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Effect of cation size on the performance of dye sensitized nanocrystalline TiO_2 solar cells based on quasi-solid state PAN electrolytes containing quaternary ammonium iodides

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ABSTRACT

The performance of dye sensitized nanocrystalline TiO_2 solar cells based on quasi-solid state PAN electrolytes containing a series of six quaternary ammonium iodide salts NH_4I, Eth_4NI, $Prop_4NI$, But_4NI, $Pent_4NI$, Hex_4NI with different cation sizes has been evaluated. Even though the total ionic conductivity decreases with increasing cation size from NH_4I to Hex_4NI, the iodide ion conductivity in the electrolytes increases with cation size. The open circuit photovoltage (V_{oc}) of the dye sensitized solar cells also increases with cation radius. The efficiency of the DSSCs varies with cation size and exhibits a maximum for $Prop_4NI$ salt. The short circuit photo current density (J_{sc}) follows a similar variation with cation size, suggesting a strong correlation between the cation size dependence of efficiency and J_{sc}. The DSSC fabricated with tetrapropylammonium iodide exhibited the maximum efficiency of 4.30% with maximum J_{sc} of 10.78 mA cm^{-2} and a V_{oc} of 0.746 V. The results have been interpreted on the basis of "the electrolyte effects" where J_{sc} is determined essentially by the iodide ion conductivity and "the electrode effects" where the J_{sc} and V_{oc} are determined by the cation adsorption in the dyed TiO_2 electrode and resulting electron dynamics at the semiconductor/electrolyte interface. For DSSCs with small cations, electrolyte effects appear to be dominating and rate determining while for DSSCs with larger cations, electrode effects appear to be dominating and rate determining.

1. Introduction

Dye sensitized, nanocrystalline TiO_2 solar cells are emerging as the next generation of solar cells due to several advantages over conventional silicon and other thin film photovoltaic solar cells. A typical dye sensitized solar cell (DSSC), first reported by O' Regan and Grätzel in 1991 [1] consists of a nanoporous dye-coated TiO_2 electrode, an electrolyte containing I^-/I_3^- redox couple, and a platinized counter electrode. An impressive power conversion efficiency of 11% has been achieved with DSSCs employing liquid electrolytes containing a I^-/I_3^- redox couple [2]. The liquid electrolytes used in these DSSCs consists of an organic solution such as acetonitrile or propylene carbonate and leads to many drawbacks such as electrolyte leakage, electrode corrosion and dye deterioration which limits the practical applications of these DSSCs. Current research efforts are therefore directed toward minimizing such drawbacks. One of the widely used techniques is to replace the volatile liquid electrolyte by a quasi-solid or gel electrolyte, in order to achieve sufficiently high power conversion efficiencies, and minimizing the problems associated with electrolyte leakage, sealing, electrode corrosion, etc [3–6].

A DSSC consists of several components such as the nanoporous semiconducting TiO_2 thin film electrode, a sensitizing dye, an electrolyte with a redox couple, and a counter electrode. In order to maximize the power conversion efficiency, each of these components needs to be optimized. Among these, electrolytes and redox couples play a major role in determining the solar cell performance in DSSCs. In DSSCs widely studied up to now, the electrolyte is an anion conductor and in majority of cases these are iodide ion (I^-) conductors. The contribution of the iodide ion conductivity to the overall ionic conductivity of the electrolyte in a DSSC is a major factor which determines the short circuit photocurrent density (J_{sc}) and hence the efficiency of a DSSC. This is because, the iodide ions

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(I^-, I_3^-), while participating in the I^-/I_3^- redox reaction, also shuttle between the photo-electrode and the counter electrode. During the solar cell action the I^- ions migrate from the Pt counter electrode to the dye sensitized TiO_2 photoanode while the tri-iodide ions (I_3^-) migrate from the TiO_2 electrode to the Pt counter electrode. Although iodide ion conductivity is an important parameter in determining the short circuit photocurrent and the efficiency of a DSSC, not much systematic research work has been reported on this aspect.

As stated earlier, quasi-solid or gel electrolytes are becoming increasingly popular as promising candidates to be used as the electrolyte medium in DSSCs. Among these, polyacrylonitrile (PAN) with chemical formula $(C_3H_3N)_n$ is a widely used polymer host for fabricating electrolytes for lithium batteries, dye sensitized solar cells, electrochromics and other electrochemical device materials. In PAN based gel electrolytes, whether they are cationic or anionic conductors, it is generally accepted that the electrolytic solution formed by dissolving the ionic salt in an ethylene carbonate/propylene carbonate (EC/PC) co-solvent is “entrapped” in cages formed by the host polymer matrix yielding almost liquid like ionic conductivities [7,8].

O’ Regan and Grätzel in their 1991 paper reported that the nature and concentration of cationic species in the electrolyte exerted a profound influence on the efficiency of dye sensitized solar cells [1]. In particular, they observed an increased photocurrent with an electrolyte containing LiI relative to an electrolyte containing tetrapropyl ammonium iodide. These findings have shown that the cation effects are important for the performance of DSSCs. Subsequent work by several groups has established that cations affect many parameters that influence solar cell performance. Among these, the attachment between the sensitizing dye molecules with the TiO_2 semiconductor surface, the dynamics of interfacial electron transfer, the adsorption to TiO_2 affecting the shifting of energy bands and changing the V_{oc} and the rate of iodide oxidation, the transport of iodide ions (I^-) within the electrolyte medium which determines the J_{sc} can be identified as strongly cation dependent processes during solar cell action [9,10]. An excellent review of cation effects in nanocrystalline solar cells has been reported by Watson and Meyer [11].

