KI as the salt.

Later the MgI_2:Pr_4NI based electrolyte also reinforced the binary cation effect for DSSCs by increasing the efficiency of quasi solid state DSSCs by almost 25% compared to that of the single salt system. In addition, the gel polymer electrolyte system studied with LiI and Hex_4NI also showed a gradual conductivity increase with increasing amount of LiI, however the best efficiency is given by the mixed salt system. Despite the ionic conductivity drop, DSSCs containing mixed salt electrolytes showed a 7.7% efficiency enhancement. In addition, the cell with the mixed alkaline salts LiI and CsI showed a 23 % efficiency enhancement compared to that of their single salt systems. In recent years, many mixed salt systems have been studied by different authors and confirmed the mixed salt effect. Since the binary salt effect is an established phenomenon the ternary salts systems have also been studied to further improve the performance for quasi-solid-state DSSCs. In addition, by using RbI and Hex_4NI mixed salt systems we obtained a remarkable energy conversion efficiency of 7.5% for a recently modified DSSC.

The current density for DSSCs is generally limited by the iodide/triiodide conductivity rather than the cation conductivity. Therefore, the cation and anion transport numbers can also govern the current density for DSSCs by differentiating the net ionic conductivity for the ionic species in the electrolyte. In addition, larger cations in the electrolyte shift the conduction band edge of the semiconductor to a more negative potential leading the cell voltage to increase whereas small cations do the opposite. Therefore, larger open circuit voltages may be reached for the DSSCs containing larger cations in the electrolyte. In general, this mutual competition of different cations tends to give higher efficiencies for mixed cation systems.

Keywords : Photoelectrochemical solar cells, electrolytes, mixed cation effect.

1. INTRODUCTION

Owing to the enormous amount of solar energy received on earth, solar cells are considered as one of the best alternatives to fulfill our energy needs. Recently, quasi-solid-state dye-sensitized solar cells (DSSCs) attracted attention since they are physically and chemically more stable compared to cells based on liquid electrolytes and therefore they offer better long term cell performance although their efficiency is relatively poor. The low cell performance of quasi-solid-state DSSCSs compared to that of the liquid electrolyte counterpart is originating mainly from the larger bulk impedance of the electrolyte and from the poor charge transfer rate at the two interfaces. Therefore, new approaches are needed to lower the impedances of charge transport and charge transfer for quasi-solid-state gel polymer electrolytes used in DSSCs to improve the performance.

Many research studies have been focused on finding a reliable and efficient gel polymer electrolyte for DSSCs. There are conventional ways to improve charge transport in these electrolytes. For example, exploring variations of types and compositions of the polymer host, the plasticizer, the nano-filler in the electrolyte are commonly used methods to improve the charge transport within the electrolyte with the intension to enhance the solar cell performance[1,2,3]. In addition, there are some additives such as 4-tert butylpyridine that improve the solar cell performance without contributing to the conductivity of the electrolyte [4,5].

Even though iodide and tri-iodide ion conduction is important to get higher photocurrents in DSSCs based on TiO_2 thin films and Ru dye complexes, the cations in the electrolyte also have an influence on solar cell efficiencies. However, as previously revealed by us using two different studies, one with the alkaline cation series and the other with the quaternary ammonium iodide series, small cations improve the short circuit current density (J_{sc}) whereas large cations improve the V_{oc} of quasi solid state DSSCs [6,7] Mutually competing effects of small and lager cations paved the way to use mixed cations (large and small) in order to get higher energy conversion efficiencies for quasi-solid-state DSSCs [8].

2. EXPERIMENTAL

The host polymer polyacrylonitrile (PAN), tetrapropylammonium iodide (Pr_4NI), tetrahexylammonium iodide (Hex_4NI), potassium iodide (KI), lithium iodide (LiI), cesium iodide (CsI), magnesium iodide (MgI_2), ethylene carbonate (EC), propylene carbonate (PC) and iodine chips (I_2) were purchased from Aldrich. Fluorine-doped tin oxide (FTO) glass substrates and Ruthenium N 719 dye (cis-diisothiocyanato-bis(2,2′-bipyridyl-4,4′-dicarboxylic acid) ruthenium(II)) also known as Ruthenizer 535-bisTBA were purchased from Solaronix SA for the TiO_2 photo-anode preparation. All the chemicals except I_2 and PC were vacuum dried at 60 °C for 24 h prior to use.

