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## Effect of alkaline cation size on the conductivity in gel polymer electrolytes and their influence on photo electrochemical solar cells

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#### Abstract

The nature and concentration of cationic species in the electrolyte exert a profound influence on the efficiency of nanocrystalline dye-sensitized solar cells (DSSCs). A series of DSSCs based on gel electrolytes containing five alkali iodide salts (LiI, NaI, KI, RbI and CsI) and polyacrylonitrile with plasticizers were fabricated and studied, in order to investigate the dependence of solar cell performance on the cation size. The ionic conductivity of electrolytes with relatively large cations,  $K^+$ ,  $Rb^+$  and  $Cs^+$ , was higher and essentially constant, while for the electrolytes containing the two smaller cations,  $Na^+$  and  $Li^+$ , the conductivity values were lower. The temperature dependence of conductivity in this series appears to follow the Vogel-Tamman-Fulcher equation. The sample containing the smallest cation shows the lowest conductivity and the highest activation energy of ~36.5 meV, while K<sup>+</sup>, Rb<sup>+</sup> and Cs<sup>+</sup>

DSSCs based on the gel electrolyte and a TiO<sub>2</sub> double layer with N719 dye exhibited an enhancement in open circuit voltage with increasing cation size. This can be attributed to the decrease in recombination rate of electrons and to the conduction band shift resulting from cation adsorption by TiO<sub>2</sub>. The maximum efficiency value, 3.48%, was obtained for the CsI containing cell. The efficiencies shown in this study are lower compared to values reported in the literature, and this can be attributed to the use of a single salt and the absence of other additives, since the focus of the present study was to analyze the cation effect. The highest short circuit current density of 9.43 mA cm<sup>-2</sup> was shown by the RbI containing cell. The enhancement of the solar cell performance with increasing size of the cation is discussed in terms of the effect of the cations on the TiO<sub>2</sub> anode and ion transport in the electrolyte. In liquid electrolyte based DSSCs, the short circuit current density has been reported to decrease with increasing size of the cation. However, in this work, it follows an opposite trend highlighting a major difference between liquid and quasi-solid electrolytes on the solar cell performance.

**Keywords:** Photo-electrochemical solar cell, alkaline cation, polymer electrolyte, quasi-solid-electrolyte, PAN, dye-sensitized solar cell

#### **1.0 Introduction**

Dye-sensitized solar cells (DSSCs) have attracted a significant interest after the groundbreaking report by O'Regan and Grätzel in 1991 [1] and soon after that the energy conversion efficiency of such cells were improved to ~12%. Subsequently, it has been further improved up to 14.3% [2]. DSSCs have attracted worldwide attention mainly due to the low production cost and the simple and environmentally friendly cell preparation methods compared to those of conventional silicon-based solar cells

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[3,4,5]. In general, the DSSC is composed of a nano-crystaline TiO<sub>2</sub> working electrode sensitized with a dye, a platinum counter electrode and an electrolyte comprising a redox couple with compatible redox potentials to the Fermi level of the photo-electrode. So far, the redox couples  $\Gamma/I_3^-$  and  $Co^{2+}/Co^{3+}$  complexes have mostly been used in order to obtain good solar cell performances [3,4,5,6].

Using a volatile liquid electrolyte for DSSCs ensures high solar cell efficiency but causes some major disadvantages such as risk for leakage, evaporation of solvents, instability, flammability at high temperatures and dye degradation especially in outdoor applications [7,8,9]. In order to overcome these drawbacks various alternatives have been investigated. For example, quasi-solid-state or gel electrolytes using a variety of host polymers, solvents and salts have been used successfully in DSSCs [7,8,9,10]. Although the gel-polymer electrolytes have exhibited many advantages including non-flammability, negligible vapor pressure and simple cell construction, the energy conversion efficiencies of DSSCs based on these electrolytes are limited basically due to charge transport limitations in the bulk of the electrolyte as well as at the electrode/electrolyte interfaces. Several efforts have been made so far to increase the conductivity in these polymer based quasi-solid electrolytes. Popular methods are to use a few different plasticizers together and/or inorganic fillers like titania, silica, or alumina [11,12,13]. The nature and the concentration of ionic species also have a profound influence on the conductivity in these polymer electrolytes [14].

Many iodide salts have been used in electrolytes intended for DSSCs and in most of the studies LiI, NaI, KI, tetrapropylammonium iodide and imidazolium iodide based ionic liquids have been widely tested. The anion transport is obviously of vital importance for the DSSC performance, but the cation also has an important role in the electron transfer dynamics in DSSCs [15,16].

