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ORIGINAL PAPER

Efficiency enhancement in dye sensitized solar cells based on PAN gel electrolyte with $Pr_4NI + MgI_2$ binary iodide salt mixture

**M. A. K. L. Dissanayake · C. A. Thotawatthage ·
G. K. R. Senadeera · T. M. W. J. Bandara ·
W. J. M. J. S. R. Jayasundara · B.-E. Mellander**

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Abstract The effect of using a binary iodide salt mixture in N719 dye-sensitized TiO_2 solar cells (DSSCs) is investigated. The cells use tetrapropylammonium iodide (Pr_4NI) and magnesium iodide (MgI_2) in a plasticized polyacrylonitrile gel in glass/FTO/nano-porous TiO_2/gel, I_2/Pt/FTO/glass solar cell structure. The salt composition in the gel electrolyte is varied to optimize the efficiency of DSSCs. The DSSCs with MgI_2 or Pr_4NI as the only iodide salt showed the efficiencies 2.56 and 4.16 %, respectively, under AM 1.5 (100 mW cm^{-2}) illumination while the DSSC with mixed cations with 18.4:81.6 MgI_2:Pr_4NI molar ratio shows the highest efficiency of 5.18 %. Thus the efficiency enhancement, relative to the high efficiency end member is about 25 %. DC polarization measurements establish the predominantly ionic behavior of the electrolytes, and show that the variation of efficiency with salt composition correlates with the change in short circuit photocurrent density (J_{sc}), which appears to be governed by the iodide ion conductivity. It is also found that J_{sc} correlates with the iodide ion transference number estimated from DC polarization data taken with non-blocking iodine electrodes. This study suggests that binary iodide mixtures may be used to obtain efficiency enhancement in different types of DSSCs based on polymeric, gel, or solvent electrolytes.

Keywords Dye-sensitized solar cells · PAN-based gel electrolyte · Efficiency enhancement · Mixed cation effect

1 Introduction

Dye sensitized solar cells (DSSCs) based on nanostructured titanium dioxide (TiO_2) are emerging as a low cost alternative to conventional silicon and thin film solar cells [1–3]. A DSSC generally consists of a semi-transparent dye-sensitized, nano-porus, nano crystalline TiO_2 film, an iodide ion containing electrolyte with a redox couple (I^-/I_3^-) in a volatile organic solvent like acetonitrile and a Pt-coated counter electrode. They have energy conversion efficiencies exceeding 10 %. However the lack of long-term stability due to liquid leakage, electrode corrosion, and photodecomposition of the dye in the solvent medium due to the usage of volatile liquids are some of the major drawbacks preventing large scale practical applications of DSSCs. Therefore, many research studies have been focused on replacing the liquid electrolyte in these DSSCs by a gel polymer electrolyte (or quasi-solid electrolyte) to

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M. A. K. L. Dissanayake (✉) · C. A. Thotawatthage ·
G. K. R. Senadeera
Institute of Fundamental Studies, Hantana Road, Kandy,
Sri Lanka
e-mail: makldis@yahoo.com

M. A. K. L. Dissanayake
Department of Physics, University of Peradeniya, Peradeniya,
Sri Lanka

G. K. R. Senadeera
Department of Physics, The Open University of Sri Lanka,
Nawala, Nugegoda, Sri Lanka

T. M. W. J. Bandara
Department of Physics, University of Rajarata, Mihintale,
Sri Lanka

W. J. M. J. S. R. Jayasundara
Postgraduate Institute of Science, University of Peradeniya,
Peradeniya, Sri Lanka

B.-E. Mellander
Department of Applied Physics, Chalmers University
of Technology, Goteburg, Sweden

minimize the above drawbacks [4–9]. In particular polyacrilonitrile (PAN)-based gel polymer electrolytes have been used successfully to fabricate quasi-solid-state DSSCs due to their relatively high anionic conductivities [10–13]. In these 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 a ethylene carbonate/propylene carbonate (EC/PC) co-solvent is "entrapped" in the host polymer matrix yielding almost liquid-like ionic conductivities [14–16].

PAN is a synthetic, semicrystalline organic polymer resin, with the linear formula $(C_3H_3N)_n$. PAN-based Li^+ ion conducting gel electrolytes have been developed as possible electrolytic membranes for high energy density rechargeable lithium batteries and other electrochemical devices [16–18]. The main advantage of these electrolytes is their high ambient temperature ionic conductivity of the order of 10^{-3} S cm^{-1} at 25 °C. However, relatively few reports are available in the literature on PAN-based, anion conducting, gel electrolytes. These have been developed mainly as electrolytes in dye sensitized solar cells [19, 20].

The Co^{2+}/Co^{3+} redox couple electrolytes containing cations have been discovered that is more suited to achieving higher efficiencies. However, one of the major shortcomings of cobalt-based complexes is that their bulky groups significantly decrease the speed at which the ions can diffuse through the electrolyte up to an order of magnitude less than conventional iodide ions [21, 22]. Therefore, in most widely studied DSSCs, the redox couple electrolytes have been anion conductors and in majority of the cases these are iodide ion (I^-) conductors with the I^-/I_3^-couple. The contribution of the iodide ion conductivity to the overall ionic conductivity of the electrolyte in these DSSCs 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 and tri-iodide ions (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 migrates 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.

By using MgI_2 as an iodide ion provider in a DSSC, one would expect that with ionic dissociation, the Mg^{++} ions in the electrolyte to be less mobile due to their double charge, favoring I^- ion conduction. Also, the smaller size of the Mg^{++} ion is expected to enhance the electron dynamics at the semiconductor/electrolyte interface. Quaternary ammonium salts such as Pr_4NI, Bu_4NI (or TBAI) and Hex_4NI are widely used as ionic salts in these electrolytes. Due to the bulky cations which are less mobile, these electrolytes are expected to have relatively higher iodide ion conductivity. Although iodide ion conductivity is an important parameter in determining the short circuit photocurrent and the efficiency of DSSCs, not much systematic research work has been reported on this subject.