2.1 Electrolyte preparation

For the electrolyte sample preparation, at first the salt/salts were dissolved in appropriate amounts of the solvents EC and PC. The salt mass fraction (x %) is given as a percentage relative to the PAN weight in the electrolyte (x : 100 = salt weight : PAN weight). After dissolving the salts in EC and PC, relevant amounts of polymer was added to the solution and stirred for few hours. Then the mixture was heated to about 100 °C under continued stirring for few minutes to get a transparent slurry. Finally iodine (iodine moles in the electrolyte = one tenth of the iodide salt moles in the electrolyte) was added and the mixture was let to cool down to room temperature with continued stirring for a few more minutes.

2.2 Photo-electrode preparation

For the fabrication of single layer photo-electrodes, titanium dioxide (TiO_2) paste was prepared by grinding Degussa P-25 with very small amount of triton X-100 and carbowax in 0.1 M HNO_3 (or in ethanol). This paste was coated on fluorine-doped tin oxide (FTO) conductive glass substrates using the doctor blade technique and calcined at about 450 °C. Dye sensitization of films were done by immersing the resulting films in an ethanolic solution of Ruthenium N719 dye for 24 h.

Double layer photo-electrodes were prepared by coating a doctor blade layer as described above on a prepared spin coated compact layer of TiO_2. For the compact layer preparation, a paste was prepared by grinding Degussa P-90 TiO_2 powder with 0.1M HNO_3. This paste was spin coated on fluorine-doped tin oxide (FTO) conductive glass substrate at 2300 RPM and then films were calcined at ~450 °C for about 30 mins. Films were immersed in an ethanolic solution of Ruthenium N719 dye for 24 h to complete the dye adsorption.

The quasi-solid-state DSSCs of configuration glass/ FTO/ TiO_2-Dye/ electrolyte/ Pt/ FTO /glass were assembled by sandwiching a small amount of gel polymer electrolyte between the dye sensitized TiO_2 photo-electrode and a platinum (Pt)-coated FTO glass. The photocurrent-voltage (I-V) characteristics of the cells under the illumination of 100 mW cm^{-2} (AM 1.5) were measured using a potentiostat.

3. RESULTS AND DISCUSSION

3.1 Tetrahexylammonium Iodide and MgI_2 system

The DSSC performance were improved by utilizing the effect of mixed cations in electrolytes used for quasi-solid-state DSSCs by blending two salts, tetrahexylammonium iodide (Hex_4NI) and MgI_2, to an electrolyte with polyacrylonitrile (PAN) host polymer and plasticizers EC and PC [9]. The work clearly highlighted the influence of the mixed cation effect on the performance of the quasi solid state DSSCs using single layer photo-electrodes. The conductivity variation for different MgI_2 and Hex_4NI compositions in the electrolyte is given in the Fig. 1 at different temperatures. Actually, at all temperatures the conductivity decreases with increasing mass fraction of MgI_2. This behavior can be understood since the small Mg^{2+} cation can cross-link the polymer and in addition it can be strongly coordinated with EC molecules in the electrolyte.

Fig. 2 shows the ionic conductivity of the electrolyte at 25°C, the short circuit current density, J_{SC}, and the energy conversion efficiency for the DSSCs with different mass fractions of MgI_2 in the electrolyte. As seen in Fig. 2 the addition of 20% MgI_2 with respect to the PAN amount in the electrolyte resulted in a ~22 % decrease of the net ionic conductivity (from 2.51 to 1.96 mS cm^{-1}) and conversely the cell efficiency improved by ~13% increasing from 3.1 to 3.5%. The maximum J_{sc} of 8.6 mA cm^{-1} is also shown for the sample with 20% KI. Therefore, it can be concluded that, the presence of small amount of MgI_2 in the electrolyte improve the DSSC performance although the ionic conductivity of the electrolyte decreases.

