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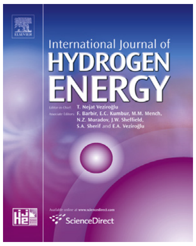

Quasi solid state polymer electrolyte with binary iodide salts for photo-electrochemical solar cells

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ABSTRACT

Quasi-solid-state polymer electrolytes can be used in dye sensitized solar cells (DSSCs) in order to overcome various problems associated with liquid electrolytes. Prior to fabricating commercially viable solar cells, the efficiency of quasi solid state DSSCs needs to be improved. Using electrolytes with a binary iodide mixture is a novel technique used to obtain such efficiency enhancement. In this work we report both conductivity and solar cell performance enhancements due to incorporation of a mixture containing LiI and tetrahexylammonium iodide in a quasi-solid-state electrolyte. The conductivity of the electrolyte increases with added amounts of LiI and thus the highest conductivity, 3.15×10^{-3} S cm^{-1} at 25 °C, is obtained for the electrolyte 100 wt% LiI. The predominantly ionic behavior of the electrolytes was established from *dc* polarization measurements. The iodide ion conductivity, measured using iodine pellet electrodes decreased somewhat with increasing amount of LiI even though the overall conductivity increased. However, the highest efficiency was obtained for the DSSC containing a polymer electrolyte with Hex_4N^+I:LiI = 1:2 mass ratio. This cell had the largest short circuit current density of about 13 mA cm^{-2} and more than 4% overall energy conversion efficiency. The results thus show that electrolytes with Hex_4N^+I/LiI mixed iodide system show better DSSC performance than single iodide systems.

1. Introduction

Photoelectrochemical (PEC) solar cells are emerging as a reliable alternative to silicon solar cells due to the advantages of ease of fabrication and lower cost [1–3]. PEC solar cells can be used to produce electricity or chemical fuels such as hydrogen directly [4]. The electrical energy from solar cells can also be stored as H_2 by electrolysis of water. Dye sensitized solar cells (DSSCs) are promising in many respects but an improvement of the components is highly important in order to fabricate reliable and more efficient photo-electrochemical solar cells.

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A DSSC consists of a dye-adsorbed nano-porous TiO_2 layer on conducting fluorine doped tin oxide (FTO) glass as a working electrode, a Pt coated counter electrode and an electrolyte. Upon irradiation dye molecules absorb photons from visible light and excite electrons in the dye and consequently inject these electrons into the conduction band of the TiO_2 layer [5]. These electrons travel through an external load and reach the counter electrode. According to the device structure, these electrons then pass three interfaces namely; TiO_2/FTO, electrolyte/counter electrode and dye/electrolyte. For the enhancement of the solar cell performance the charge transport between these interfaces should be improved [6].

Since the report of the first DSSC by Grätzel et al. extensive research studies have been focused on DSSCs in order to improve their performance [7]. Especially, the photo-electrode [8–10] and the electrolyte [11,12] need improvements in order to fabricate commercially viable DSSCs. The present work is focused on improving the performance of DSSCs via optimization of the quasi-solid state (gel) polymer electrolyte.

Both the iodide/tri-iodide and Co^{+2}/Co^{+3} redox couples have shown good DSSC performance with liquid type electrolyte systems. The Co^{+2}/Co^{+3} redox couple based electrolytes have shown the best efficiency reported so far for a DSSC, but for the widely used ruthenium based dye complexes the best reported electrolytes contain the iodide/tri-iodide redox couple [1,3,14]. The recently reported highest efficiency with $Co^{(II/III)}$ tris(bipyridyl) – redox couple for porphyrin-sensitized DSSCs is an important development [2]. However, for Co^{+2}/Co^{+3} as well as for I/I_3 redox couples tested, volatile solvent based electrolytes have been used in laboratory scale cells when the highest efficiencies of about 10–13% are reported [3,13,14]. The use of volatile liquids in the electrolyte causes stability problems for DSSCs. Consequently, in order to fabricate practical and commercially viable DSSCs the replacement of liquid type electrolytes by solid or quasi-solid-state electrolytes is important [11,15–17]. The major drawback of DSSCs using solid or quasi-solid electrolytes is their low efficiency basically due to resistive losses both in the bulk and at the interfaces [11,15–17].