Several studies have revealed that the cation in the electrolyte has a profound influence not only in determining the J_{sc} but also on the electrolyte/semiconductor interface electron dynamics and hence on the efficiency of DSSCs [23–27]. However, there are only very few published reports on the use of binary iodide mixtures as electrolytes in DSSCs. According to these reports, electrolytes with iodide salt mixtures have shown better DSSC performance compared to using only a single-iodide salt [28–30].

Studies of DSSCs containing aqueous electrolytes with various cations have shown that short circuit current density increases with the increasing charge density of the cation in the electrolyte while the fill factor, open circuit voltage, and efficiency decreases [31, 32]. While bulky cations such as Pr_4N^+ and Hex_4N^+ are expected to minimize the cationic conductivity and enhance the iodide ion conductivity in the electrolyte, cations with high charge density, such as K^+, Li^+, or Na^+ and also Mg^{++} get adsorbed into the TiO_2 electrode and contribute toward better photogeneration of electrons at the dye and faster diffusion dynamics at the dye-semiconductor interface. Therefore, it would be natural to explore the combined effect of using a binary mixture of two iodide salts consisting of a bulky cation and a small cation with high charge density in the electrolyte to benefit from both above-mentioned mechanisms.

In order to systematically study the effect of mixed cation systems on the performance of DSSCs, our group has focussed on the beneficial effect of using binary iodide salt mixtures on the efficiency enhancement in several different types of DSSCs [30, 33]. In the present system we have used the quaternary ammonium salt, Pr_4NI as the salt with a bulky cation and MgI_2 as the salt with a small cation in a DSSC with a PAN-based gel electrolyte.

2 Materials and methods

PAN (MW 150,000) magnesium iodide (MgI_2) and tetrapropyl ammonium iodide (Pr_4NI), all of purity greater than 98 % were purchased from Aldrich and ethylene carbonate (EC), propylene carbonate (PC), and iodine chips (I_2) with purity greater than 99 % were purchased from Fluka. Ru N 719 dye was purchased from Solaronix SA. All the chemicals except MgI_2, I_2, and PC were vacuum dried for 24 h prior to use. MgI_2 was kept in a nitrogen (N_2) environment with relative humidity less than 10 %.

Table 1 Compositions of the electrolytes prepared by varying $MgI_2/Pr_4N^+I^-$ iodide salt ratio

Electrolyte	MgI_2 % (w/w)	MgI_2 (mol%)	Relative I^- (mol%)	MgI_2 (g)	$Pr_4N^+I^-$ (g)	I_2 (g)
A	0	0.0	1.81	0	0.06	0.0049
B	8.3	9.3	1.83	0.005	0.055	0.0049
C	16.6	18.4	1.85	0.01	0.05	0.0050
D	33.3	36.0	1.89	0.02	0.04	0.0051
E	50	53.0	1.93	0.03	0.03	0.0052
F	100	100.0	2.04	0.06	0	0.0055

2.1 Electrolyte preparation

For preparing the electrolyte samples, the weights of PAN (0.10 g), EC (0.40 g), and PC (0.40 g) were kept unchanged while the total weight of MgI_2 and $Pr_4N^+I^-$ was kept at 0.06 g. Six different compositions of the gel polymer electrolyte, with PAN:EC:PC: $(100 - x)$ wt% Pr_4NI + x wt% MgI_2, I_2, for $x = 0, 8.3, 16.6, 33.3, 50.0, 100$ were prepared by changing the weight ratio of Pr_4NI and MgI_2. The weight of I_2 was taken to be one tenth of the mole amount of the iodide salt. Appropriately weighed quantities were mixed in a glass bottle by magnetic stirring. Initially EC, PC, PAN, $Pr_4N^+I^-$, and MgI_2 (was added inside a N_2 filled and humidity <10 % controlled glove box) and the mixture were stirred at room temperature for about 2 h until MgI_2 was fully dissolved. Finally, the electrolyte was mixed by continuously stirring at 80 °C for about for 10 min until the entire polymer has been dissolved. The mixture was then allowed to cool down to room temperature and I_2 chips were added. Then, the mixture was again continuously magnetically stirred overnight (12 h) to obtain a homogeneous gel electrolyte. This procedure was repeated for all the compositions shown in Table 1.

2.2 Ionic conductivity and DC polarization measurements

Ionic conductivity of the six electrolyte samples was measured by AC impedance spectroscopy using a computer controlled Metrohm Autolab (PGSTAT 128 N) impedance analyzer in the frequency range 0.1–1 MHz. The electrolytes were sandwiched between two polished stainless steel (SS) electrodes with configuration SS/electrolyte/SS for impedance measurements. The temperature of all the samples was varied from 30 to 55 °C. Measurements were taken at 5 °C intervals after keeping the sample for about 15 min at the pre-selected temperature for thermal equilibrium. The conductivity values were extracted from the impedance data.

2.2.1 Wagner's DC polarization method

For a solid, gel, or liquid electrolyte to be used as an electrolyte separator in electrochemical devices, such as rechargeable batteries, fuel cells, super capacitors, and dye sensitized solar cells, the electronic conductivity of the electrolyte must be negligibly small compared to the ionic conductivity to minimize the internal short circuiting and to achieve higher power densities and power conversion efficiencies. Due to its simplicity, the most widely used technique to estimate the ionic and electronic contributions to the total conductivity in an electrolyte has been the Wagner DC polarization method.