Our group has already observed the beneficial effect of using iodide electrolytes containing two cations of different sizes, one containing a quaternary ammonium ion and the other containing an alkali or magnesium ion (KI + Pr_4NI and MgI_2 + Hex_4NI) [12,13]. This type of binary iodide salt mixtures has improved the efficiency in quasi-solid state DSSCs.

The influence of electrolytes containing LiI, LiBr and tetraalkylammonium iodides on the photovoltaic performance of mercurochrome-sensitized nanocrystalline TiO_2 solar cells has been studied by Hara et al. They have observed that the short-circuit photocurrent density J_{sc} and the open-circuit photovoltage V_{oc} depend strongly on the cations in the electrolyte used [14]. Influence of electrolyte cations, Li^+, Na^+, Mg^{2+} and tetrabutyl ammonium (TBA^+) on electron transport in TiO_2 dye sensitized solar cells has been reported by Wang et al. [15]. However, a systematic study of the influence of a series of quaternary ammonium iodides on the electrolyte conductivity, photocurrent, photovoltage and power conversion efficiency of TiO_2 based dye sensitized solar cells is still lacking in the literature. In this report we present the results of the influence of PAN based quasi-solid (gel) electrolytes containing a different quaternary ammonium iodide salt from the series: ammonium iodide (NH_4I), tetraethylammonium iodide (Eth_4NI), tetrapropylammonium iodide ($Prop_4NI$), tetrabutylammonium iodide (But_4NI), tetrapentylammonium iodide ($Pent_4NI$) and tetrahexylammonium iodide (Hex_4NI). Ionic conductivity, differential scanning calorimetry, DC polarization measurements and characterization of solar cells have been performed in order to understand the influence of the quaternary ammonium cations on solar cell performance.

2. Experimental

2.1. Materials

Quaternary ammonium iodides $R_4N^+I^-$ (R = ethyl, propyl, butyl, pentyl, hexyl) and ammonium iodide (NH_4I) as salts, PAN, iodine (I_2), ethylene carbonate (EC) and propylene carbonate (PC) all with purity greater than 98%, from Aldrich were used as starting materials. Prior to use PAN was vacuum dried for 24 h at 50 °C in a vacuum oven. Other materials were used as received. Conducting glass substrates (FTO glass, fluorine doped tin oxide over-layer with sheet resistance of 7 $\Omega\,cm^{-2}$) and sensitizing dye ruthenium 535-bis TBA were purchased from Solaronix SA. TiO_2 P25 and P90 were from Degussa Germany.

2.2. Electrolyte sample preparation

Six different gel electrolyte samples were prepared by selecting the appropriate weights of PAN, EC, PC, salt, I_2 according to the chemical formula $(PAN)_{10}(EC)_{25}(PC)_{20}(salt)\,(I_2)_{0.1}$. Where PAN represent one monomer of the polymer.

The above composition used in the present work expressed in molar ratios, corresponds to the weight ratio: (PAN)10:(EC)40(PC)40:(Salt,I_2)10 which has been used in several earlier studies by our group as well as by other groups, as given in the references [5,6,8,12,13]. Our experience in both Li^+ ion conducting PAN based gel electrolytes as well as PAN based gel electrolytes used in dye sensitized solar cells shows that, as long as the polymer gel structure with these compositions (for PAN, EC, PC) is retained, the ionic conductivity can be optimized by varying the salt concentration while keeping the total weight of the other three components unchanged. In all our previous studies, we have started with this base composition ratio and further optimized with the particular iodide salt selected.

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 hour. Finally, iodine was added to the mixture and heated to ~100 °C along with continuous stirring for a few more minutes until a homogeneous viscous solution was obtained. This procedure yielded a visually homogeneous and gel-type polymer electrolyte. Our attempt to prepare the electrolyte containing tetramethylammonium iodide was not successful as this salt was not soluble in the polymer gel medium (Table 1).

2.3. Fabrication of DSSCs

To prepare the photo anode two layers of TiO_2 were made on the conducting glass substrate. For the first layer preparation, 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. Subsequently, the second layer of TiO_2 was coated on the first layer using P25 TiO_2 powder according to the published procedure [13]. 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 24 h followed by rinsing with acetone.

Table 1
Compositions of the six different gel electrolytes with different salt masses. The number of moles of [I] from the salt is 0.0001885 for all the samples.

Sample	Electrolyte salt	Mass/g				
		PAN	EC	PC	Salt	Iodine
A	Ammonium iodide	0.1	0.4149	0.3848	0.0273	0.0048
B	Tetraethylammonium iodide	0.1	0.4149	0.3848	0.0485	0.0048
C	Tetrapropylammonium iodide	0.1	0.4149	0.3848	0.0590	0.0048
D	Tetrabutylammonium iodide	0.1	0.4149	0.3848	0.0696	0.0048
E	Tetrapentylammonium iodide	0.1	0.4149	0.3848	0.0802	0.0048
F	Tetrahexylammonium iodide	0.1	0.4149	0.3848	0.0908	0.0048

The prepared gel electrolyte was casted onto the 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 configuration glass/FTO/dye/TiO_2/electrolyte/Pt/FTO/glass. At least three cells for each electrolyte were fabricated and the stable result was considered for discussion.