Various host polymers, plasticizers and fillers have been tried out in order to develop quasi-solid or solid polymer electrolytes intended for PEC solar cells. For instance, Polyvinylidenefluoride (PVDF), Polyacrylonitrile (PAN) and Polyethylene oxide (PEO) based gel electrolytes have shown reasonably good solar cell performance. The best performing PVDF based quasi-solid state solar cells have used volatile solvents like acetonitrile [16] or acetone [17]. The advantages expected by replacing liquid electrolytes by gel electrolytes are obviously difficult to attain with electrolytes containing such volatile solvents. Polyacrylonitrile (PAN) emerged as a reliable host polymer for DSSCs since 7.27% energy conversion efficiency has been obtained for using a PAN based electrolyte without any volatile solvents [18]. Hence, in the present work, PAN has been selected as the host polymer in order to optimize the quasi-solid state electrolytes intended for DSSCs.

Some recent research has shown that quasi-solid electrolytes with binary salt mixtures give higher efficiencies for DSSCs [19–21,25] than the corresponding single salt systems. For example, the mixed iodide system, LiI and KI in a polyethylene oxide (PEO) based gel electrolyte has been studied by Agarwala et al. [21]. They found that the short circuit current density, J_{sc}, reaches a maximum at 14.5 wt% KI and then decreases as the KI concentration increases. The authors explain the drop of J_{sc} beyond 14.5 wt % KI concentration was due to the formation of ion pairs in the electrolyte. PAN based electrolytes with Pr_4NI and KI salts have also been studied in order to optimize the performance of DSSCs [20]. An efficiency enhancement of about 12% was in that case recorded for the mixed salt electrolyte system compared to the single salt system.

The present work is focused on the study of the role played by two cations of different sizes on conductivity and solar cell performance in quasi-solid-state electrolytes since polymer based quasi solid electrolytes give the advantage of better chemical and dimensional stability.

2. Experimental

2.1. Materials

PAN (Mw.150,000), Hex_4N^+I, LiI, iodine (I_2), EC and PC all with purity greater than 98% from Aldrich were used as starting materials. Prior to use, Hex_4N^+I and PAN were vacuum dried for 24 h at 50 °C and LiI was vacuum dried for 4 h at 150 °C. Conducting glass substrates (FTO glass, Fluorine doped tin oxide over-layer with sheet resistance of 7 $\Omega\ cm^{-2}$) and sensitizing dye cis-diisothiocyanato-bis(2,2-bipyridyl-4,4-dicarboxylate) ruthenium(II) bis(tetrabutylammonium) (N719) were purchased from Solaronix SA. TiO_2 P25 and P90 were supplied from Degussa Germany.

2.2. Preparation of quasi-solid state (gel) electrolyte

A series of gel electrolytes were prepared by keeping the mass fractions of PAN (1.0 g), EC (4.0 g), PC (4.0 g) unchanged and varying the amounts of Hex_4N^+I and LiI according to Table 1. The amount of iodine added was fixed at 0.1 times the total number of moles of salts (Hex_4N^+I + LiI) in the electrolyte.

Initially the relevant weights of EC, PC and salts were mixed in a closed glass bottle by continuous stirring at 50 °C for about 2 h. Then PAN was added to the mixture which was stirred further keeping it at 40 °C for about 1 h. Finally, iodine was added to the mixture and heated to ~100 °C along with continuous stirring for a few more minutes until a homogenous viscous solution was obtained. The resulting hot viscous gel was pressed between two glass plates. This procedure yielded a visually homogenous thin film gel electrolyte.

2.3. Assembly of DSSCs

Two layers of TiO_2 were deposited on the conducting glass substrate in order to prepare the photo-anode. To prepare the first layer, 0.5 g of P90 TiO_2 powder was ground well for ~30 min with ~2 ml of HNO_3 (pH = 1) in an agate mortar. The resulting slurry was coated on the well cleaned glass substrate with a spin coater using a multi-speed program. The first stage was done at 1000 rpm for 2 s and the second stage at 2350 rpm for 60 s. During the spin-coating a part of the glass plate was covered with adhesive tape to prevent coating TiO_2 on the part needed for electrical contacts. After drying in air for ~30 min, the coated substrate was sintered at 450 °C for ~30 min.

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Table 1 – Electrolyte composition, where the amount of PAN, EC and PC were kept at 1.0 g, 4.0 g and 4.0 g respectively.