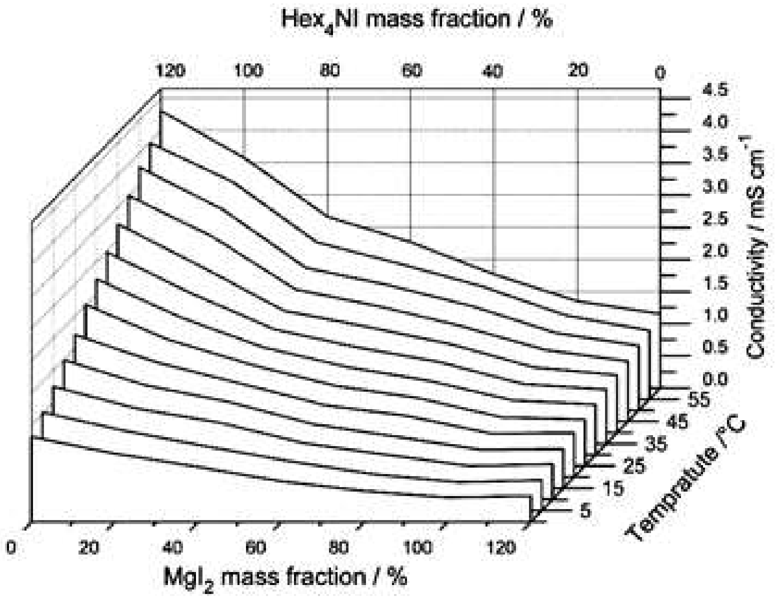

Fig.1. Conductivity variation of PAN/EC/PC:Hex_4NI:MgI_2 electrolytes containing different Hex_4NI and MgI_2 mass fractions at different temperatures.

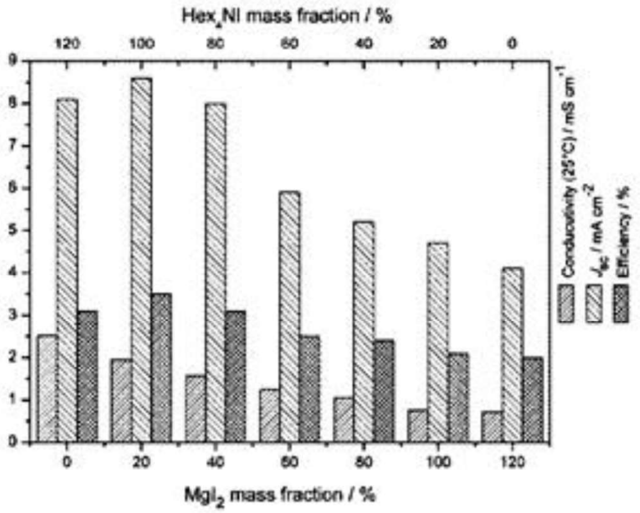

Fig.2. The ionic conductivity of PAN/EC/PC/(Hex_4NI:MgI_2) electrolytes at 25°C and J_{SC} as well as the energy conversion efficiency of the DSSCs with respective electrolytes containing different mass fractions of the MgI_2 in the electrolyte.

3.2 Tetrapropylammonium Iodide and KI system

The mixed cation effect in quasi solid state DSSCs has been thoroughly investigated by studying a binary iodide salt mixture of KI and tetrapropylammonium iodide (Pr_4NI) [10]. In this work, single layer photo-electrodes were fabricated by the doctor blade method using a TiO_2 slurry prepared using ethanol.

The ionic conductivity of PAN/EC/PC/(Pr_4NI:KI) electrolytes at 25°C and J_{SC} as well as the energy conversion efficiency of the DSSCs with respective electrolytes containing different mass fractions of KI and Pr_4NI in the electrolyte are shown in Fig. 3. In the study a conductivity increase was shown with increasing amount of KI and decreasing amount of Pr_4NI in the electrolyte. Consequently, the cell with the electrolyte containing 16.6 % KI and 83.4% Pr_4NI showed the highest DSSC efficiency, which was 20% higher compared to that of the cell with the highest conducting electrolyte, containing only KI as the salt. The maximum J_{sc} of 13.4 mA cm^{-1} is also shown for the sample with 16.6 % KI and 83.4% Pr_4NI. This study also proved the advantage of the presence of small amounts of KI in the electrolyte, although it did not exhibit the maximum ionic conductivity.