2.4. Measurements

The gel polymer electrolytes were subjected to electrical and thermal characterization prior to their use in DSSCs. The complex impedance measurements were performed on disk shaped gel electrolyte samples, sandwiched between two stainless steel (SS) blocking electrodes using a HP 4292A RF impedance analyzer in the 10 Hz–10 MHz frequency range and the ionic conductivity was extracted from complex impedance spectra. During impedance measurements, SS/electrolyte/SS cells were kept inside a hollow metal cylinder covered with a lid (Faraday cage) and the temperature was controlled using a water bath connected to a GRANT heating system (type KD, England) and a cooling system (HETOIFRIGE, Denmark). The temperature of each sample was increased from 0 °C to 60 °C and the measurements were taken at 5 °C intervals keeping the sample for about 30 min at each pre-set temperature to achieve thermal equilibrium. A thermocouple connected to a HEWLETT PACKARD 344401A millimeter was used to measure the temperature.

DSC thermograms were obtained using a Mettler Toledo DSC 30 differential scanning calorimeter to understand the thermal behavior of the sample. The glass transition temperature (T_g) was extracted from DSC thermograms. Each sample was scanned between −140 °C and 100 °C with a rate of 10 °C min^{-1}. Thermal measurements were carried out with several consequent heating and cooling cycles with the same sample. A flow of nitrogen gas was maintained over the perforated pan to avoid any contact with atmospheric moisture.

DC polarization tests were carried out at room temperature by sandwiching an electrolyte sample between two stainless steel blocking electrodes (SS) or between two iodine non-blocking electrodes with respective configurations SS/electrolyte/SS and SS/I_2/electrolyte/I_2/SS. Fabricated solar cells were illuminated under a LOT-Oriel GmbH solar simulator 1.5 AM, 1000 Wm^{-2} (one sun). I–V characteristics of the cells were obtained using a computer controlled eDAQ Potentiostat and e-coder. The area of the cell exposed to light was 11 mm^2.

3. Results and discussion

The variation of ionic conductivity with temperature is depicted in Fig. 1. As expected for PAN based gel electrolytes, the ln(σT) vs. $1/T$ plots are linear with essentially similar activiation energies and the conductivity appears to follow Arrhenius type behavior with increasing temperature. Hence, the data can be fitted to the Arrhenius equation,$\sigma T = B \exp\left(\frac{-E_a}{kT}\right)$where E_a is the activation energy, B is the pre-exponential factor and k is the Boltzmann constant.

It is now well established that these PAN based gel electrolytes are formed essentially by "trapping" the EC/PC (ethylene carbonate/propylene carbonate) based electrolytic solution in the matrix formed by PAN [13]. Therefore, we would expect the conducting properties of the gel electrolyte system to be determined essentially by the properties of the electrolytic solution at all concentrations. According to Fig. 1, the activation energy values, which correspond to the Arrhenius plots, are constant for all the gel electrolyte samples studied and independent of the salt type. The temperature dependence of conductivity in organic polar solvent electrolytes has been discussed by Fuoss et al. in 1933 [16]. In two recent publications by Petrowsky and Frech, the temperature dependent ion transport in organic liquid electrolytes and amorphous polymer electrolytes is discussed [17,18]. These authors suggest that ion transport in these electrolytes is governed by a single activation process which depends on the solvent family. For a given salt, the activation energy is largely independent of the salt concentration for low and moderate concentrations and the type of salt used but depends essentially on the type of solvent, in particular on the nature of the solvent heteroatom. Their results show that the ion transport in these systems involves a single activated process, which depends on the solvent functional group. This activation process is very likely the dipole re-orientation which depends on the dipole relaxation rates.

A similar interpretation can explain the observed conductivity vs. temperature variation shown in Fig. 1 because each gel electrolyte sample essentially consists of an ionic salt dissolved in the

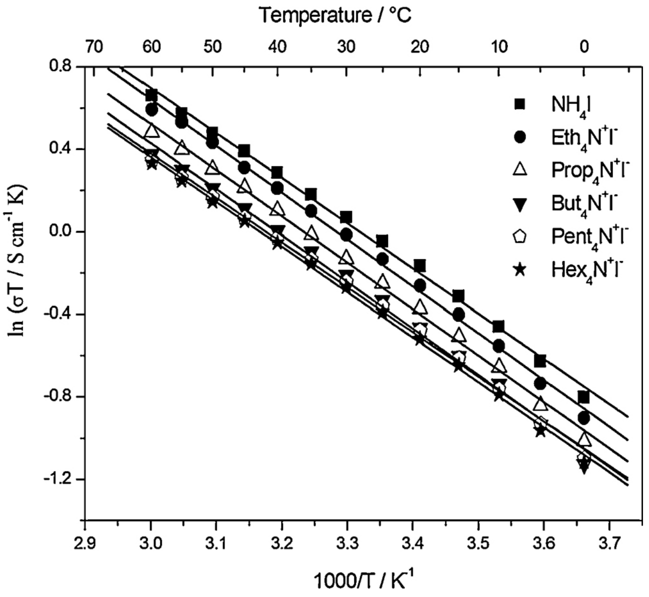

Fig. 1. Variation of ln(σT) vs. $1/T$ for the six quaternary ammonium iodide salts in quasi-solid state PAN based electrolyte: PAN:EC:PC: Quat. Ammonium iodide salt.