Some reports can be found in the literature that investigated the best candidate salt for electrolytes by changing the cation. Yushuai Shi *et al.* [17] investigated the dependence of the photovoltaic performance of DSSCs for cations with different charge densities, such as lithium, sodium, potassium, and dimethylimidazolium ions in a liquid electrolyte system. They observed an improvement in the cell photovoltage with the decrease of charge density of the cations, and the results are basically correlated to a negative shift of the titania conduction band edge. However, in DSSCs solid and gel polymer electrolytes appear to behave different to liquid electrolytes. It is well known that the conductivity in electrolytes largely depends on ionic strength. Furthermore, in a quasi-solid (gel) polymer electrolyte, the size, shape and charge density of ions have independent and profound influences on both the conductivity and the ionic strength.

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Shen *et al.* [18] have studied the effect of alkali-metal cations in polyethylene oxide (PEO) based gel electrolytes in quasi-solid state DSCCs using acetonitrile as a solvent. The results showed that the open circuit voltage ( $V_{oc}$ ) increased with increased radius of the alkali metal cation, and it has been correlated to the shift of electron Fermi level ( $E_F$ ) of TiO<sub>2</sub> which in turn is caused by a decrease in the I<sub>3</sub><sup>-</sup> concentration. However, they could not observe a clear trend for the short circuit current density variation, which in general correlates with the ion conduction in the electrolyte and in particular with the iodide ion conduction. In a previous work reported by us, aimed at investigating the best salt candidate out of a series of quaternary ammonium iodide salts in polyacrylonitrile (PAN) based quasi-solid state

electrolytes intended for DSSCs, it was found that the best efficiency was shown by tetrapropylammonium iodide with cationic radius of 0.46 nm [19].

At present, DSSCs and perovskite solar cells (PSCs) are playing the leading role in the field of third-generation photovoltaic technologies according to the recent advancement of the field [20]. Especially, the success of DSSCs has been attributed to the introduction of polymer electrolytes [20,21]. In addition, novel ways to improve gel polymer electrolytes for are reported in literature. For instance, DSSCs with water based gel polymers have recorded higher stability and efficiency of about 2.3% [22]. Light-designed polymer electrolytes based DSSCs have showed an energy conversion efficiency of about 0.679% [23].

The present work is focused on finding the best alkaline iodide to be used in PAN based quasi-solid state dye sensitized solar cells without using any volatile solvents as plasticizers, and on investigating the cation effect on electrolyte conductivity and on the performance of DSSCs. In this work, electrolytes based on single salts were investigated without using additives such as 4-tert-butylpyridine, etc., since the focus of the study is to investigate cation effects, and hence, as expected, the efficiencies are not as high as that of the reported best quasi-solid state DSSCs containing various additives and binary iodide salts etc

#### 2.0 Experimental

#### 2.1 Materials

Alkaline metal iodides MI (M = Li, Na, K, Rb, Cs) as salts, polyacrylonitrile (Mw = 150,000), iodine (I<sub>2</sub>), ethylene carbonate (EC) and propylene carbonate (PC), all purchased from Aldrich and with purity greater than 98%, were used as starting

materials. Prior to use, PAN was vacuum dried for 24 h at 50 °C in a vacuum oven. The other materials were used as received. Conducting glass containing fluorine doped tin oxide (FTO) with a sheet resistance of 7  $\Omega$  cm<sup>-2</sup> and sensitizing dye ruthenium 535-bis TBA were purchased from Solaronix SA. TiO<sub>2</sub> of two different particles sizes, P25 and P90, were purchased from Degussa.

#### 2.2 Electrolyte sample preparation

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For the gel electrolyte preparation the method described in our previous work is used [19]. Five different gel electrolyte samples were prepared according to the stoichiometric formula  $(PAN)_{10}(EC)_{25}(PC)_{20}(MI)_{1.2}(I_2)_{0.12}$  in order to get a good gel and to keep the molar concentration of the electrolyte constant. In this formula PAN represents one monomer of polyacrylonitrile. The compositions of the electrolytes are given in Table 1.

**Table 1.** The composition of electrolyte series  $(PAN)_{10}(EC)_{25}(PC)_{20}(MI)_{1.2}(I_2)_{0.12}$ .

Sample	Salt (MI)	PAN/g	EC/g	PC/g	Salt/mg	I <sub>2</sub> /mg
A	LiI	0.10	0.4151	0.3851	30.384	5.76
В	NaI	0.10	0.4151	0.3851	34.025	5.76
С	KI	0.10	0.4151	0.3851	37.682	5.76
D	RbI	0.10	0.4151	0.3851	48.208	5.76
Ε	CsI	0.10	0.4151	0.3851	58.977	5.76

2.3 Fabrication of DSSCs

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In order to prepare the TiO<sub>2</sub> photo-anode, two layers of TiO<sub>2</sub> were deposited on the conducting glass substrate. The first layer was spin-coated on the FTO substrate using a slurry containing TiO<sub>2</sub> P90 powder. The second layer was coated on the first layer with a slurry containing TiO<sub>2</sub> P25 powder using the doctor blade method. The photoelectrode preparation is described in detail in a previously published work [24]. The dye adsorption to the TiO<sub>2</sub> coated glass plate was conducted by immersing the TiO<sub>2</sub> coated glass plates in a 0.5 mM ethanolic solution of ruthenium 535-bis TBA at about 60 °C and kept 24 h at room temperature. After taking out, the dye-adsorbed TiO<sub>2</sub> electrode was rinsed with acetone to remove the unbound TiO<sub>2</sub> particles and loosely bound dye prior to assembly of the cell.