Electrolyte	*a*	*b*	*c*	*d*	*e*	*f*	*g*
LiI/g	0.0	0.2	0.4	0.6	0.8	1.0	1.2
$Hex_4N^+I^-$/g	1.2	1.0	0.8	0.6	0.4	0.2	0.0
I_2/g	0.063	0.090	0.118	0.145	0.173	0.200	0.227
Wt. ratio PAN:$Hex_4N^+I^-$:LiI	1:1.2:0	1:1:0.2	1:0.8:0.4	1:0.6:0.6	1:0.4:0.8	1:0.2:1	1:0:1.2

Subsequently, the second layer of TiO_2 was coated on the first layer using P25 TiO_2 powder. For the preparation of this layer, 0.5 g of Degussa powder (TiO_2) was ground well for ~30 min with ~2 ml of HNO_3 (pH = 1) in an agate mortar. The resulting colloidal suspension was diluted to get a 5% (*w*/*w*) solution and subsequently, it was stirred overnight at 60 °C and 25% (*w*/*w*) solution was obtained. Then ~0.1 g of carbowax and few drops of Triton × 100 (surfactant) were added and mixed well. This colloidal suspension was casted using the doctor blade method followed by sintering in air at 450 °C for 30 min to obtain a porous TiO_2 layer. The final film thickness was ~10 μm. The adsorption of sensitizing dye was carried out by soaking the TiO_2 coated glass plates in an ethanolic solution of the dye while both were hot (~60 °C) and kept for 24 h followed by rinsing with acetone.

The DSSCs were assembled by sandwiching an electrolyte film between the sensitized TiO_2 electrode and a platinum (Pt) coated conducting glass plate (counter electrode). At least three cells were prepared for each electrolyte composition and the stable results were used for the analysis.

2.4. *Characterization*

Complex impedance measurements were made on disc shaped samples with a thickness of ~0.5 mm sandwiched between two stainless steel electrodes of 10.5 mm diameter, using a computer controlled HP 4192 impedance analyzer in the frequency range 10 Hz–10 MHz. Prior to measurements the samples were heated to 60 °C and thereafter the temperature of the sample was varied from 60 to 0 °C and the measurements were taken at 5 °C intervals. The ionic conductivities were derived from the complex impedance data.

DSC thermograms of the electrolyte samples were obtained using a Mettler Toledo DSC 30 differential scanning calorimeter. Each sample was scanned at a rate of 10 °C min^{-1} from −140 °C to 100 °C. The measurements were carried out by performing several consequent heating and cooling cycles with the same sample. A flow of nitrogen gas was purged in order to avoid contact with atmospheric moisture.

The fabricated solar cells were irradiated by a LOT-Oriel GmbH solar simulator 1.5 AM, 1000 W m^{-2}. *I*–*V* characteristics of the cells were obtained using a computer controlled eDAQ Potentiostat and e-coder. The effective area of the cell was 11 mm^2.

3. Results and discussion

Fig. 1 shows the conductivity versus salt composition in the electrolyte for different temperatures between 0 and 60 °C (step 5 °C). The compositions of salts are expressed with respect to one gram (1.0 g) of PAN in the electrolyte as given in Table 1 and the total weight of salt was kept unchanged at 1.2 g. The conductivity of electrolyte without LiI is low and has values1.2 × 10^{-3}(0 °C) 2. 3 × 10^{-3} (25 °C) and 3.5 × 10^{-3} S cm^{-1} (50 °C) for the electrolyte with 1.2 g of Hex_4NI. The conductivity is gradually increased with increasing amount of added LiI. Accordingly, the electrolyte containing the maximum amount of LiI salt shows the highest conductivity at all temperatures. This electrolyte showed conductivity values of 1.51 × 10^{-3}(0 °C) 3.15 × 10^{-3} (25 °C) and 5.41 × 10^{-3} S cm^{-1} (50 °C) respectively.

Fig. 2 shows the conductivity versus 1000/T for PAN/EC/PC:Hex_4N^+I/LiI electrolytes with different LiI and Hex_4N^+I compositions. The temperature dependence of the conductivity (σ) of all electrolyte samples show Vogel–Tammann–Fulcher (VTF) behavior and were fitted to the VTF equation,

$$\sigma = AT^{-1/2}\exp\left(-\frac{E_a}{k_B\left(T - T_g^{/}\right)}\right) \tag{1}$$

where σ is the conductivity, *T* the absolute temperature, *A* a pre-exponential factor, E_a a pseudo activation energy and $T_g^{/}$ a reference temperature which is related to the equilibrium state glass transition temperature [22]. In this work the measured glass transition temperature, T_g, was employed as the reference temperature $T_g^{/}$ for the fitting. *A*, and E_a values obtained by fitting conductivity data to eq. (1) are shown in