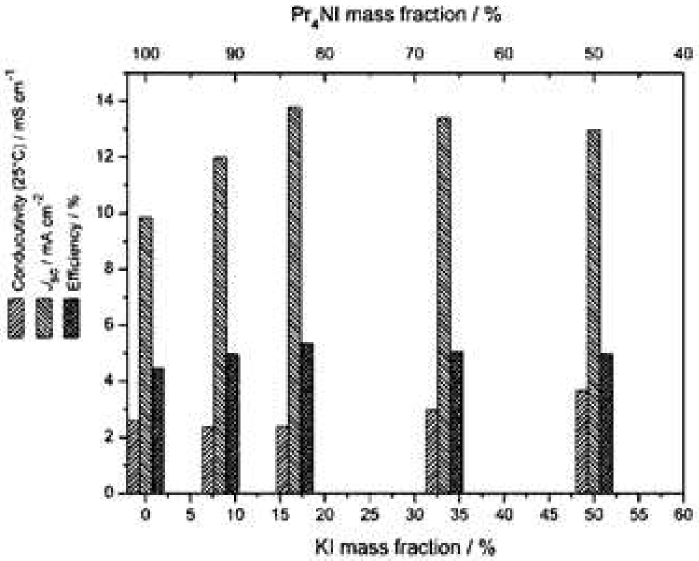

Fig.3. The ionic conductivity of PAN/EC/PC/(Pr_4NI:KI) electrolytes at 25°C and J_{SC} as well as the energy conversion efficiency of the DSSCs with respective electrolytes containing different mass fractions of KI and Pr_4NI in the electrolyte.

3.3 MgI_2 and Tetrapropylammonium Iodide system

The MgI_2:Pr_4NI system also reinforced the binary cation effect in DSSCs by increasing the efficiency in the quasi solid state DSSCs by almost 25% compared to that of the single salt system [11,12]. Single layer photo-electrodes were fabricated by doctor blade method using a TiO_2 slurry prepared by mixing with ethanol. The ionic conductivity of the PAN/EC/PC/(MgI_2:Pr_4NI) electrolyte series at 27°C and J_{SC} as well as the energy conversion efficiency of the DSSCs with this electrolyte series containing different mass fractions of MgI_2 and Pr_4NI are shown in Fig. 4. The study uncovered that the conductivity decreases with increasing amount of MgI_2 as already observed in the comparable Hex_4NI and MgI_2 mixed salt system (Fig. 1). The maximum efficiency and the maximum J_{sc} is exhibited by the cell containing the electrolyte with 16.6 wt% MgI_2 and 83.4 wt.% Pr_4NI. This composition exhibited a ~5.18 % energy conversion efficiency and a J_{sc} of ~12 mA cm^{-2}. The investigation thus also provided evidence for the mixed salt effect for enhancing the DSSC performance. Small amounts of MgI_2 in the electrolyte reduces the ionic conductivity, however, it benefits the cell performance. More interestingly the net ionic conductivity of the electrolyte does not govern the efficiency nor the J_{sc}

in these gel polymer electrolytes based DSSCs. Therefore, evidently there are some other effects that offer a DSSC performance enhancement from mixed counter ions. It is important to investigate these positive effects given by mixed salt systems for further improvements of DSSCs.

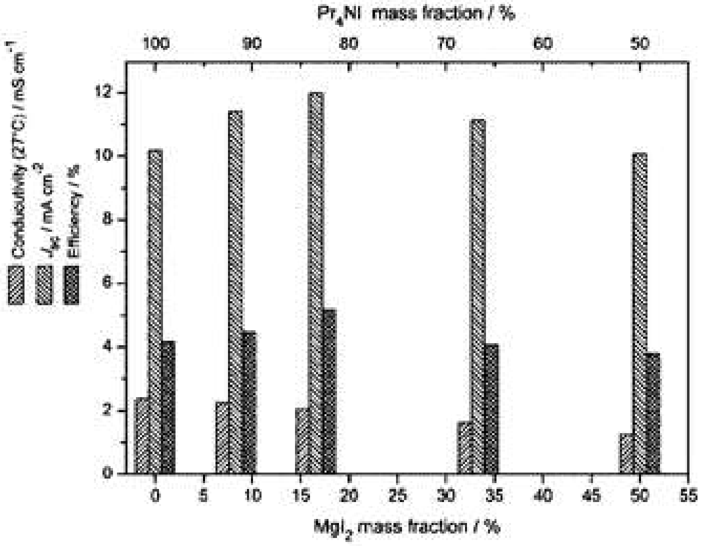

Fig. 4. The ionic conductivity of PAN/EC/PC/(Pr_4NI:MgI_2) electrolytes at 27°C and J_{SC} as well as the energy conversion efficiency of the DSSCs with respective electrolytes containing different mass fractions of the salts in the electrolyte.