The prepared gel electrolyte was casted onto the dye-sensitized  $TiO_2$  electrode and then a platinum (Pt) coated conducting glass plate (counter electrode) was pressed on top of the  $TiO_2$  electrode to form a DSSC with the configuration glass/FTO/dye/TiO<sub>2</sub>/electrolyte/Pt/FTO/glass. At least three cells for each electrolyte were fabricated and tested and the stable result was considered for discussion.

#### 2.4 Measurements

The complex impedance measurements were performed using a HP 4192A RF impedance analyzer in the 10 Hz – 10 MHz frequency range to evaluate the ionic conductivity of the samples. The sample cell was prepared by sandwiching the electrolyte by two stainless steel electrodes. The temperature of the sample varied from 60 to 0  $^{\circ}$ C during the measurements. The measurements were thus made on cooling runs. Differential scanning calorimetry (DSC) thermograms were obtained using a Mettler Toledo DSC 30 differential scanning calorimeter. Each sample was scanned between -140 and 100  $^{\circ}$ C at a rate of 10  $^{\circ}$ C min<sup>-1</sup>. The glass transition

temperatures ( $T_g$ ) were extracted using the 2<sup>nd</sup> heating cycle. The attenuated reflectance infrared spectra were recorded for gel electrolyte sample, and raw material at room temperature on a computer interfaced Platinum-ATR spectrometer from Bruker in the range of 4000-400 cm<sup>-1</sup> with resolution of 1 cm<sup>-1</sup>. Fabricated solar cells were illuminated by a LOT-Oriel GmbH solar simulator 1.5 AM, 1000 W m<sup>-2</sup> (one sun) in order to obtain *I-V* characteristics using a computer controlled eDAQ Potentiostat and e-coder. The area of the cell exposed to light was 11 mm<sup>2</sup> and the scan rate was 100 mV s<sup>-1</sup>.

#### **3.0 RESULTS AND DISCUSSION**

#### 3.1 Electrolyte Characterization

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The ionic conductivity of the series of electrolytes was calculated using the highfrequency intercept with the real axis of Nyquist plots. Within the measured frequency range the linear parts of the curves were visible while the semicircular parts were not visible. The ionic conductivity isotherms for all the electrolyte samples are shown in Fig. 1. The conductivity for electrolytes with larger cations ( $K^+$ ,  $Rb^+$ ,  $Cs^+$ ) is higher and more or less equal, while that for electrolytes containing Na<sup>+</sup> and especially Li<sup>+</sup> is lower. This behavior was same at all measured temperatures ranging from 0 to 60 °C. The samples containing larger cations K<sup>+</sup>, Rb<sup>+</sup> and Cs<sup>+</sup> gave conductivities, around 2.6 and 4.3 mS cm<sup>-1</sup> at 20 and 50 °C, respectively. The ionic conductivity in these electrolytes is due to both cations as well as iodide anions. We shall discuss the implications of the variation of the cation size or, in a Coulombic model, the cation charge density on the ionic conductivity. It has to be noted that salt dissociation, polymer crosslinking, mobility of ions, ion coordination and shielding by polymer chains all are linked to cation size and charge density.



**Fig. 1.** Ionic conductivity variation with the alkaline iodide salt (MI = LiI, NaI, KI, RbI and CsI) in  $(PAN)_{10}(EC)_{25}(PC)_{20}(MI)_{1.2}(I_2)_{0.12}$  electrolyte samples at different temperatures.