In the present study, we have used the Wagner DC polarization technique where the electrolyte sample was sandwiched between two SS ion blocking electrodes, in the cell configuration SS/electrolyte/SS, and a constant DC potential of 2 V was applied across the sample by a potentiostat and the resulting current was monitored by a sensitive digital multimeter (Keithley 2000) as a function of time. Under the influence of the DC field, cations migrate to the negative electrode and anions to the positive electrode thus polarizing the material. When the back potential created by the concentration gradient exactly opposes the applied potential the ions no longer carry current and the cell becomes completely polarized. Thus, any resulting steady-state current is only due to electronic conductivity in the electrolyte material. Just after switching on the circuit, the initial total current I_t started to quickly decrease with time, corresponding to the polarization of ionic species in the electrolyte and becomes constant in the fully polarized situation. At this steady-state, the residual current is only electronic current (I_e) which is expected to be negligibly small (<5 %). We have used the DC polarization measurements to establish that all six gel electrolyte samples are predominantly ionic conductors. The calculated ionic and electronic transport numbers from this method is only approximate because experimentally, the actual value of the initial total current (at time $t = 0$) is sometimes difficult to measure accurately. This is an inherent limitation of this method. Also, for a measurement with reasonable accuracy, the electrode over-potential which is the potential drop at the two blocking electrodes should be taken into account unless they are negligibly small. If one is interested in actually determining the ionic and electronic transport numbers accurately, a better method would be to use a four probe technique instead of the usual two electrode method.

The Wagner DC polarization method can also be used to estimate the cationic or anionic contribution to the ionic conductivity by sandwiching the electrolyte between appropriately selected electrodes for the symmetrical cell. For example to estimate the Li^+ ion conductivity contribution in a lithium ion (Li^+) conducting electrolyte, Li^+X^-, a polarizing cell with lithium metal (Li) non-blocking electrodes must be used in the configuration Li/LiX/Li and the resulting steady-state current is then only due to Li^+ ions.

In the present work, the electronic contribution to the total ionic conductivity in our gel electrolyte samples was estimated using the standard Wagner's DC polarization method by sandwiching the electrolyte between two polished SS blocking electrodes in the configuration SS/electrolyte/SS. Similarly, Iodide ion (I^-) conductivity contribution to the total ionic conductivity was estimated by the same method, but using iodine (I_2) pellet, non-blocking electrodes in the cell configuration I_2/electrolyte/I_2. Out of all the six samples, the sample *C*, exhibiting the highest solar cell efficiency and highest J_{sc}, had the highest iodide ion conductivity of about 80 % as shown in Fig. 3. Similarly, the electrolyte sample *F*, having only MgI_2 as the iodide salt, appears to be a good ionic conductor (from SS/electrolyte, *F*/SS cell configuration) but a poor Mg^{++} ion conductor (from Mg/electrolyte, *F*/Mg cell configuration).

2.3 TiO_2 electrode preparation

TiO_2 paste was prepared by grinding 0.20 g of TiO_2 (Degussa P-25) with 12 drops of glacial acetic acid, one drop of triton X-100 and about 2 ml of ethanol. This paste was spread on a pre-cleaned, fluorine-doped conducting tin oxide (FTO) glass (Nippon sheet glass 10–12 Ω sq^{-1}). An active cell area of 0.25 cm^2 was obtained by spreading the paste using the doctor blade technique and sintering at 450 °C for 45 min. The resulting TiO_2 nano-porous film was allowed to cool down to room temperature. The thickness of the film on FTO glasses was measured with the help of a homemade, calibrated profilometer and the average film thickness of the TiO_2 film was found to be around 12 µm. Dye absorbance was carried out by immersing the above film in an ethanolic dye solution containing Ruthenium dye N719 ($RuL_2(NCS)_2$:2TBA where, L = 2,2′-bipyridyl-4′,-dicarboxylic acid; TBA = tetrabutylamonium) for 24 h.

2.4 Solar cell fabrication and characterization

Dye sensitized solar cells (DSSC) of configuration Glass/FTO/TiO_2/Dye/electrolyte/Pt/FTO/glass were fabricated by sandwiching the polymer electrolyte between the dye adsorbed TiO_2 electrode and a platinum (Pt)-coated FTO glass. The current–voltage (*I–V*) characteristics of the cells were measured under the illumination of 100 mW cm^{-2} (AM 1.5) simulated sunlight using a homemade computer controlled setup coupled to a Keithley 2000 mm with potentiostat/galvonostat HA-301. A Xenon 500 lamp was used with AM 1.5 filter to obtain the simulated sunlight with above intensity.

2.5 Measurement of the flat band potential using Mott-Schottky plots

We have performed Mott-Schottky (*C–V*) measurements by immersing a TiO_2 electrode in an electrolyte solution containing EC, PC, MgI_2, and Pr_4NI salts, but without PAN. The salt ratio of MgI_2 to Pr_4NI in the electrolyte solution samples (in EC, PC) was identical to the salt ratios used in the PAN-based gel electrolyte, used for the DSSCs. In both cases, the weights of EC and PC were kept fixed at 0.4 g each, while the MgI_2 to Pr_4NI weight ratio was changed from 0: 0.06 to 0.06:0 which corresponds to the MgI_2 wt% ratio of 0–100 %. In each solution, the TiO_2 electrode was immersed for 1 min and the stabilized voltage was measured with respect to a standard calomel electrode (SCE) using Mertohm Autolab PGSTAT128 N potentiostat. The scanned frequencies were 1 and 1.5 kHz.

3 Results and discussion

3.1 Characterization of the PAN-based gel polymer electrolyte

The compositions of the six gel polymer electrolytes with PAN:EC:PC: $(100 - x)$ wt% Pr_4NI + x wt% MgI_2, I_2, for $x = 0$, 8.3, 16.6, 33.3, 50.0, 100 prepared by changing the weight ratio of Pr_4NI and MgI_2, while keeping the total weight of the two iodide salts constant at 0.06 g are shown in Table 1. The "gel" nature of the six electrolyte samples has been verified by the "inverted bottle test" as shown in Fig. 1.