3.4 CsI and LiI system

In addition, the gel polymer electrolyte system containing the two alkaline salts LiI and CsI was also investigated to study the mixed salt effect [13]. In this work, double layer TiO_2 photo-electrodes were fabricated by the doctor blade and spin coating methods using a TiO_2 slurry prepared in a 0.1 M HNO_3 solution. Fig. 5 shows the ionic conductivity of the electrolyte at 25°C as well as J_{SC} and energy conversion efficiency for the DSSCs with different mass fractions of LiI and CsI with respect to PAN. In this study the electrolyte containing only LiI salt showed the lowest conductivity, 2.24 mS cm^{-1} (at 25 °C), and the sample with of only CsI showed a conductivity of 2.55 mS cm^{-1}. The highest conductivity, 2.94 mS cm^{-1}, was shown for the 30 % CsI and 30 % LiI containing sample with respect to PAN weight. The maximum energy conversion efficiency, 4.8 %, was in this case shown by the cell containing the highest conducting electrolyte. The cell with mixed salts showed a 23 % efficiency enhancement compared to that of the single salt system. The highest J_{sc}, 13.5 mA cm^{-2}, was shown by the device with 20 % CsI and 40 % LiI.

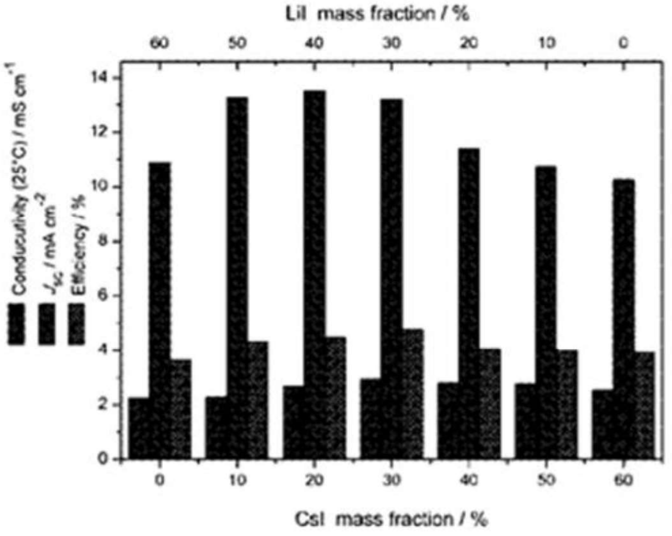

Fig.5. The ionic conductivity of PAN/EC/PC/(CsI:LiI) electrolytes at 25°C. The J_{SC} as well as the energy conversion efficiency of the DSSCs with electrolytes containing different mass fractions of the salts (CsI:LiI) with respect to the in the electrolyte.

3.5 CsI and Hex$_4$NI system

Fig. 6 shows the ionic conductivity of the electrolyte at 25°C, as well as J_{SC} and energy conversion efficiency for the DSSCs with different mass fractions of LiI and Hex$_4$NI with respect to PAN weight. The study was described in detail in a previous publication [14]. In order to assemble DSSCs, double layer TiO$_2$ photo-electrodes were fabricated by the doctor blade and spin coating methods using a TiO$_2$ slurry prepared using 0.1 M HNO$_3$ as described in the experimental section. In this electrolyte series, the conductivity increased with added amount of LiI and thus the highest conductivity, 3.15 mS cm^{-1} at 25 °C, was shown by the electrolyte with only LiI. However, the highest energy conversion efficiency was obtained for the DSSC containing a polymer electrolyte composition of Hex$_4$NI:LiI = 1:2 mass ratio. This cell exhibited the largest short circuit current density, ~13 mA cm^{-2}, and an energy conversion efficiency of ~4%. Despite the ionic conductivity drop, the DSSCs containing mixed salt electrolytes showed an efficiency enhancement of up to 7.7%. The results thus show that electrolytes with a mixed Hex$_4$NI:LiI iodide system showed a better DSSC performance than single iodide salt systems.