Spherical symmetry is the common electronic feature of the alkaline ion series since the electronic structure is basically that of a rare gas, so modeling the ion as a single positive charge in a coulombic field or as a positive charge density is a reasonable simplification in this study. The small (0.76 Å)  $\text{Li}^+$  ion can strongly coordinate with the CN groups of the polymer chains via intra- and inter-chain bonds stiffening and crosslinking the polymer and restricting in this way the flexibility. The effect of the coordination will be a reduction of the concentration of free  $\text{Li}^+$  ions as well as a decrease of the mobility of the free ions due to the stiffening of the polymer matrix. Anions might conversely be more free to move because the ionic bond is weakened by the "solvation" of the cation by the heteroatoms in the polymer and plasticizers. The anion will be more loosely bound to the  $\text{Li}^+$  cation, a lithium cation that is now stuck so the mechanism of the conduction will, instead of a collective movement of the anion accompanied by the movement of the cation, rather be a mechanism where the anion will have to move from a stuck cation to the next, and this in a system which has been stiffened by the intra- and inter-chain crosslinks. In this vision what determines the intensity of the interactions is the charge density of the cation or in other words its Lewis acid property. Consequently, the conductivity of the NaI containing sample is larger than that of the LiI containing sample as shown in Fig. 1. Na<sup>+</sup> ions are not such a strong crosslinker as Li<sup>+</sup> due the comparatively lower charge density of the former. The Lewis acid base interaction between the alkaline ion and the CN groups are weaker for Na<sup>+</sup> compared to that of Li<sup>+</sup>. Thus iodide ions in Na<sup>+</sup> containing samples can also attain greater mobility than those in Li<sup>+</sup> containing samples when considered the polymer flexibility and the local viscosity. Since there are so many effects imposed by the nature of cations for the conductivity in solid or gel polymer electrolytes and some of the major effects are summarized in Table 2 with respect to cation radius [25].

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**Table 2.** Some of the parameters that influence the ionic conductivity in gel/solid polymer electrolyte containing alkaline metal diodes.

Alkaline ion	Li <sup>+</sup>	Na <sup>+</sup>	$\mathbf{K}^{+}$	$\mathbf{Rb}^+$	Cs <sup>+</sup>	Expected influences from left to right
<ol> <li>Radius /pm (6 coordination) [25]</li> </ol>	76 $102$ $138$ $152$ $167$ Increases from Li <sup>+</sup> to Cs <sup>+</sup>			152 i <sup>+</sup> to C	167 2s <sup>+</sup>	Increasing cation size increases ionic dissociation, increases the separation of the polymer chains and decreases the viscosity.
2. Charge density	Decreases from Li <sup>+</sup> to Cs <sup>+</sup>		$Cs^+$	Weakening coordination bond strength, activation energy decreases. Salt dissociation decreases (but can compensated by an increasing coordination number, see point 4).		

3.	Acidity (as a Lewis acid)	Decreases from Li <sup>+</sup> to Cs <sup>+</sup>	Weaker interactions with electronegative/donor sites in the electrolyte.		
4.	Coordination Number	Increases more or less from $Li^+$ to $Cs^+$	Salt solvation improves		
5.	Polymer flexibility	Increases from Li <sup>+</sup> to Cs <sup>+</sup>	Improves the ion conduction		
6.	Local viscous force (of cation moving in the media)	Increases from Li <sup>+</sup> to Cs <sup>+</sup>	Reduces the cation conduction		
7.	Viscosity change in the electrolyte	Decreases from Li <sup>+</sup> to Cs <sup>+</sup>	Anion conductivity improves		
8.	Ionic dissociation of salts	Increases from Li <sup>+</sup> to Cs <sup>+</sup>	Enhance the carrier density and conductivity		
9.	Free volume and voids in the electrolyte	Increases from Li <sup>+</sup> to Cs <sup>+</sup>	Improves the ion conduction		

The following effects can enhance the cation conductivity when the size of the alkaline cations in the series increases:

- The increasing cation size makes the polymer chains spaced apart resulting in an increase of polymer flexibility and size of voids, as illustrated in the schematic diagram in Fig. 2. This reduces viscosity and helps to improve the segmental motion and the transport of ions.
- Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup> are hard Lewis acids and their strength decreases with decreasing charge density. Thus the Lewis acid-base interactions with the electronegative sites in the electrolyte become weaker with decreasing charge density, thus improving the cation mobility.

- 3. The coordination number is increasing with the increase of cation size, resulting in a decrease in hindrances to the cation movement especially if the coordination is to a template compound like PAN.
- A lower charge density can reduce the local viscosity of the electrolyte due to swelling effect or conversely shrinkage of the polymer with increasing charge density of cations, as shown in Fig. 2.
- 5. The increase in the local viscous force acting on the moving cation with increasing size of the cation can generate a drop of the conductivity since the viscus force is proportional to the radius of the traveling particles according to Stokes' law. Conversely the bulk viscosity in the electrolyte medium has the opposite trend as mentioned above.
- 6. For the sequence Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>, the size of the ions increases resulting in a drop of the mobility of the ions, thus increasing the activation energy.

When the size of the cation in this alkaline series is increased, the following effects can influence the anion (iodide ion) conductivity:

- 1. Flexibility of host polymer chains (increases) and bulk viscosity (decreases).
- 2. Local viscosity (increases)

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- 3. Size of voids (increases)
- Binding energy of cations and anions decreases which increases the salt dissociation.