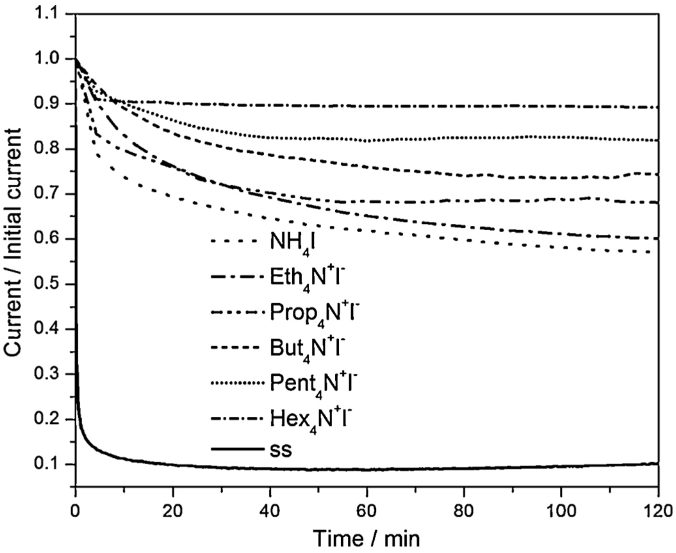

Fig. 2. DC polarization curves taken with PAN based electrolyte samples sandwiched between two non-blocking iodine electrode pellets in the configuration SS/I_2/Electrolyte/I_2/SS, where SS stands for stainless steel current collectors.

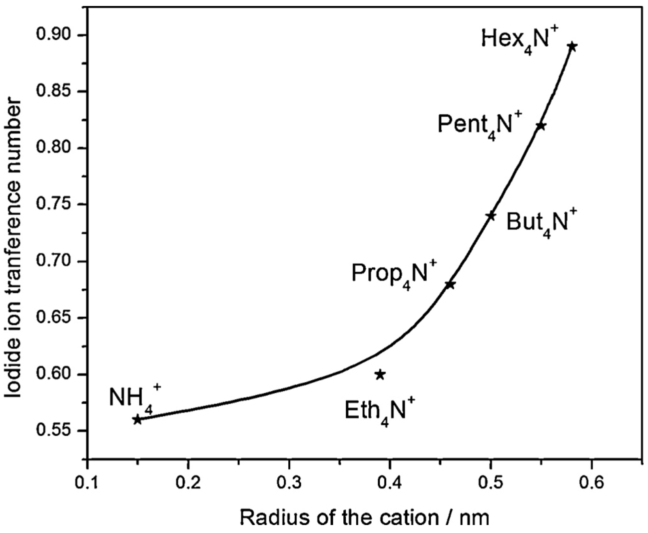

Fig. 3. Variation of iodide ion transference number estimated from DC polarization data for the PAN based electrolyte with the cation radius of the quaternary ammonium iodide salt.

organic polar co-solvent EC/PC. The energy of activation, therefore, depends on the nature of the co-solvent and is essentially unaffected by the type and the concentration of the salt. This is very likely the reason for the similar activation energies seen for the conductivity plots depicted in Fig. 1. As shown in Table 3, the activation energy calculated by fitting the data to Arrhenius equation is 0.19 eV. At a given temperature the conductivity increases with decreasing size of the cation, with the NH_4I containing electrolyte showing the highest ionic conductivity. The contributions to the total ionic conductivity in these gel electrolytes come from two types of ionic species in the electrolyte; from quarternery ammonium cations and from anions ($I^-/I_3{}^-$). The increasing trend in the total conductivity from the largest tetrahexyl ions to smallest ammonium ions clearly suggests that the cation size plays a major role in determining the overall ionic conductivity. Cation radii of the six quaternary ammonium iodide salts are given in Table 2.

Fig. 2 shows the results of the DC polarization test taken with iodine pellet non-blocking electrodes for all the gel electrolyte samples. The DC polarization curve taken with stainless steel blocking electrodes for one representative sample is also shown as evidence for the low electronic conductivity. As can be seen from the steady state values of the DC current in this figure, the iodide ion conductivity contribution increases from NH_4I to tetrahexyl ammonium iodide (Hex_4NI), with the largest cation (Hex_4N^+) exhibitting the highest iodide ion conductivity and the highest iodide ion transference number estimaed from steady state DC polarization curves (Fig. 4).

Based on Figs. 1 and 2, and considering the ionic conductivity in the electrolyte alone, it is clearly seen that for small cations such as NH_4N^+, Eth_4N^+, the high total ionic conductivity is evidently due to the high cationic mobility, but the iodide ion contribution is low. Similarly, for large cations such as Pen_4N^+ and Hex_4N^+, the total ionic conductivity is low evidently due to the lower cationic mobility, but the iodide ion conductivity is high due to high ionic dissociation caused by large size cations. The variation of the iodide ion transference number with cation radius for the six electrolyte samples is shown in Fig. 3.

DSC thermogrammes of different electrolytes are shown in Fig. 4. Although the change in glass transition temperature (T_g) observed is not so significant, a definite decreasing trend with cation size can be observed from NH_4I to Hex_4NI. This would imply that the disorder and hence the local mobility of the polymer host is increasing with increasing cation size. In general, in polymer electrolytes, the conductivity increases with decreasing glass transition temerature since the mobilty of the ions can be related to the polymer flexibility. In the prsent case, however, although the overall ionic conductivity actually decreases, the iodide ion contribution to conductivity increases with increasing cation size, evidently due to the increased mobility of iodide ions caused by the increased disorder of the polymer host. The overall ionic conductivity after

Table 2
Variation of iodide ion transference number estimated from DC polarization data with ionic radii of the quaternary ammonium ions in the PAN based electrolyte.