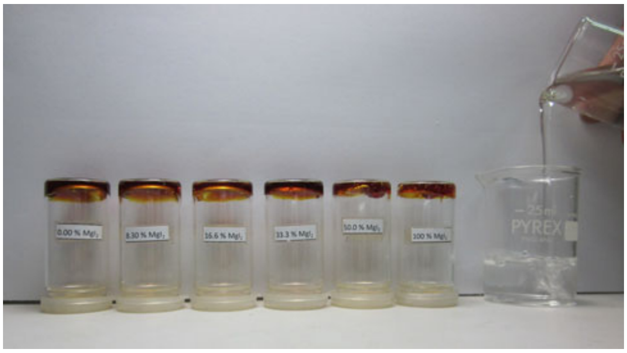

Fig. 1 The six gel electrolyte samples prepared with different MgI_2/Pr_4NI weight ratios in "inverted" sample bottles to show the gel nature of the electrolytes. From *left to right*, the MgI_2 wt% are: 0, 8.3, 16.6, 33.3, 50, 100

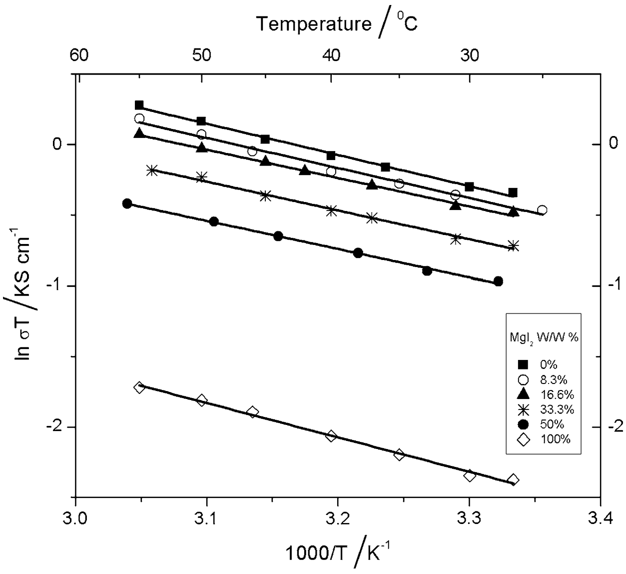

Fig. 2 The variation of ln σT plotted against the reciprocal absolute temperature for PAN/EC/PC/MgI_2/Pr_4NI/I_2 gel electrolytes containing different MgI_2/Pr_4NI ratios

The variations of ln σT plotted against the reciprocal temperature for six different electrolyte compositions are shown in Fig. 2. The electrolyte containing only Pr_4NI as the salt (sample *A*) has the highest conductivity at all measured temperatures. It has a conductivity of 2.37×10^{-3} S cm^{-1} at 27 °C. The conductivity of the electrolytes gradually decreases with the addition of MgI_2 and the electrolyte containing only MgI_2 (sample *F*) shows the lowest conductivity of 3.1×10^{-4} S cm^{-1} at 27 °C.

From the linear shapes shown in Fig. 2, the conductivity appears to follow 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.

In order to explain the observed variation of conductivity with reciprocal temperature, we make use of the fact that these PAN-based gel electrolytes are formed essentially by "entrapping" the EC/PC co-solvent-based electrolytic solution in the matrix formed by PAN [10, 34, 35]. PC is a solvent with low viscosity and high dielectric constant. While the high dielectric constant favors salt dissociation, the low viscosity would lead to high ionic mobility in the electrolytic solution. Therefore, one would expect the conducting properties of the PAN-based gel electrolyte system to be determined essentially by the properties of the entrapped electrolytic solution at different salt concentrations.

According to Fig. 2, the activation energy values, which correspond to the Arrhenius plots, are almost constant for all six gel electrolyte samples studied and essentially independent of the salt concentration ratios [MgI_2]/[Pr_4NI]. The average value of the activation energy for the six electrolyte sample is 0.18 eV. The ion transport in organic solution electrolytes appears to be governed by a single activation process which depends on the solvent family [36–38]. According to some recent reports, for a given salt (or a salt mixture), the activation energy is largely independent of the salt concentration for low and moderate concentrations and the type of salt used but depends essentially only on the type of solvent, in particular on the nature of the solvent heteroatom [37, 38]. 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. On the other hand, in a solid electrolyte, the ion transport would consist of thermally activated hopping from an occupied site to a vacant site, with an energy barrier equal to the activation energy, E_a. In the case of organic liquid electrolytes and amorphous polymer electrolytes, the immediate environment surrounding the mobile ionic species undergoes dipole rearrangement in response to the change in position of the mobile ion, and therefore, the energy of activation would involve the energy required for rearrangement of the local structure.

It is possible to use a similar interpretation to explain the observed conductivity vs temperature variation of the present gel electrolyte system. The energy of activation, therefore, depends to a large extent, on the nature of the EC/PC co-solvent and essentially unaffected by the type and the concentration of the salt(s). This would explain the essentially similar activation energies seen for the linear conductivity plots depicted in Fig. 2.

The ionic conductivity of the gel electrolyte sample with only MgI_2 as the iodide salt (sample *F*) originates from two types of ions, namely Mg^{++} ions and iodide (I^-/I_3^-) ions and all these ions contribute to the conductivity of this sample. On the other hand, the ionic conductivity of the gel electrolyte sample with only Pr_4NI as the iodide salt (sample *A*) is the highest. As the cation Pr_4N^+ in this electrolyte sample is bulky, the iodide ions (I^-) are expected to make the dominant contribution to the ionic conductivity of this sample. Ionic dissociation also should be high for Pr_4NI rich samples. As the weight percentage of MgI_2 in the electrolyte increases from sample *A* to *F*, and Pr_4NI is gradually replaced by MgI_2, the drop in ionic conductivity is evidently due to the low mobility of the doubly charged Mg^{++} cations and also due to low dissociation of MgI_2 salt (Fig. 2).