The Li<sup>+</sup> ion, having the highest charge density in the series, can be cross-shielded by the polymer chains, owing to much tighter and close bonds between electro-negative sites in the polymer chain and the resulted shrinkage of the polymer chain network.

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The interactions of the (alkaline cation) – CN groups in the polymer can be classified as coordination due to Lewis acid base interactions and the strength of this interaction depends on the charge density of ions. In this kind of electrolytes the cation motion is attributed to making and breaking of coordinate bonds thus resulting in transport between coordinating sites while the anion (iodide ion) motion is assisted by a flexible and weak interacting surrounding [26,27,28]

Thus the net ionic conductivity variation depicted in Fig. 1 is due to the combined consequences of above mentioned, sometimes competing effects for cations and anions. As shown in Fig. 1 the net ionic conductivity in the electrolyte series increases with increasing cation size and the iodide ion conductivity should also have a similar trend since some of the effects imposed by increasing size of the cation is favorable also for iodide ion conductivity, as mentioned above.



**Fig. 2.** Schematic illustration in 2 dimensions to show the increase of polymer chain flexibility due to swelling effect of the electrolyte with increasing size of the cation. The size of variation of cations are relative to their actual sizes while the other atoms are not drawn to the actual scale.



**Fig. 3.**  $\sigma T^{1/2}$  plotted against 1000/(*T*-*T*<sub>g</sub>) for different alkaline iodide (MI) in quasisolid state (PAN)<sub>10</sub>(EC)<sub>25</sub>(PC)<sub>20</sub>(MI)<sub>1.2</sub>(I<sub>2</sub>)<sub>0.12</sub> electrolyte. The symbols are experimental data and each solid line is fitted to the VTF equation.

The conductivity of all samples appears to follow the Vogel-Tammann-Fulcher (VTF) [29,30] behavior with increasing temperature. Hence, the data were fitted to the VTF equation,

$$\sigma(T) = AT^{-\frac{1}{2}} \exp\left[\frac{-E_a}{k_B(T-T_0)}\right]$$
(1)

where  $E_a$  is a pseudo-activation energy, A is a pre-exponential factor and k is the Boltzmann constant. The pseudo-activation energy  $E_a$  is in general related to polymer segmental motion, which is linked with the mobility of charge carriers.  $T_0$  is a reference temperature, the ideal glass transition temperature, usually associated with the temperature at which the free volume disappears. In this study the glass transition

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temperature ( $T_g$ ) obtained using DSC measurements was used as  $T_o$  The calculated  $E_a$ and pre-exponential factors are shown in Fig. 4. The high  $E_a$  value of about 36.5 meV is exhibited by the LiI containing sample as expected due to stiffening of the polymer via stronger crosslinks restricting the lithium and iodide ion motion in the electrolyte. Clearly high conducting samples (KI, RbI, CsI containing samples) shows lower activation energy,  $E_a$  values, favoring better ion conduction [29] with increasing size of the cation (or decreasing charge density) for these gel polymer electrolytes. Interestingly the three highest conducting samples have shown almost similar activation energies. However, the slight increase of the  $E_a$  values with cation size shown in Fig. 4 for samples containing K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup> can be due to hindrances to ion conduction due to the action of the local viscous force with increasing size as mentioned above.

The pre-exponential factor *A* is a constant that is proportional to the number of charge carrier ions [29] and thus the values obtained in this study and shown in Fig. 4 are in agreement with the conductivity variation shown in Fig. 1, since the conductivity is mainly governed by the charge carrier density. The highly conducting samples, namely the KI, RbI, and CsI containing samples, have larger density of charge carriers and lower activation energies because these large cations are not sequestered by the coordination like for LiI.



Fig. 4. Activation energy,  $E_a$ , and pre-exponatial factor, A, values as a function of cation in the salt.

Fourier transform infrared spectroscopy (FTIR) is a powerful technique for identifying the nature of bonding and different functional groups in a sample by observing the vibrational energies of molecules, which are essentially the fingerprint of different molecules [29, 31]. Fig. 5 shows the FTIR spectra of the  $(PAN)_{10}(EC)_{25}(PC)_{20}(MI)_{1.2}(I_2)_{0.12}$  electrolyte series and EC, PC,  $(EC)_{25}(PC)_{20}$  and  $(PAN)_{10}(EC)_{25}(PC)_{20}$  mixtures obtained in order to understand the interactions between functional groups and ionic species.

16



Fig. 5 The FTIR spectra of  $(PAN)_{10}(EC)_{25}(PC)_{20}(MI)_{1.2}(I_2)_{0.12}$  electrolyte series and EC, PC,  $(EC)_{25}(PC)_{20}$  and  $(PAN)_{10}(EC)_{25}(PC)_{20}$  mixtures.