Salt	Iodide ion transference no.	Radius of the cation/nm	Reference
Ammonium iodide	0.56	0.15	[19]
Tetraethylammonium iodide	0.60	0.39	[20]
Tetrapropylammonium iodide	0.68	0.46	[20]
Tetrabutylammonium iodide	0.74	0.50	[20]
Tetrapentylammonium iodide	0.82	0.55	[21]
Tetrahexylammonium iodide	0.89	0.58	[21]

Table 3
Ionic conductivity (20 °C), activation energy and glass transition temperature of the six PAN based quasi solid electrolytes containing the quaternary ammonium iodide salts.

	Electrolyte	Molecular weight (g/mol)	Molecular formula	T_g (°C)	Conductivity at 20 °C ($S\,cm^{-1} \times 10^3$)	Activation energy (eV)
A	Ammonium iodide	144.94	NH_4I	−100.7	2.88	0.19
B	Tetraethylammonium iodide	257.16	$(C_2H_5)_4NI$	−101.2	2.62	0.19
C	Tetrapropylammonium iodide	313.26	$(CH_3CH_2CH_2)_4NI$	−101.4	2.35	0.19
D	Tetrabutylammonium iodide	369.37	$[CH_3(CH_2)_3]_4NI$	−101.5	2.14	0.19
E	Tetrapentylammonium iodide	425.47	$[CH_3(CH_2)_4]_4NI$	−101.8	2.11	0.19
F	Tetrahexylammonium iodide	481.58	$[CH_3(CH_2)_5]_4NI$	−102.2	2.03	0.19

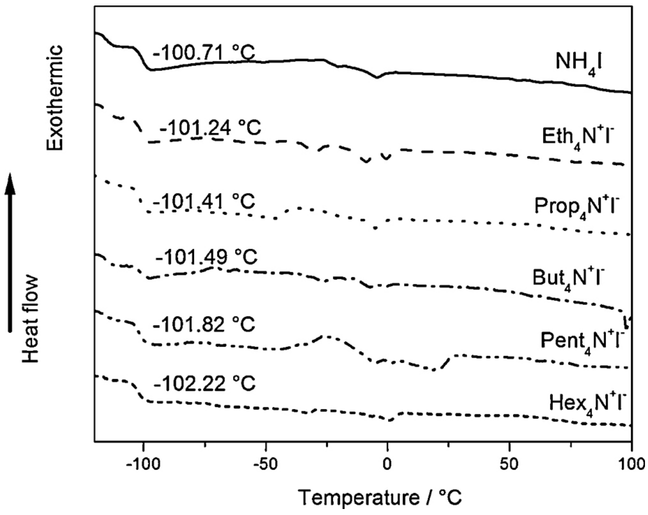

Fig. 4. DSC thermograms used to extract the glass transition temperature (T_g) of the six PAN based electrolytes with quaternary ammonium iodide salts.

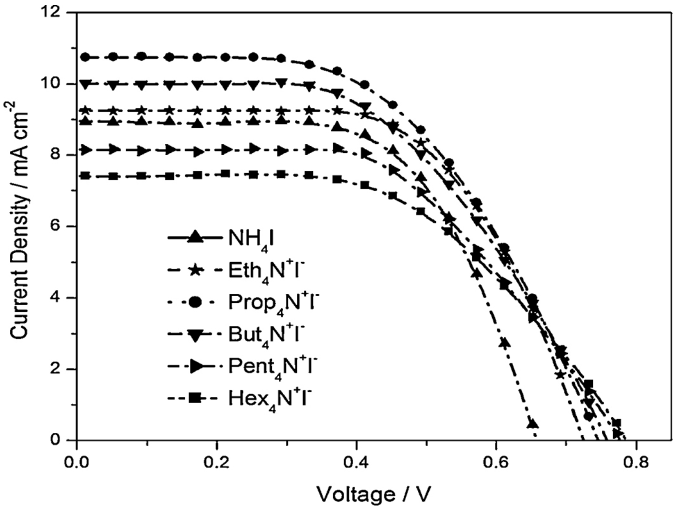

Fig. 5. *J–V* characteristics of dye sensitized solar cells fabricated with PAN based electrolytes containing six quaternary ammonium iodide salts.

all decreases due to the considerable size and hence the reduced mobility of the cations. As reflected from the very small change in T_g, the polymer-salt interactions in these PAN based gel polymer electrolytes are very minimal. This has been observed even in PAN based Li^+ ion electrolytes [8].

J–V characteristic curves for the DSSCs fabricated with six different quaternary ammonium salts are shown in Fig. 5. These curves were used to calculate solar cell parameters J_{sc} V_{oc}, ff, and energy conversion efficiency (η, %) which are shown in Table 4. Variation of η and J_{sc} with cation radius is shown in Fig. 6 and the variation

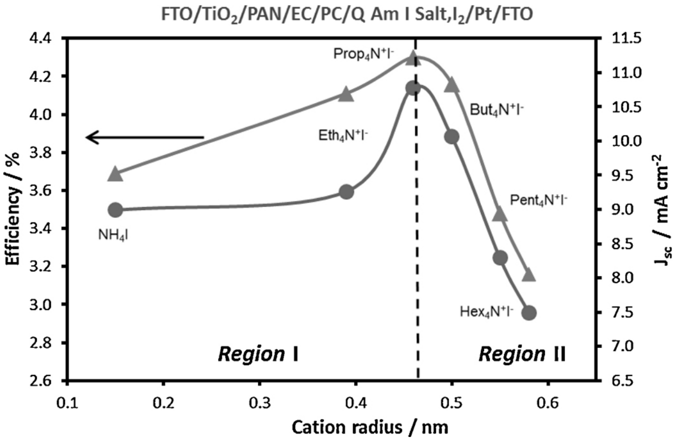

Fig. 6. Variation of the power conversion efficiency and the short circuit photo current density as a function of the cation radius for the dye sensitized solar cells fabricated with six quaternary ammonium iodide salts.