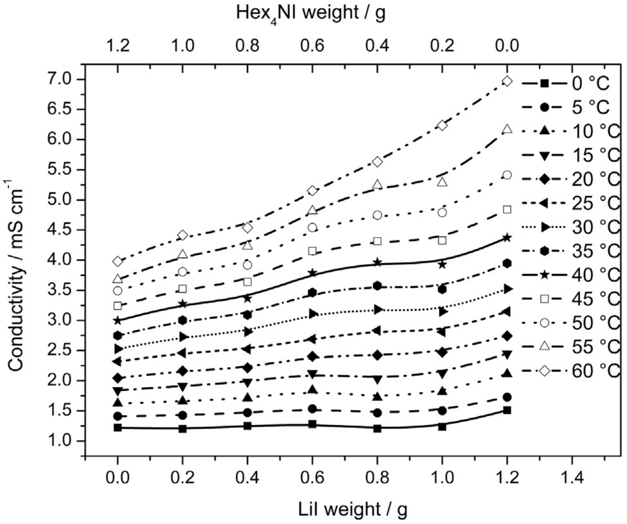

Fig. 1 – Conductivities for different LiI and $Hex_4N^+I^-$ composition in PAN/EC/PC: $Hex_4N^+I^-$/LiI electrolytes at different temperatures.

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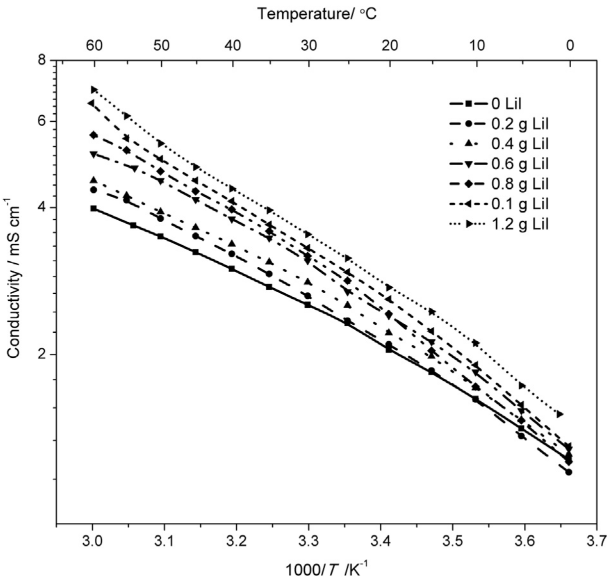

Fig. 2 – Conductivity versus 1000/T for PAN/EC/PC:$Hex_4N^+I^-$/LiI electrolytes for different LiI $Hex_4N^+I^-$ and compositions.

Fig. 3. In general, the pre-exponential factor, A, is proportional to the number of ionic charge carriers in the electrolyte and E_a reveals the energy characteristics [22,23,24.] Calculated E_a values fluctuate between 30 and 40 meV. A trend of activation energy increase is observed with increasing amount of LiI in the electrolyte, with some exceptions. The small discrepancy in activation energies shown for samples "b" "f" and "g" against the increasing trend of E_a may have arisen from disparity imposed by the use of single salt and mixed salt system. The increase of activation energy may be attributed to the decrease of the local segmental motion of polymer electrolyte by increase in complexion points between the polymer and the ionic species [23] because, with added LiI the density of ionic species in the electrolyte is increased since the molar weight of the Li is very much less than that of the Hex_4N. As shown in Fig. 3, A increases more or less with increasing amount of LiI, suggesting that the number of ionic charge carriers increases with added LiI as expected [23,24]. Hence, the conductivity increase with increasing LiI mass fraction can be attributed basically to an increase of the number of charge carriers.

Fig. 4 shows differential scanning calorimetry (DSC) thermograms of PAN/EC/PC: Hex_4N^+I/LiI electrolyte samples containing different LiI and Hex_4N^+I compositions taken during the 2nd heating run. Significant dissimilarities were not observed between the 1st and 2nd heating runs, however, data obtained from the 2nd heating run were selected in order to make the thermal history identical for all samples. In general, in this kind of gel polymer electrolytes the liquid components EC and PC are trapped in cages formed by the polymer host [6,25]. Fig. 4 includes the DSC traces of the raw materials used. The melting peaks due to the raw materials are, however, more or less absent for the electrolyte complex and only small effects of recrystallization and melting are shown for some of the samples. These effects are anyway occurring at temperatures below the normal operating range of the electrolyte and for all measurements of electrical properties and solar cell performance the electrolyte is in gel state. A clear glass transition around −100 °C was observed for all samples. The glass transition temperatures, T_g, (mid-point) obtained using the 2nd heating cycle are given in Fig. 5. These measured T_g values were used to fit conductivity data to the VTF equation (1) as mentioned above. A glass transition around −100 °C has been reported earlier in literature for PAN/EC/PC electrolytes for other comparable systems [11]. The T_g increases with added amount of LiI for all samples but for sample "b". This decrease in T_g against the increasing trend observed for sample "b" might be attributed to the disorder imposed to the single salt system by incorporating a small amount of LiI. The general increasing trend of T_g shown can be