The band attributed to the C=N stretching in the infrared spectrum appears at 2247 cm<sup>-1</sup> for pure PAN and it shifts to about 2243 cm<sup>-1</sup> when it interacts with solvent molecules [32]. In this study the observed peaks for the C=N stretching band are small and thus enlarged and shown in Fig. 6. The shift in vibrational frequency can be used to assess the interactions of the sample. Before adding any salt the C=N stretching band is shown at 2242.6 cm<sup>-1</sup> due to solvent effects as shown in Fig. 6. However, when salts were added, it shifts to 2243.5, 2242.8, 2242.9, 2243.6, 2243.8 cm<sup>-1</sup> for LiI, NaI, KI, RbI and CsI containing samples, respectively, owing to the interactions with alkaline cations. The peaks have shifted very slightly (essentially they are at ~2243 cm<sup>-1</sup>) due to the salt indicating very mild interaction.



Fig. Peaks 6. corresponding to C≡N stretching band for  $(PAN)_{10}(EC)_{25}(PC)_{20}(MI)_{1.2}(I_2)_{0.12}$ electrolyte series and  $(EC)_{25}(PC)_{20}$ and  $(PAN)_{10}(EC)_{25}(PC)_{20}$  mixtures (MI = LiI, NaI, KI, RbI and CsI).

Qing-Yun Wu et al. have shown antiparallel alignment of interacting pairs of PAN and solvent complexes between the C=N group of PAN and the polar group of solvents such as C=O by the optimized configurations of PAN–solvent complexes [32]. The authors have suggested that the dissolution of PAN in solvents includes the dissociation of the solvent–solvent complex and the inter/intra-molecular interaction of PAN chains. Our results show that EC has three carbonyl group stretching peaks as illustrated in Fig. 7 and given in Table 3 [33, 34]. The stretching mode of the carbonyl (C=O) group in PC is assigned to the characteristic frequency shown at 1786.5 cm<sup>-1</sup> and it moves to 1794.6 cm<sup>-1</sup> when EC is incorporated and to 1796.7 cm<sup>-1</sup> when PAN+EC is added. However, additions of salts haven't shifted this peak significantly and thus the peak remains at 1796.7 cm<sup>-1</sup> for salt added samples. Scrutinizing of these peaks through deconvolution will help the further investigation

of cation solvent interactions. However, the major focus of this paper is to study the

cation effects for DSSCs.

**Table 3**. Wavenumbers of carbonyl group stretching peaks of raw materials their mixtures and electrolyte samples.

Sample	Wavenumber	Wavenumber	Wavenumber	Wavenumber	Total peak
name	/cm <sup>-1</sup>	$/cm^{-1}$	$/cm^{-1}$	$/cm^{-1}$	area
	(C=O stretch	(C=O stretch	(C=O stretch	(C=O stretch	(relative to
	peak of PC)	peak 1of EC)	peak 2 of	peak 3 of	EC+PC
			EC)	EC)	peak)
PC	1786.5	-	-	-	-
EC		1737.5	1770.2	1790.6	-
EC+PC	1794.6	-	1774.3	1794.6	1.00
PAN+EC+P		-	1774.3		0.89
С	1796.7			1796.7	
Sample A	1796.7	-	1774.3	1796.7	0.82
Sample <i>B</i>	1796.7	-	1774.3	1796.7	0.87
Sample C	1796.7	-	1774.3	1796.7	0.87
Sample D	1796.7	-	1774.3	1796.7	0.87
Sample E	1796.7	-	1774.3	1794.6	0.89



Fig. 7. FTIR peaks corresponding to C=Ostretching band for  $(PAN)_{10}(EC)_{25}(PC)_{20}(MI)_{1.2}(I_2)_{0.12}$ electrolyte series and  $(EC)_{25}(PC)_{20}$ and (PAN)<sub>10</sub>(EC)<sub>25</sub>(PC)<sub>20</sub> mixtures.

The ratio of peak areas in the FTIR spectrum can be used as an indication of the degree of dissociation of solvent-solvent interaction and thus this is an indicator for the ion-solvent association. The normalized peak areas assigned for C=O stretching bands relative to the peak area of  $(EC)_{25}(PC)_{20}$  mixture, is given in Table 3. When PAN is incorporated to the EC and PC mixture the carbonyl stretching peak area is reduced to 0.89 and this can be due to dissociation of solvent-solvent interaction with added PAN. However, the lowest peak area, 0.82, is shown by LiI containing samples indicating stronger Li<sup>+</sup> ion attachment with the solvents in the electrolyte that exhibited the lowest conductivity. The highly conducting electrolyte sample have shown a larger peak area for carbonyl stretching indicating a lower degree of interaction with K<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup> ions. Out of the salt added samples the largest peak area, 0.89, is shown by the CsI containing sample indicating poor ion interaction with solvents of this highly conducting sample.