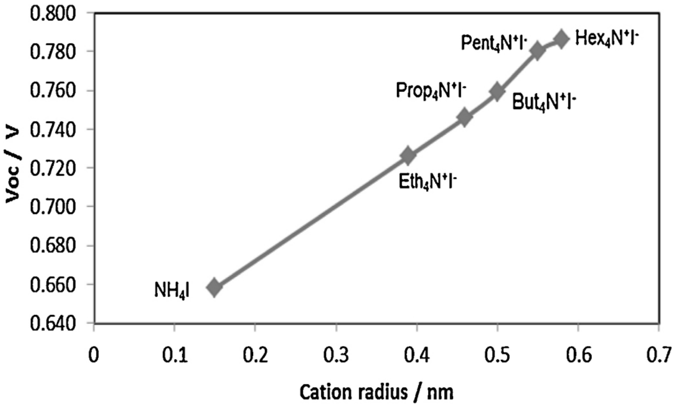

Fig. 7. Dependence of the open circuit voltage (V_{oc}) on the cation radius for the dye sensitized solar cells fabricated with six quaternary ammonium iodide salts.

of V_{oc} with cation radius is shown in Fig. 7. The power conversion efficiency (η, %) of a solar cell is given by the following equation:

$$\eta = \frac{J_{sc}V_{oc}\mathrm{ff}}{\text{Total incident power density}}$$

where the symbols have their usual meanings. From Table 3 and Fig. 6, it is clear that the variation of efficiency with cation radius correlates with the variation of the short circuit photocurrent density, J_{sc}. This suggests that the J_{sc} dominates the performance of these solar cells.

For the DSSCs fabricated with mercurochrome-sensitized nanocrystalline TiO_2 photocathode and electrolytes containing LiI and tetraalkyl-ammonium iodides in acetonitrile solvent Hara et al. have obtained J_{sc} of 3.42 mA cm^{-2} and V_{oc} of 0.52 V for the LiI containing electrolyte and J_{sc} of 2.10 mA cm^{-2} and V_{oc} of 0.86 V for the Pr_4NI containing electrolyte [14]. This difference in DSSC performance has been attributed to the difference in the shifts of the

Table 4
J_{sc}, V_{oc}, field factor, and the efficiency (η) of dye sensitized solar cells fabricated with PAN based electrolytes containing six quaternary ammonium iodide salts.

Sample	Electrolyte	Cond. at 20 °C (mS cm^{-1})	J_{sc} (mA cm^{-2})	V_{oc} (V)	ff (%)	η (%)
A	Ammonium iodide	2.88	8.99	0.658	62.41	3.69
B	Tetraethylammonium iodide	2.62	9.26	0.726	61.09	4.11
C	Tetrapropylammonium iodide	2.35	10.78	0.746	53.40	4.30
D	Tetrabutylammonium iodide	2.14	10.06	0.759	54.48	4.16
E	Tetrapentylammonium iodide	2.11	8.29	0.780	53.82	3.48
F	Tetrahexylammonium iodide	2.03	7.49	0.786	53.68	3.16

conduction band level of the TiO_2 electrode caused by the two cations, Li^+ and Pr_4N^+. These authors have also obtained the J_{sc} and V_{oc} values for DSSCs with solution electrolytes containing the quaternary ammonium salts, Me_4NI, Et_4NI, Bu_4NI, and Hex_4NI. One of the major differences in their work and our present work is that while they have used mercurochrome-sensitized TiO_2 and organic solution electrolytes, we have used ruthenium N 719 dye and PAN based gel electrolytes. Their DSSC efficiencies are much lower compared to ours even though they have used liquid type electrolytes. However, out of the J_{sc} values obtained by these authors for Et_4NI, Pr_4NI and Bu_4NI electrolytes, Pr_4NI has shown the highest J_{sc} value, similar to what we have observed in our work using PAN based gel electrolytes. However, their J_{sc} value for the Hex_4NI electrolyte is higher than that for the Pr_4NI electrolyte and the J_{sc} values have not followed any specific trend with cation size.

From a quantitative study of the influence of different cations (Li^+, Na^+, Mg^{2+} and TBA^+ or Bu_4N^+), on TiO_2 conduction band and electron life times, Wang et al. have found that the separation between the TiO_2 conduction band (E_c) and the redox Fermi level has decreased as the charge/radius ratio of the cations increased [15]. Thus E_c in the Mg^{2+} electrolyte was found to be 170 meV lower than that in the Na^+ electrolyte and 400 meV lower than that in the TBA^+ electrolyte. The rate of electron back reaction was also higher in the TBA^+ electrolyte compared with the Na^+ and Li^+ electrolytes.