Results of the DC polarization tests are shown in Fig. 3. To check the electronic conductivity, DC tests were performed on electrolyte samples sandwiching them between two SS electrodes in the cell configuration SS/electrolyte/SS, and only the curve taken for the 100 wt% MgI_2 containing electrolyte (sample *F*) is shown in the figure as a

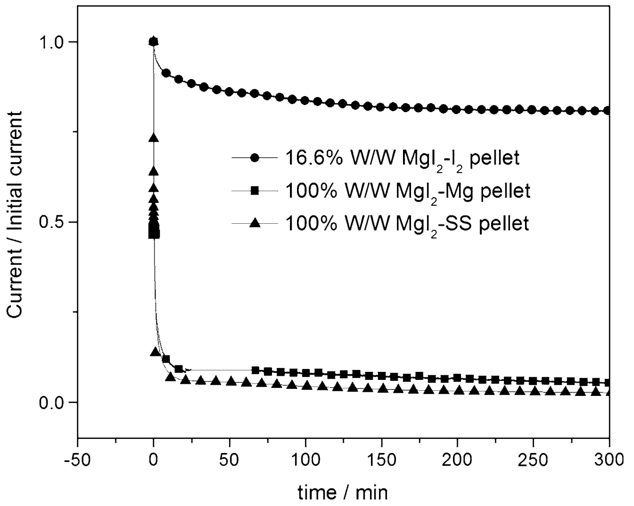

Fig. 3 Current/initial current versus time plots for the some selected electrolyte samples obtained by DC polarization test with iodine non-blocking electrodes, Mg non-blocking electrodes, and stainless steel blocking electrodes

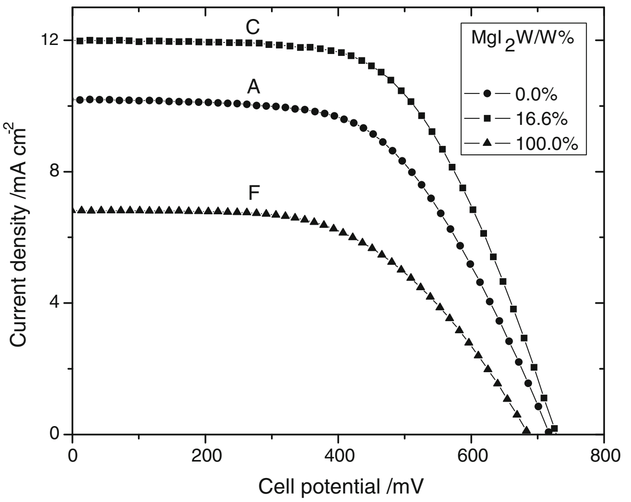

Fig. 4 The photocurrent–photovoltage (*I*–*V*) characteristics of three solar cells where the gel electrolyte salt compositions are: (*A*) 0 wt% MgI_2 (only Pr_4NI) (*C*) 16.6 wt% MgI_2 + 83.4 wt% Pr_4NI and (*F*) 100 % MgI_2. (100 mW cm^{-2}, A.M. 1.5, active area 0.25 cm^{-2})

representative example. All the electrolyte samples exhibited negligible electronic conductivity. The DC polarization curve for the 100 wt% MgI_2 sample, taken with metallic magnesium (Mg) electrodes in the cell configuration Mg/electrolyte/Mg, shows that, even in this sample which has the highest Mg^{++} content, the Mg^{++} ion conductivity is small. The DC curve taken with iodine pellet (I_2) non-blocking electrodes for the gel electrolyte sample with 16.6 wt% MgI_2 (Sample *C*, which corresponds to the highest efficiency DSSC) in the I_2/electrolyte/I_2 cell configuration, clearly shows that this sample has the highest iodide ion (I^-/I_3^-) conductivity contribution of about 80 %. All the other five samples showed lesser iodide ion conductivity values. The ionic transference number was estimated by measuring the height of the DC polarization curve from the DC curve taken with SS electrode. As estimated from the steady-state DC polarization curves, the electronic transference number is 0.02 and the Mg^{++} ion transference number is 0.10 for the 100 wt% MgI_2 sample *F* and the iodide ion (I^-) transference number is 0.79 for the sample *C* containing 16.6 wt% MgI_2 + 83.4 wt% Pr_4NI as the iodide salt mixture in the gel electrolyte. Thus, the sample *C* has exhibited the highest iodide ion conductivity.

3.2 Characterization of dye-sensitized solar cells

The photocurrent–photovoltage (*I*–*V*) characteristics of six solar cells of configuration glass/FTO/TiO_2/electrolyte/Pt/FTO/glass were measured using gel electrolyte samples with six different $MgI_2/Pr_4N^+I^-$ salt ratios (samples *A* to *F*). However, for clarity only the *I*–*V* curves for three solar cells fabricated with the gel electrolyte with 0 wt% MgI_2 (Sample *A*), 16.6 wt% MgI_2 (Sample *C*), and 100 wt% of MgI_2 (sample *F*) are shown in Fig. 4. Solar cell parameters such as the open circuit voltage (V_{oc}), the short circuit current density (J_{sc}), the fill factor (FF %), and the efficiency (η) for all six solar cells are shown in Table 2.

The efficiency (η) and the short circuit current density (J_{sc}) of all six solar cells as a function of MgI_2 wt% in the gel electrolyte are shown in Fig. 5. It is interesting to see that the efficiency variation follows a similar trend as the J_{sc}. As seen from this figure, the solar cell *C* fabricated with the gel electrolyte containing the binary iodide mixture with 16.6 wt% MgI_2 +83.4 wt% Pr_4NI has shown the highest energy conversion efficiency of 5.18 % and has the highest short circuit photo current density of 11.99 mA cm^{-2}. The solar cells fabricated using the electrolyte with only MgI_2 (sample *F*) and with only Pr_4NI (sample *A*) as

Table 2 Parameters of solar cells with PAN:EC:PC: (100 − *x*) Pr_4NI + *x* wt% MgI_2, I_2 gel electrolyte samples of six different MgI_2/Pr_4NI wt% ratios

Electrolyte	MgI_2 % (w/w)	Relative I^- (mol%)	J_{sc} (mA cm^{-2})	V_{oc} (mV)	FF (%)	η (%)
A	0	1.81	10.19	718.0	56.80	4.16
B	8.3	1.83	11.41	731.0	53.61	4.47
C	16.6	1.85	11.99	727.5	59.40	5.18
D	33.3	1.89	11.12	697.6	52.42	4.07
E	50	1.93	8.08	689.8	55.22	3.08
F	100	2.04	6.82	684.0	54.83	2.56