#### 3.2 DSSC Characterization

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The short circuit current density ( $J_{sc}$ ) and open circuit photovoltage ( $V_{oc}$ ) of the DSSCs are shown in the Fig. 8 as a function of the alkaline salt in the electrolyte. The observed 39% enhancement in  $V_{oc}$  (from 0.49 to 0.68 V) with increasing size of the cation can be attributed to the decrease of the recombination of electrons in the conduction band of TiO<sub>2</sub> with I<sub>3</sub><sup>-</sup> in the electrolyte at the vicinity of the TiO<sub>2</sub> electrode and to the specific shift of the conduction band resulted by cation adsorption or intercalation to TiO<sub>2</sub>.

In a study to find the influence of different cations (Li<sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup> and a tetrabutyl ammonium cation) using a liquid electrolyte based on acetonitrile/valeronitrile and 4TBP, Wang et al. found that the separation between the TiO<sub>2</sub> conduction band edge ( $E_c$ ) and the electrolyte redox level decreased when the charge/radius ratio of the cations increased [35]. Their results have shown that  $E_c$  in the Mg<sup>2+</sup> electrolyte was 77 and 178 meV lower than that in the Li<sup>+</sup> and Na<sup>+</sup> electrolyte, respectively. This indicates that the  $E_c$  of TiO<sub>2</sub> in the presence of Na<sup>+</sup> is 101 meV higher than that of Li<sup>+</sup>. This explains that the reported increase of the cell potential with decreasing of cation charge density is related to the shift of  $E_c$  of TiO<sub>2</sub> away from the redox potential of I<sub>3</sub><sup>-</sup>/ $\Gamma$  as implied in this study by sequential variation of  $V_{oc}$  with the cation charge density and a similar trend have been observed even for Li<sup>+</sup>, Na<sup>+</sup> and Mg<sup>2+</sup> based liquid electrolytes [35].



**Fig. 8.** Short circuit current density  $(J_{sc})$  and open circuit cell potential  $(V_{oc})$  of the cells as a function of salt in the electrolyte.

In addition, this trend in  $V_{oc}$  was confirmed by the observations made by Liu et al. [36] using a series of alkali-iodides with EC and PC solvent based liquid electrolytes. Their results are comparable to the present work (Fig. 8), but in the present work, a quasi-solid state electrolyte containing PAN, EC and PC has been employed. This variation in  $V_{oc}$  can be attributed to the shift of  $E_c$  of TiO<sub>2</sub> electrode due to the adsorption or intercalation of cations onto the TiO<sub>2</sub> electrode. The conduction band edge,  $E_c$ , of the porous TiO<sub>2</sub> film shifts to a more positive potential with decreasing cation radius, due to higher adsorption of small cations [36]. In addition, this increasing trend of cell potential with decreasing charge density has been reported for quasi-solid state cells by using a PEO based alkaline iodide series and a PAN based quaternary ammonium iodide based system [18,19]. Results in this work also confirms the trend of  $E_{\rm c}$  that shifts towards more negative potentials when cation size is increased. For better understanding, a schematic diagram is shown in Fig. 9 which illustrates the trend of possible shift of the conduction band edge  $(E_c)$  to more negative potentials, which is seen in this study by a shift of the Fermi level ( $E_F$ ). In this type of DSSCs the  $V_{oc}$  is resulting from the difference of the Fermi level ( $E_F$ ) in the semiconductor and the redox potential of the electrolyte. Therefore, the resulting shift of  $E_{\rm F}$  when the cell is irradiated (1000 W m<sup>-2</sup>) is shown in Fig. 9 with respect to NHE.

22



Fig. 9. A schematic diagram to illustrate the trend of shift of the conduction band edge (*E*c) to more negative potentials and the resulting shift of Fermi level ( $E_F$ ) when the cation size is increased. Potentials are shown relative to NHE and at 1000 Wcm<sup>-2</sup> irradiation.

However, a completely opposite trend of  $J_{sc}$  variation is shown in the present work (Fig. 8) where the gel electrolyte based DSSCs are compared with their liquid electrolyte based counterparts reported in literature [36]. This difference can be understood by studying the differences in charge transport in the two media. As shown in Fig. 8, the  $J_{sc}$  of the DSSC increases with cation size except for the CsI containing cell. In general, the  $J_{sc}$  of a DSSC can be tuned by the cation choice in the electrolyte through at least two mechanisms.