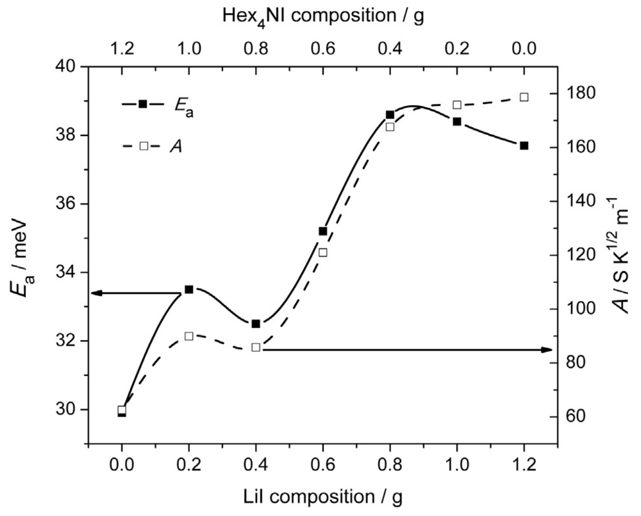

Fig. 3 – Variation of activation energy, E_a, and pre-exponential factor, A, with LiI and Hex_4NI composition in PAN/EC/PC; $Hex_4N^+I^-$/LiI electrolyte.

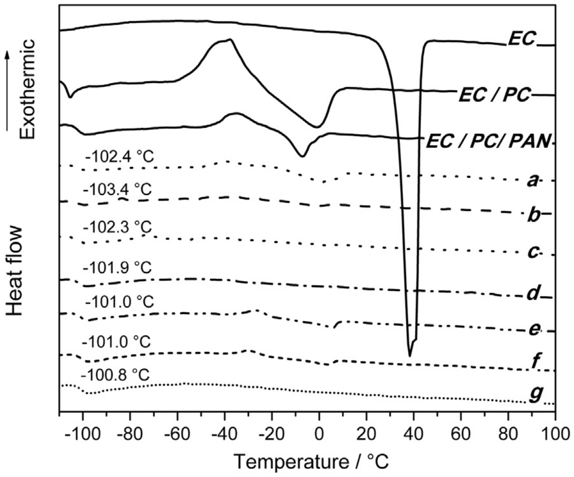

Fig. 4 – DSC thermograms of PAN/EC/PC electrolytes containing different weights of $Hex_4N^+I^-$ and LiI with respect to PAN under heating rate of 10 °C min^{-1}. The compositions of samples a,b,…,g are given in Table 1. DSC traces of raw materials also shown.

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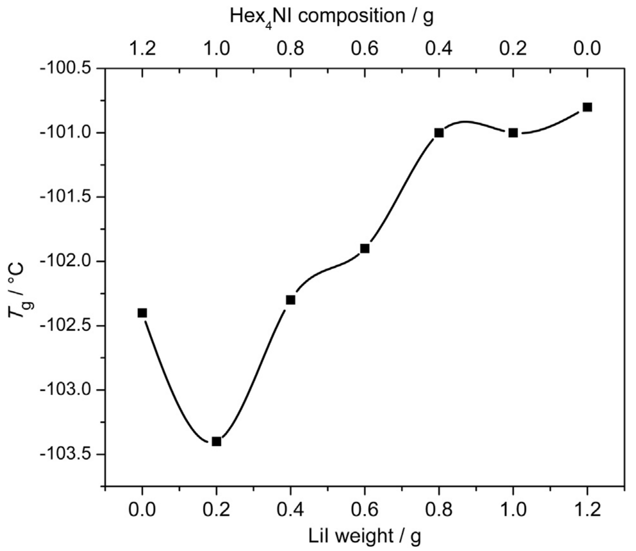

Fig. 5 – Variation of glass transition temperature, T_g, with LiI and $\text{Hex}_4\text{N}^+\text{I}^-$ composition in PAN/EC/PC/$\text{Hex}_4\text{N}^+\text{I}^-$/LiI electrolyte.