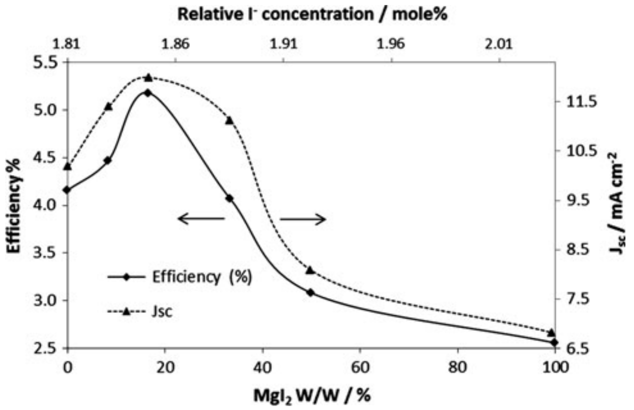

Fig. 5 The variation of (*thin line*) the efficiency (η) and (*dotted line*) the short circuit photo current density (J_{sc}) of all six solar cells as a function of the wt% MgI_2

the iodide salt in the gel electrolyte have shown efficiencies of 2.56 and 4.16 %, respectively. The use of the binary iodide mixture has clearly enhanced the solar cell efficiency in all the six DSSCs and for the best DSSC the efficiency is increased by a factor of about 25 % compared to the higher efficiency end member. It is also important to note that from Table 2, although the relative molar iodide ion concentration in the six gel electrolyte samples increases gradually with the addition of MgI_2, the short circuit current density J_{sc} goes through a maximum at 1.85 molar % of [I^-]. The remaining iodide ions at higher [I^-] concentrations evidently do not contribute to J_{sc} and solar cell action and very likely remain in the electrolyte as neutral and higher ionic aggregates.

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. According to Table 2, the V_{oc} value and the fill factor (FF) of the solar cells also vary with MgI_2 wt% but these variations do not follow a definite trend. However, the variation of the efficiency with MgI_2 wt% follows an identical trend as the J_{sc}. Therefore, the dominant contribution to the solar cell efficiency clearly comes from the J_{sc} and is determined essentially by the relative amount of iodide/tri-iodide (I^-/I_3^-) ion conductivity in the electrolyte.

3.3 Cation influenced charge-transfer dynamics in DSSCs

It is well-established that cations in the electrolytes used play an important role in the performance of DSSCs. In addition to contributing to ionic dissociation to generate iodide (I^-) ions which essentially determines the J_{sc}, 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. Cations in the electrolyte can efficiently screen the photo-injected electrons on the TiO_2 film, insuring that electro-neutrality is maintained throughout the TiO_2 network. Ionic migration in the electrolyte is therefore strongly correlated with electron transport in the TiO_2 film.

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 of TiO_2, and the cations in the electrolyte become adsorbed into the TiO_2 film for charge compensation. The V_{oc} is determined by the relative positions of the flat-band potential and the redox potential of the electrolyte ($V_{oc} = |V_{fb} - V_{red}|$). The flat-band potential of TiO_2 is moved positively due to the cation adsorption and it is associated with the drop in photovoltage of the DSSC. The associated drop in photovoltage depends upon the size and charge density of the cations. As compared to the bulky cations, small-sized cations could easily be adsorbed onto the TiO_2 grain surface resulting in a larger potential drop. However, due to this positive shift of the TiO_2 flat-band potential, the driving force for the charge injection from the excited dye molecules to TiO_2 increases, resulting in large injection efficiency and thus a higher photocurrent at the expense of the photovoltage.

3.4 Flat-band potential (V_{fb})

The positions of the flat-band potential, V_{fb} determined from Mott–Schottky ($1/C^2$ vs V) plots taken on a dye sensitized TiO_2 electrode immersed in an electrolyte solution containing EC, PC, MgI_2, and Pr_4NI salts, but without PAN are shown in Fig. 6 along with V_{oc} values of the corresponding solar cell. However, it should be noted that the electrolyte used in the solar cell was the "gel" electrolyte, containing PAN. This experiment clearly shows the movement of the flat-band potential of the TiO_2 electrode in contact with the electrolyte solution containing Mg^{++} and Pr_4N^+ cations. From this figure, it is clear that the two end member compositions agree well with expected results, that the V_{fb} value for the 100 wt% MgI_2 electrolyte is lower than that for the 100 wt% Pr_4NI electrolyte. Also, the V_{fb} value gradually decreases from 8.3 wt% MgI_2 composition to 100 wt% MgI_2 composition evidently due to the increased concentration of Mg^{++} ions adsorbed into the TiO_2 film. The apparent "maximum" in V_{fb} seen at 8.3 wt% MgI_2 composition is due to the lower V_{fb} value of the 100 wt% Pr_4NI electrolyte. It is interesting to see that

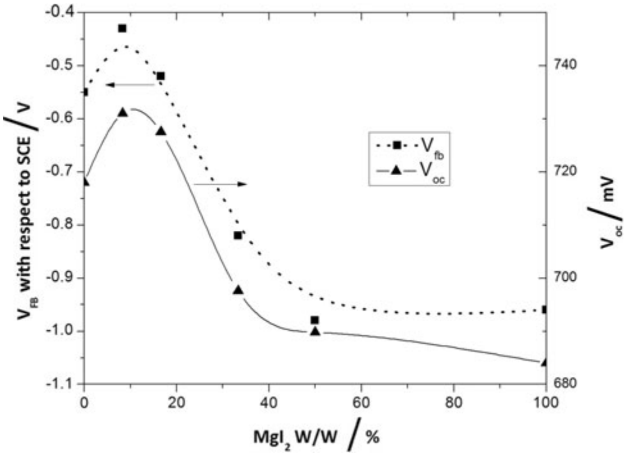

Fig. 6 Variation of the flat-band potential (V_{fb}) with wt% MgI_2 for the TiO_2 electrode immersed in the solution electrolyte EC/PC/MgI_2/Pr_4NI. Variation of the open circuit photovoltage (V_{oc}) of the DSSC with PAN/EC/PC/MgI_2/Pr_4NI/I_2 gel electrolyte is also shown for comparison

the V_{oc} values of the DSSC with corresponding "gel" electrolyte compositions follow the same order. This is a further evidence that the PAN host matrix essentially has no interaction with the electrolyte solution other than holding it, giving the electrolyte the "gel" character in agreement with several reports on similar PAN-based Li^+ ion conducting gel electrolytes [14–16].