In their very first paper on DSSCs published in 1991, O'Regan and Grätzel reported that the incident photon-to-current conversion efficiency (IPCE) of the DSC increased from 68% to 84% when Pr_4N^+ in the electrolyte was replaced by Li^+ [1]. The effect of alkali metal cations Li^+, Na^+, K^+, Rb^+, and Cs^+ on J_{sc} and V_{oc} of DSSCs was later investigated by Liu et al. who observed that largest J_{sc} and smallest V_{oc} were obtained for the Li^+ electrolyte solution compared to solutions with other cation species, and that V_{oc} was proportional to the cationic radius [22]. These studies have been extended to cover ionic liquids as well. Park et al. have compared the photovoltaic properties of DSSCs due to the influence of Li^+ and 1.2-dimethyl-3-hexyl imidazolium ions in the electrolyte [10]. The electrolyte with Li^+ ions have produced a lower V_{oc} compared to the electrolyte with the imidazolium ions. The influence of cation charge density on the photovoltaic performance of DSSCs by electrolytes containing Li^+, Na^+, K^+ and dimethyl imidazolium (DMI^+) ions have been reported by Yushuai Shi et al. whose results generally agree with other reports mentioned above [9].

Our results on the effect of different quaternary ammonium iodide salts on J_{sc} and V_{oc} of DSSCs based on PAN gel electrolyte (see Table 4) are generally in agreement with the observations reported above for DSSCs based on organic solution electrolytes. However, as a major research finding we observe that the J_{sc} exhibits a maximum value for the Pr_4NI containing gel electrolyte and that the cell efficiency appears to be governed largely by the J_{sc} rather than by the V_{oc} as evidenced from Fig. 6. As V_{oc} is derived from the energy gap between the conduction band level of TiO_2 and the I^-/I_3^- redox potential, smaller V_{oc} is expected for small cations in the electrolyte compared to larger cations. In our results, V_{oc} has increased gradually from NH_4I (658 mV) to Hex_4NI (786 mV) in agreement with the expected trend (Fig. 7).

In order to explain the observed variation of J_{sc} and V_{oc} with cation radius of the quaternary ammonium iodide salt series, it is necessary to understand the factors contributing to these parameters in a DSSC. J_{sc} in a DSSC is determined by two competing mechanisms which we shall label as "Electrolyte Effects" and "Electrode Effects" respectively. Electrolyte effects refer to the anionic or iodide ion (I^-/I_3^-) conductivity in the electrolyte medium. This iodide ion conductivity and iodide ion transference number can generally be estimated by the DC polarization test using iodine "non-blocking" electrodes. Iodide ion conductivity depends on the degree of ionic dissociation which determines the number of "free" iodide ions available for conduction as well as the viscosity of the electrolyte which determines the iodide ion mobility. In an electrolyte containing an iodide salt like LiI, both Li^+ ions and I^- ions contribute substantially toward the total ionic conductivity. However, in an electrolyte containing an iodide salt like $Prop_4NI$ or Hex_4NI, due to the large size of the cation, the iodide anion (I^-) conductivity dominates. As seen in Fig. 7, the iodide ion conductivity in the electrolyte increases gradually from NH_4I to Hex_4NI evidently due to higher degree of ionic dissociation in the electrolyte containing larger cations. It should be emphasized that, the iodide ion conductivity results are taken from DC polarization measurements on gel electrolyte samples sandwiched between two non-blocking iodine electrodes in the $SS/I_2/Electrolyte/I_2/SS$, where SS stands for stainless steel current collectors, and not in an illuminated DSSC structure.

Once the DSSC of configuration glass/FTO/dye/TiO_2/electrolyte/Pt/FTO/glass is fabricated and illuminated, the electron dynamics at the dye sensitized TiO_2 semiconductor electrode/redox electrolyte interface starts to affect the J_{sc} through redox reactions. The dependence of J_{sc} and V_{oc} on the type and the nature of the cation take place due to interfacial kinetics of the dyed TiO_2 film. Upon light illumination of the dyed nanoporous TiO_2 film, the injected electrons from the excited dye molecules are accumulated at the conduction band (CB) of TiO_2, and the cations in the electrolyte become adsorbed into the TiO_2 film for charge compensation. We have labeled these as electrode effects.

The cation/TiO_2 interactions cause two effects in a DSSC: (i) a positive shift of the flat band potential of the semiconductor and (ii) the creation of deeper electron-trapping states, which play an important role in electron transport through TiO_2 to the current collector. The charge transfer process in a TiO_2 based dye sensitized solar cell with a typical electrolyte containing an iodide/tri-iodide (I^-/I_3^-) redox couple involves several steps. Under light illumination, the photoexcited electrons are injected from the excited dye sensitizer (D^*), ($D^* \rightarrow D^+ + e^-$) into the conduction band of the nanocrystalline TiO_2 and reach the external circuit. The oxidation of I^- anions ($3I^- \rightarrow I_3^- + 2e^-$) takes place on the surface of the dyed TiO_2 film and therefore, the resulting dye cations in the previous step are reduced by I^- anions ($2D^+ + 3I^- \rightarrow 2D + I_3^-$). Meanwhile, the oxidized I_3^- species migrate from the photoelectrode to the platinized counter electrode and become reduced to I^- by accepting electrons from the external circuit. Cations in the electrolyte can efficiently screen the photo-injected electrons on the TiO_2 film, ensuring that electro-neutrality is maintained throughout the TiO_2 network. The iodide and tri-iodide ions (I^-/I_3^-), while participating in the redox reaction, also shuttles between the photo-electrode and the counter electrode where the iodide ion conductivity in the electrolytes becomes important. Thus, the ionic migration in the electrolyte is strongly correlated with electron transport in the TiO_2 film.