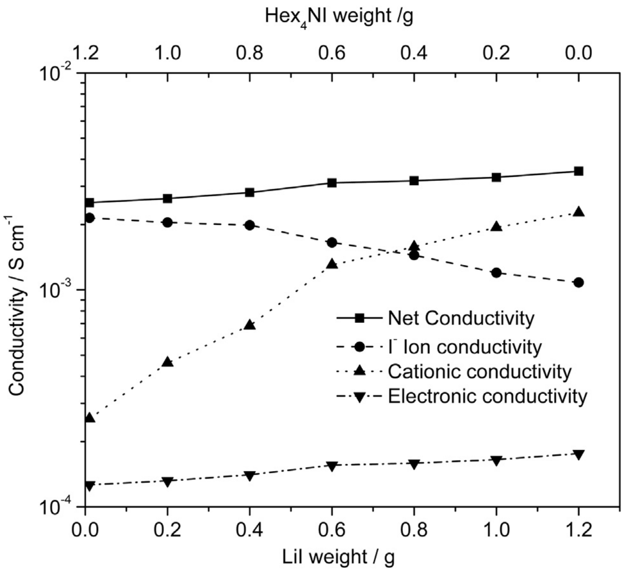

Fig. 6 – Conductivity contributions from different species to total conductivity as a function LiI salt mass fraction with respect to PAN in PAN/EC/PC:$\text{Hex}_4\text{N}^+\text{I}^-$:LiI electrolyte at 30 °C.

attributed to the cross-linking of long polymer chains by Li^+ ions and geometrical constrictions imposed by non-dissociated LiI to the polymer. It is clear that the flexibility of the polymer electrolyte has been more or less reduced by increasing the LiI concentration. The increase of E_a with increasing amount of LiI could possibly be due to increased local viscosity in the polymer gel medium caused by cross linking of the polymer and the presence of ionic complexes and undissolved solutes etc at higher LiI concentrations. This behavior is evident by the T_g increase with added LiI which would reduce ionic mobility. However, the contribution to the conductivity due to the increase of mobile Li^+ ion and I^- ion concentrations with added LiI, as shown by an increase in A, appears to be much greater than the contribution due to the reduced mobility. Thus the general trend is conductivity an increase with increasing amount of LiI.

The conductivity contributions were estimated using DC Polarization measurements performed using 1.0 V bias voltage and at 30 °C, the results are shown in Fig. 6. When stainless steel (SS) electrodes were used in SS/Electrolyte/SS blocking electrode configuration, an abrupt current drop is observed within the first 10 min, subsequently the current reached to a more or less stable value after about 60 min. Hence, these electrolytes exhibited a predominantly ionic nature (about 95%). The estimated electronic contribution to the conductivity is also shown in Fig. 6. Polarization measurements in the SS/I_2/Electrolyte/I_2/SS symmetrical, non-blocking configuration were used to estimate I^- ion and cation contributions to the conductivity. With the increase of LiI a current drop (or drop of plateau value) could be observed in polarization curves. This is possibly owing to a gradual decrease of I^- ion conductivity and an increase of that of cations as shown in Fig. 6. This small decrease in I^- ion conductivity can be attributed to effects from the reduction of segmental flexibility of polymer chains owing to the increase of complexion points with added LiI and this behavior is confirmed by the gradual increase of T_g with increasing amount of LiI. Since Hex_4N^+ is essentially immobile [26], the results ensures a Li^+ conductivity enhancement with increasing amount of LiI as expected in this system.

The variation of the real part of the dielectric constant (high frequency plateau value) obtained using complex impedance data are shown in Fig. 7 for different PAN/EC/PC:$\text{Hex}_4\text{N}^+\text{I}$/LiI electrolyte compositions at 30 °C. The real part of the dielectric constant is calculated using;

$$\varepsilon_r' = \frac{-Z''}{\omega C_o(Z'^2 + Z''^2)} \tag{2}$$

where Z', Z'', ω, C_o are the real part of complex impedance, imaginary part of complex impedance, angular frequency of

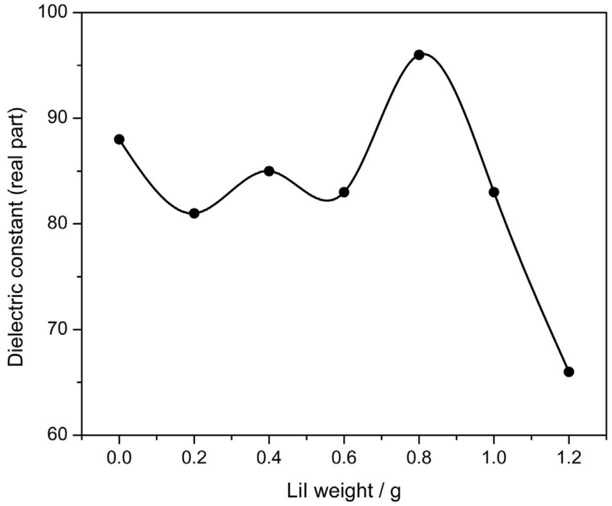

Fig. 7 – Variation of real part of dielectric constant, ε'_r, with LiI composition in the PAN/EC/PC/$\text{Hex}_4\text{N}^+\text{I}^-$/LiI electrolyte.