- 1. Variation of the ionic conductivity, in particular the triiodide conduction in the electrolyte. The increase of ionic conductivity contributes to enhance the photo-current of the DSSC contributing to a  $J_{sc}$  increase.
- 2. Variation of charge injection rates of from oxidized dye to  $TiO_2$  due to adsorbed cations. When the conduction band shifts to an even more negative potential as illustrated in Fig. 9, the driving force for the injection of electrons from the excited dye to the conduction band decreases, leading to a low injection efficiency [36, 37, 38]. This can consequently decrease the photocurrent with the increase of cation size.

In liquid electrolytes the variation of conductivity is small compared to that in gel polymer electrolytes when the molar concentration of salts is kept unchanged and the alkaline cation is varied. Thus the poor  $J_{sc}$  values shown by LiI and NaI containing samples in the present investigation can be attributed to the low ionic conductivity of the electrolytes as shown in Fig. 1. KI, RbI and CsI containing electrolytes have shown almost similar conductivities and the low  $J_{sc}$  value shown by CsI containing sample compared to that of KI and RbI can be due to the second mechanism discussed above, namely the variation of charge injection rates due to shift of conduction band as shown in Fig. 9.

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**Fig. 10.** The efficiency and fill factor (*FF*) of the cells as a function of salt in the electrolyte.

The energy conversion efficiency in DSSCs increases with the cation size and exhibits a maximum of 3.48% for the CsI containing sample while the LiI containing cell gives the lowest efficiency of 0.75%. Thus in this work a remarkable efficiency enhancement of 364% is recoded only due to the change of cation in the electrolyte. The efficiency enhancement is governed by the dominant increase of  $V_{oc}$ , *FF* and to some extent on the increase of  $J_{sc}$ . The highest  $J_{sc}$  of 9.43 mA cm<sup>-1</sup> and a corresponding efficiency of 3.46% is shown for the RbI containing sample while the CsI containing cell shows a  $J_{sc}$  of 8.34 mA cm<sup>-1</sup>. The cation dependence of the quasisolid state DSSC performance can be understood in terms of the shift in energy levels due to the co-ordination, the intercalation and the adsorption of the cations by the TiO<sub>2</sub> as well as by studying the charge transport in the electrolytes. The efficiencies reported in this study are somewhat lower compared to other quasi-solid state electrolyte based DSSCs due to the use of a single salt and to the absence of other additives such as 4-tert-butylpyridine, ionic liquids or mixed salts because the focus of this study is to analyze cation effect.

In summary, the major trend for the ionic the conductivity in electrolyte and all the DSSC parameters,  $J_{sc}$ ,  $V_{oc}$ , FF and power efficiency of this series of quasi-solid state DSSCs is that they increase with decreasing charge density of alkaline cations in the electrolytes. The only exception is a slightly lower  $J_{sc}$  for the CsI containing DSSC. These findings will help the future selection of iodide salts for quasi-solid state electrolytes for DSSCs.

#### 4.0 Conclusions

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The ionic conductivity variation with alkaline cation size for the series of PAN based gel polymer electrolytes is the result of several combined and competing effects and it is mainly attributed to the interactions among the ions and the electro-negative sites in the polymer and in the plasticizers. The LiI containing electrolyte showed the lowest conductivity and this can be attributed to stronger crosslinking and related to other effects which result in the stiffening of the polymer chains. Larger cations contribute to a conductivity enhancement and K<sup>+</sup>, Rb<sup>+</sup> and Cs<sup>+</sup> containing samples gave the highest conductivities, about 2.6 and 4.3 mS cm<sup>-1</sup> at 20 and 50 °C, respectively. The temperature dependence of conductivity in this series adheres to the VTF equation. In addition, FTIR spectra can be utilized to understand ion-solvent and ion-polymer interactions in relation to the ionic transport in this series of gel polymer electrolytes.

The efficiency and the fill factor of the DSSCs increase with the cation size and exhibit a maximum of 3.48% of efficiency and 61.6% *FF* for the CsI containing sample with this single salt electrolyte. The efficiency improvement of the DSSCs is

predominantly governed by the  $V_{\rm oc}$  change of about 39%. However, the highest  $J_{\rm sc}$  of

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Physical Chemistry Chemical Physics Accepted Manuscript

9.43 mA cm<sup>-1</sup> and the corresponding efficiency of 3.46% are shown by the RbI containing sample under 1000 W m<sup>-2</sup> irradiance. The ionic conductivity for the electrolyte and all the DSSC parameters,  $J_{sc}$ ,  $V_{oc}$ , *FF* and power efficiency of this series of quasi-solid state DSSCs generally increase with decreasing charge density of alkaline cations in the electrolytes. The only exception is a slightly lower  $J_{sc}$  given for the CsI containing DSSC. One of the important observation made in this work is the reported increasing trend of  $J_{sc}$  with cation size in contrast to the variation seen for liquid electrolyte based DSSCs, emphasizing the difference of charge transport mechanisms in quasi-solid state electrolytes and liquid

electrolytes.

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