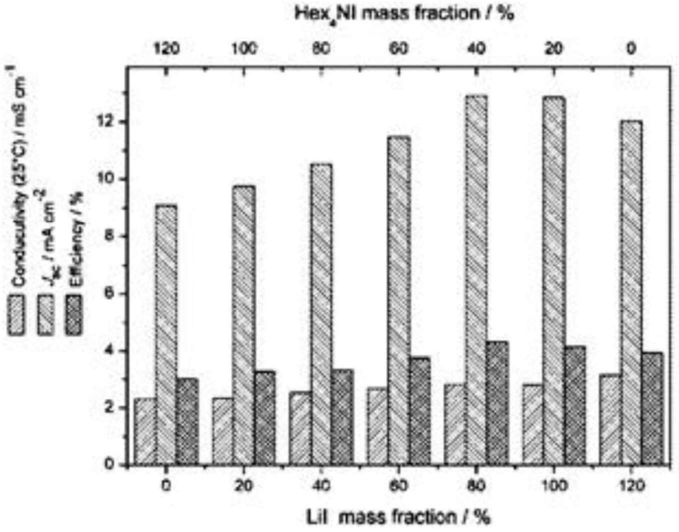

Fig.6. The ionic conductivity of PAN/EC/PC/(LiI:Hex$_4$NI) electrolytes at 25°C together with J_{SC} and the energy conversion efficiency of the DSSCs with respective electrolytes containing different mass fractions of the salts.

The current density in DSSCs is generally limited by the iodide/tri-iodide conductivity rather than the cation conductivity. Therefore, the cation and anion transport numbers can also govern the current density in DSSCs by differentiating the net ionic conductivity for the ionic species in the electrolyte. In addition, larger cations in the electrolyte shift the conduction band edge of the semiconductor to more negative potentials leading the cell voltage to increase whereas small cations do the opposite. Thus, larger open circuit voltages can be offered for the DSSCs containing larger cations in the electrolyte. These mutual competition of different cations tend to give higher efficiencies for mixed cation based DSSC systems. Recently, by using RbI and Hex4NI mixed salt systems we obtained a remarkable energy conversion efficiency of 7.5% for a modified DSSC using spin coating method.

In order to interpret the cation dependence of the DSSC performance we have to consider so many effects that govern the cell performance. May cations in the electrolyte contribute to charge regeneration and charge recombination process or to iodide tri-iodide diffusion? The diffusion of iodide and tri-iodide will limit the total amount of materials reacting at the photo electrode. Dye regeneration is faster when the iodide (I^-) conduction at the photo electrode electrolyte interface. On the other hand higher tri-iodide concentration at the interface increase the conduction band electron recombination with tri-iodide. This will result in a cell performance drop. It should be noted that the iodide concentration is ten times higher than the tri-iodide concentration. The study done with several mixed salt systems proves that the DSSCs performance improves when appropriate mixtures are used in the electrolyte.

4. CONCLUSIONS

The studies with several electrolyte systems revealed that higher DSSC performance is shown for mixed iodide salt containing electrolytes. Higher tri-iodide diffusion is important for the DSSCs performance and therefore the cation and anion transport numbers can also govern the current density in DSSCs by differentiating the net ionic conductivity for the ionic species in the electrolyte. In addition, the larger cations in the electrolyte shift the conduction band edge of the semiconductor to a more negative potential leading the cell voltage to increase whereas small cations do the opposite according to studies done with single salt systems. Larger open circuit voltages can be offered for the DSSCs containing larger cations in the electrolyte. In order to interpret the cation dependence of the DSSC performance we have to consider many effects that govern the cell performance. The diffusion of iodide and tri-iodide can limit the charge transport kinetics at the photo electrode. Dye regeneration is faster when the iodide (I^-) conduction at the photo electrode electrolyte interface. On the other hand higher tri-iodide concentration at the interface increase the conduction band electron recombination with triode decreasing the cell performance. Cations in the electrolyte may contribute to charge regeneration and charge recombination processes or to iodide and tri-iodide diffusion in order to give higher energy conversion efficiency for mixed salt systems.

5. ACKNOWLEDGEMENT

The authors wish to acknowledge the research support provided by, Carl Tryggers Foundation for Scientific Research, the Swedish Research Council and Magnus Bergvalls Stiftelse.

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