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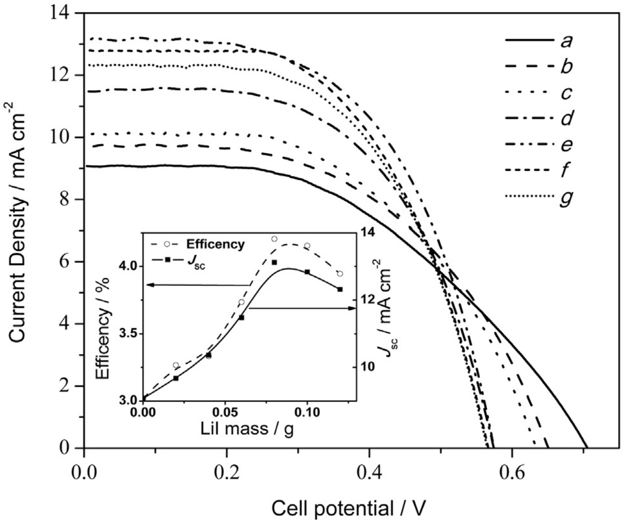

Fig. 8 – Photocurrent density versus cell potential for seven different DSSCs fabricated using PAN/EC/PC:LiI/$Hex_4N^+I^-$ electrolyte containing a total of 1.20 g salt under irradiation of 1000 W m^{-2} (1.5 AM). The DSSCs are labeled using the same labeling used for electrolyte samples given in Table 1. The inset shows the variation of the efficiency and J_{sc} with LiI mass fraction in the electrolyte.

the signal and geometric capacitance of the cell respectively. The highest value for the real part of the dielectric constant is shown by the electrolyte sample "*e*" though the highest conductivity is shown by sample "*g*". Therefore polarization effects should be high for sample "*e*". The double-layer capacitance of an electrolyte sandwiched between blocking electrode can be estimated by;

$$C_e = \varepsilon_r \varepsilon_\circ \frac{A}{d} \tag{3}$$

where, ε_r ε_o A and *d* are dielectric constant, vacuum permittivity, cross section area and Debye length respectively. A high double layer capacitance is actually favorable for the solar cell performance since it prevents internal short circuits or recombination of electrons.

I–V characteristic curves for DSSCs fabricated using PAN/EC/PC:Hex_4N^+I/LiI quasi-solid-state electrolytes with different Hex_4N^+I/LiI salt mass ratios are shown in Fig. 8; the figure also shows the efficiency and short-circuit-current density variation with LiI composition. Seven different cells were fabricated using the seven different electrolyte compositions shown in Table 1. The short-circuit photocurrent density (J_{SC}) and open-circuit voltage (V_{OC}) under the irradiation of 1000 W m^{-2} (1.5 AM) of each of the cells are shown in Table 2. The fill factor, *ff*, and the power conversion efficiency, η, were calculated using;

$$ff = \frac{J_{opt}V_{opt}}{J_{SC}V_{OC}} \tag{4}$$

$$\eta = \frac{J_{SC}\ V_{OC}\ ff}{\text{Total incident power density}} \tag{5}$$

where, J_{opt} and V_{opt} are the current density and voltage at maximum power output. The fill factor and the energy conversion efficiency, η, of the seven cells are also shown in Table 2.

All quasi-solid state DSSCs studied in this work exhibited energy conversion efficiencies of more than 3%. Since the conductivity of the electrolyte increases with increasing amount of LiI one can expect a performance enhancement, especially for J_{SC}, of the DSSC with added LiI. On the other hand there are positive effects on solar cell performance by incorporated small cations such as Mg^{++} or Li^+, due to an enhancement of the electron injection yields from dye to TiO_2 film, electron diffusion through the TiO_2 layer, dye regeneration and effects imposed to the semiconductor band positions with increasing amount of LiI.