As shown by several authors previously, the conduction band level of the TiO_2 electrode shifts positively due to the adsorption of cations by nanoporous TiO_2 increasing the energy gap between the LUMO level of the dye and the CB of TiO_2 [13–15,22]. This shift is greater for the smaller cations like Li^+, K^+, NH_4^+ compared to larger cations like $Prop_4N^+$. Therefore, an adsorbed smaller cation, due to the larger potential drop is expected to increase the driving force for the electron injection process from the LUMO level of the dye into the CB of TiO_2 leading to faster electron dynamics at the semiconductor/electrolyte interface and generating a larger photocurrent compared to an adsorbed larger cation. At the same time, the V_{oc} of a DSSC using an iodine redox electrolyte is determined by the energy gap between the positively shifted CB of TiO_2 and the I^-/I_3^- redox potential. Thus the V_{oc} is expected to be lower in DSSC s containing smaller cations and higher for larger cations in the electrolyte and gradually increase with cation size from NH_4I

to Hex_4NI. This is in excellent agreement with our observations (Fig. 7).

Based on these electrolyte and electrode effects, it is now possible to explain the variation of J_{sc} and V_{oc} with cation radius in the present system. For the purpose of the discussion, it is convenient to divide the gel electrolytes containing different quaternary ammonium iodide salts into two regions, labeled in Fig. 6 as Region I (from NH_4I to $Prop_4NI$) and Region II (from $Prop_4NI$ to Hex_4NI).

In region I (Fig. 6), the electrolyte effects appear to be dominating and rate determining for the solar cell performance. According to Fig. 1, NH_4I electrolyte has the highest total ionic conductivity but according to Fig. 2, this electrolyte also has the lowest iodide (I^-/I_3^-) ion conductivity and lowest iodide ion transference number as measured by the DC polarization test with iodine non-blocking electrodes. If electrode effects were dominating, NH_4^+ should have produced a larger J_{sc} compared to $Prop_4N^+$. However, in the present case, the NH_4^+ cation has produced the lowest J_{sc} value of 8.99 mA cm^{-2} evidently due to the lowest iodide ion conductivity in the electrolyte. The iodide ion conductivity (I^-) also increases from NH_4^+ to $Prop_4N^+$ (Fig. 2) in accordance with higher ionic dissociation of the salts with larger cations. This mechanism is valid for DSSCs containing NH_4^+, Eth_4N^+ and $Prop_4N^+$ cations in Region I as expected from the increasing iodide ion conductivity contribution and the iodide ion transference number from NH_4^+ to Pr_4N^+ (Figs. 2 and 3). Therefore, the efficiency increase from NH_4I to Pr_4NI appears to be largely due to the increase in J_{sc}. In this region, a contribution toward the efficiency increase may also come from the V_{oc} increase as the cationic radius increases.

For the four salts (Table 2) in region II, from Pr_4NI to He_4NI, the J_{sc} has decreased from 10.78 mA cm^{-2} to 7.49 mA cm^{-2} in the order $Prop_4NI > But_4NI > Pent_4NI > He_4NI$ with the increasing size of the cation despite the increasing iodide ion conductivity and iodide ion transference number (Figs. 2 and 3) and in agreement with the observations made by other groups for related systems with organic solution electrolytes. In this region, due to the relatively larger downward shift of the TiO_2 CB caused by adsorption of relatively smaller size cations ($Prop_4N^+$), there is a greater driving force for electron injection from the LUMO of the Rh dye to the conduction band of TiO_2, compared to larger cations ($Pent_4^+$, Hex_4^+). This effect, which determines the value of J_{sc} in this region, decreases in the order $Prop_4NI > But_4NI > Pent_4NI > Hex_4NI$ despite the increasing iodide ion conductivity contribution to J_{sc}. Therefore, in region II, electrode effects on J_{sc} appear to be dominating and rate determining for the solar cell performance. The decrease in efficiency in this region with increase in cation size, despite the increase in iodide ion conductivity and V_{oc} both is appears to be due to the decrease in J_{sc} caused by the increasing cation size from $Prop_4NI$ to He_4NI.

4. Conclusions

In this work we have studied the dependence of performance of dye sensitized TiO_2 solar cells based on quasi-solid state PAN electrolytes containing quaternary ammonium iodide salts on the size of the quaternary ammonium ion. The total ionic conductivity decreases with increasing cation size from NH_4I to Hex_4NI. However, the iodide ion conductivity in the electrolytes increases with cation size. The open circuit photovoltage (V_{oc}) of the dye sensitized solar cells also increases with cation radius. The variation of efficiency of the DSSCs with cation size exhibits a maximum for $Prop_4NI$ salt. The variation of short circuit photo current density (J_{sc}) follows a similar variation with cation size, suggesting a strong correlation between the cation size dependence of efficiency and J_{sc}. The DSSC fabricated with PAN based electrolyte with tetrapropylammonium iodide ($Prop_4NI$) exhibits the maximum power conversion efficiency of 4.30% with maximum J_{sc} of 10.78 mA cm^{-2} and a V_{oc} of 0.746 V. The results have been explained on the basis of “the electrolyte effects” where the J_{sc} is determined essentially by the iodide ion conductivity in the electrolyte and “the electrode effects” where the J_{sc} and V_{oc} are determined by the cation adsorption in the dyed TiO_2 electrode and resulting electron dynamics at the semiconductor/electrolyte interface. For DSSCs with small size cations from NH_4N^+ to $Prop_4N^+$, electrolyte effects appear to be dominating and rate determining while for DSSCs with large size cations from $Prop_4N^+$ to Hex_4N^+, electrode effects appear to be dominating and rate determining.

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