3.5 The role played by mixed cation salt systems

We find that only very few reports in the literature deals with the mixed cation binary iodide salt mixtures emphasizing on the effect of cations on the performance of DSSCs. For the binary iodide system LiI + KI in a PEO-based gel electrolyte, the maximum solar cell efficiency of 4.5 % has been achieved at 14.5 wt% of KI [28]. In this system, the J_{sc} has also reached a maximum at 14.5 wt% KI concentration. However, these authors have not attempted to correlate the solar cell efficiency directly with the J_{sc} and the iodide ion conductivity in the electrolyte. The influence of different single iodide salts on the performance of dye sensitized solar cells containing phosphozene-based non-volatile electrolytes has been reported [39]. The photovoltage was highest in the 1-methyl-3-propylimidazolium (PMII) system and decreased in the order PMII > NH_4I > NaI > LiI. The LiI salt has produced the lowest V_{oc}. The effect of cations on the open circuit photo-voltage and charge injection efficiency of dye has been reported for Li^+ and 1,2-dimethyl-3-hexylimidazolium ion [40]. The electrolyte containing Li^+ has produced a lower V_{oc} compared to the cell with imidazolium ion.

The influence of cation charge density on the photovoltaic performance of DSSCs has been studied for Li^+, Na^+, K^+, and dimethyeimidazolium (DMI^+) ions by Shi et al. [41]. The results show that, from DMI^+ to Li^+ the short circuit current density (J_{sc}) increases due to the increase in electron injection rates with increase in cation charge density. The drop in V_{oc} is higher for the Li^+ ions due to a larger downward shift of the conduction band edge induced by the adsorption of Li^+ cations on the surface of nano titania grains. From the above findings, it is clear that different cations in the electrolyte can show different effects on V_{oc}. Small radius cations such as Li^+ and K^+ can intercalate into the lattice of nano TiO_2 causing a positive shift of the conduction band edge potential. This increases the driving force for charge injection and typically leads to a higher J_{sc} at the expense of V_{oc}. In our binary system also we observe a similar behavior with respect to the two end members. The 0 wt% MgI_2 (or 100 wt% Pr_4NI) cell exhibiting a V_{oc} of 718.0 mV and the 100 wt% MgI_2 cell exhibiting a V_{oc} of 684.0 mV are consistent with above findings.

In the present system the adsorption of cations, Mg^{++} and Pr_4N^+ ions, on the surface of nano titania grains would cause the conduction band edge to move to the positive side (downward shift), thereby decreasing the V_{oc} values. This effect is expected to be more pronounced for smaller Mg^{++} ions (ionic radius, 0. 072 nm) than for bulky Pr_4N^+ ions (ionic radius, 0.46 nm) as the number of adsorbed Mg^{++} cations per unit area of nano titania grain surface would be much greater than the number of Pr_4N^+ ions adsorbed, due the difference in their sizes. Therefore, the drop in V_{oc} due to this effect should be greater for the solar cell with electrolyte with 100 wt% MgI_2 concentration (V_{oc} = 684.0 mV for sample *F*) compared to the drop in V_{oc} for the cell with 100 wt% Pr_4NI electrolyte (V_{oc} = 718.0 mV for sample *A*). The observed drop in the V_{oc} value due to the effect of both types of cations for the cell with highest efficiency (sample *C*) is the second smallest (compared with the two end members), resulting a V_{oc} of 727.5 mV (see Table 2). This is also the second highest V_{oc} value in the series.

3.6 The occurrence of the maxima in efficiency and J_{sc}

3.6.1 *Electrolyte effect*

Up to the maximum efficiency composition of 16.6 wt% MgI_2 which corresponds to the molar iodide ion concentration [I^-] of 1.85 %, the total conductivity decreases gradually with increasing MgI_2 content although the iodide ion conductivity contribution and hence the J_{sc} increases (Figs. 2, 3). Drop in total conductivity is clearly due to the dominating negative effect of Mg^{++} ions in reducing the cationic conductivity very likely due to the low ionic dissociation and low ionic mobility by doubly charged Mg^{++} cations. However, Pr_4NI provides additional iodide ions through higher salt dissociation, which helps to boost up the iodide ion conductivity and J_{sc} at these low MgI_2 concentrations, up to J_{sc} max resulting in the steeper rise in J_{sc} (Fig. 5) and hence the efficiency. The contribution from bulky Pr_4N^+ cations to overall ionic conductivity is low due to their low mobility. However, due to high ionic dissociation of Pr_4NI, the number of "free" iodide ions (I^- and I_3^-) increases resulting maximum iodide ion conductivity at 16.6 wt% MgI_2 composition. Beyond this MgI_2 salt concentration, both the iodide ion conductivity as well as the total conductivity drops with increasing MgI_2 content. This is evidently due to the dominating negative effect by the Mg^{++} cations as described above, and due to the formation of ion pairs, ionic triplets, and higher aggregates, which do not contribute to conductivity. Also the increase in viscosity due to high concentration of salts and solutes and possible cross linking of the polymer by the high charge density Mg^{++} cations can contribute to the ionic mobility drop. Therefore, due to both, the reduced number of free ions and the reduced mobility, the total ionic conductivity as well as the iodide ion conductivity drops at high MgI_2 salt concentrations.