The presence of lager cations have some positive effect on the performance of DSSCs, for instance Y. Shi et al. [27] have shown using liquid electrolytes that J_{SC} of a DSSC increases with increasing cation charge density, due to enhanced electron injection rates. On the other hand, the V_{OC} and *ff* of the DSSCs increased in the order $Li^+ < Na^+ < K^+ < DMI^+$ (dimethylimidazolium) when the charge density decreased. They have shown that the increase of the V_{OC} mainly correlates with the upward shift of the conduction band edge induced by the adsorption of low-charge-density cations on the surface of titania nanocrystals. Therefore, the V_{OC} increase shown in the present study for quasi solid-state DSSCs with Hex_4N^+ content, having very low charge density compared to Li^+ (sample "*a*" and "*g*"), is in agreement with the studies by Y. Shi et al. using liquid electrolytes [27].

However, since the quasi-solid state electrolyte system was prepared by mixing two iodide salts with cations having large and small charge density, this system has two competing effects. The presence of the LiI would tend to improve the J_{SC} whereas Hex_4NI would tend to improve

Table 2 – The performance of DSSCs prepared using electrolytes containing different LiI and Hex_4N^+I compositions given in Table 1.

Electrolyte	J_{sc}/mA cm^{-2}	V_{oc}/mV	J_{opt}/mA cm^{-2}	V_{opt}/mV	*ff*/%	Efficiency/%
a	9.08	704	7.12	424	47.2	3.0
b	9.76	650	7.60	430	51.5	3.3
c	10.11	634	8.01	416	52.0	3.3
d	11.48	574	9.39	398	56.7	3.7
e	13.12	574	10.54	404	56.3	4.2
f	12.84	566	10.60	386	57.2	4.1
g	12.32	566	10.17	388	56.8	3.9

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the V_{OC} [27]. Owing to the combined effect of these two mechanisms the best energy conversion efficiency is shown by the cell containing electrolyte sample "*e*". Even though electrolyte "*g*" shows the best total conductivity, the efficiency of the cell with electrolyte sample "*g*" is lower than that of the cell with electrolyte sample "*e*" indicating the influence of the cation in the electrolyte to the DSSC performance in addition to the iodide ion conductivity.

For quasi-solid-state DSSCs that use Ru based dye complexes, a high iodide ion conductivity in the electrolyte is important for the cell performance. This is because the iodide ion conductivity is expected to make the dominant contribution to the short circuit photocurrent density, J_{sc}. However, apart from the iodide ion conductivity there are other factors that influence the efficiency of the DSSCs. Especially the cations in the electrolyte can have profound influence on the performance of the DSSCs. The V_{OC} increases with the increase of cation size whereas electron injection and charge separation in the photo-electrode have a positive influence, which enhances the J_{SC}, when the size of the cation decreases.

As shown in Fig. 8, the photocurrent density, J_{sc} initially increases up to the maximum of 13.1 mA cm^{-2} (sample "*e*"). This increase can result from the increased molar iodide ion concentration [I^-] due to an increased LiI content. At low LiI concentrations, one expects a high ionic dissociation and all the LiI molecules are expected to dissociate in to Li^+ and I^- ions. However, after reaching the maximum J_{sc} and maximum efficiency (sample "*e*"), the efficiency as well as the J_{sc} start to decline, even though the molar iodide ion concentration keeps on increasing with added LiI content. Also, the total ionic conductivity keeps on increasing throughout the studied concentration range.

The drop in J_{sc} beyond this maximum can be attributed to several mechanisms. The decrease of double layer capacitance between electrolyte and photo-electrode can also be a cause to drop J_{sc} as discussed above.

This work shows that an electrolyte system containing mixed cations gives better solar cell performance, compared to a single cation system due to the beneficial effects from both types of cations.

4. Conclusions

In the PAN/EC/PC:Hex_4N^+I:LiI quasi solid-state polymer electrolyte system, the composition with 1.20 g of LiI (and no Hex_4NI, sample "g") showed the maximum conductivity out of all the compositions. This electrolyte showed conductivity values of 1.51×10^{-3}, 3.15×10^{-3} and 5.41×10^{-3} S cm^{-1} at 0, 25 and 50 °C respectively and a T_g value of −100.83 °C.

The electrolyte with the highest conductivity (sample "*g*"), however, did not show the best energy conversion efficiency when applied in a DSSC. The V_{OC} increases with increasing amounts of iodides with larger cations (Hex_4N^+I). The solar cell efficiency variation with LiI content correlates with the J_{sc} variation and both shows maxima for electrolyte sample "*e*". This cell has an energy conversion efficiency of 4.2% and a short circuit current density of 13.1 mA cm^{-2}. The results conclude that electrolyte with Hex_4N^+I/LiI mixed iodide system (containing small and large cations) shows better DSSC performance than single iodide systems.

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