3.6.2 Electrode effect

Electron dynamics at the TiO_2 electrode also play a major role in determining the J_{sc}. As described earlier, small cations are more readily absorbed into the TiO_2 electrode than cations having larger size, and in return, the conduction band of TiO_2 is shifted to the more positive side, which reduces the V_{oc}. The difference could be due to the fact that bulky Pr_4^+ cations can hardly coordinate to oxygen of complexation sites in the sensitizer. Moreover, Pr_4^+ hardly penetrates the space between the adsorbed dye molecule and the surface of TiO_2. It could remain only at a certain distance of the TiO_2 surface forming some cloud of positive charges, inducing just a slight positive shift of the CB of TiO_2. This could have as consequence a poor electron injection because of the poor overlap between dye excited level and CB of TiO_2.

It can be remarked that the smaller the cation size, the higher is the photogenerated current. This is due to the fact that small cations can be adsorbed or intercalated easily on the TiO_2 surface forming a thin electric double layer resulting in higher concentration of I^- at the TiO_2/dye interface where regeneration of the oxidized dye cation can be facilitated. On the other hand, intercalated small size cations screen-well the injected electrons and enhance the J_{sc}. In addition to the electrolyte effect, the initial increase in J_{sc} with Mg^{++} ion concentration in the present study can also be linked to a high screen effect generated by Mg^{++} to the photogenerated electron–hole pair (oxidized dye and injected electron). Kelly et al. [26] attributed such cation-dependent electron injection yield to a thermodynamic effect, in which cation adsorption induce a positive shift of TiO_2 acceptor states, resulting in more favorable energetics for electron injection producing an increase in J_{sc} followed by a decrease in V_{oc}. They attributed the change in J_{sc} and V_{oc} to the lowering of the TiO_2 conduction band level in the presence of cations. However, surface adsorption of Mg^{++} ions on TiO_2 can reduce the recombination of injected electrons and the mediator. In fact, the electron injected into the TiO_2 network and the negative charges of the mediator are screened effectively over a diameter of the ionic cloud due to Mg^{++} ions. This could substantiate the initial steep increase of J_{sc} with Mg^{++} ion concentration.

Wang et al. [42] and Grätzel et al. [43]. have also reported that, an increase in photocurrent is in the order of $Mg^{++} > Li^+ > Na^+$ and attributed that to the charge density of the metal ions which are found to be potential-determining. While J_{sc} is increased in devices when the concentration of cations in the electrolyte is augmented, the open circuit voltage, V_{oc}, in contrast decreases but not linearly.

In this DSSC system, as seen from the variation of the efficiency,η and the short circuit photo current density, J_{sc} with MgI_2 concentration (Fig. 5), the solar cell performance appears to be governed essentially by the short circuit photocurrent, which exhibit a maximum at 16.6 wt% MgI_2 electrolyte composition. Although the molar iodide ion concentration $[I^-]$ continues to increase with MgI_2 content (Table 2), the iodide ion conductivity which determines the value of J_{sc} exhibits a maximum at 16.6 wt% MgI_2 composition.

If the gel electrolyte had only the Pr_4NI as the iodide salt, the iodide ion concentration would decrease with decreasing salt concentration giving rise to a decrease in J_{sc} and hence a drop in DSSC efficiency. Similarly, if the gel electrolyte had only MgI_2 as the iodide salt, the iodide ion concentration would decrease with increasing salt concentration due to reduced ionic dissociation by doubly charged Mg^{++} cations, resulting a decrease in J_{sc} and hence the efficiency. However, the presence of both these iodide salts in the electrolyte has given rise to the occurrence of the J_{sc} maximum as the concentration ratio of the iodide salts changes. The beneficial electrolyte effect of using two dissimilar cations in increasing the J_{sc} and enhancing the DSSC efficiency is evident from this mechanism.

Electrode effects arises when small size Mg^{++} cations are adsorbed into the nanoporous TiO_2 film causing enhancement in J_{sc} due to improved electron dynamics at the semiconductor/electrolyte interface. This results in increasing the J_{sc} at the expense of the V_{oc}. The presence of Pr_4NI, with a bulky cation, would insure that the drop in V_{oc} is small due to the adsorption of bulky Pr_4^+ cations into TiO_2 surface. A relatively higher V_{oc} is therefore maintained. The combined effect of these two types of cations, therefore, would insure that the DSSC efficiency reaches a maximum at some optimal slat ratio in the electrolyte, although the J_{sc} continue to be the dominating parameter.

4 Conclusions

This paper reports the enhancement of efficiency of a N719 dye sensitized solar cell, due to the mixed cation effect in a PAN-based gel polymer electrolyte with a binary iodide system consisting of a small alkali cation (K^+) and a bulky cation (Pr_4N^+). The variation of efficiency with wt% MgI_2 follows a similar trend as J_{sc} which appears to be governed by the I^-/I_3^- conductivity in the electrolyte. High iodide conductivity in the best solar cell is further supported by the iodide ion transference number estimated from DC polarization data taken with iodine non-blocking electrodes. The dependence of the short circuit photocurrent and the open circuit photovoltage on the cation type of the two end member compositions is generally in agreement with the reported data for related but single salt systems. The maximum efficiency and the maximum in J_{sc} occur at 16.6 wt% MgI_2 concentration, which corresponds to a relative molar iodide ion concentration of 1.85 %. With 100 wt% MgI_2 and 100 wt% Pr_4NI, efficiencies under AM 1.5 illuminations are 2.56 and 4.16 %, while 16.6:83.4 MgI_2:Pr_4NI weight ratio shows the highest efficiency of 5.18 %. The efficiency enhancement, relative to the high efficiency end member is about 25 %. It should be mentioned here that, a similar efficiency enhancement due to mixed cations has also been observed by us for DSSCs based on solution electrolyte, EC/PC, $MgI_2 + Pr_4NI$ without PAN.

The efficiency enhancement achieved by employing the binary iodide mixture in the gel electrolyte instead of a single iodide salt, could be utilized in different types of dye sensitized solar cell systems studied so far (and to be studied hence forth) using polymeric, gel or solution electrolytes to increase the efficiency by a considerable percentage.

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