



Short communication

Dye-sensitized, nano-porous TiO₂ solar cell with poly(acrylonitrile): MgI₂ plasticized electrolyte

T.M.W.J. Bandara^{a,c,*}, M.A.K.L. Dissanayake^a, I. Albinsson^b, B.-E. Mellander^c^a Department of Physics and Postgraduate Institute of Science, University of Peradeniya, Peradeniya, Sri Lanka^b Department of Physics, Gothenburg University, Göteborg, Sweden^c Department of Applied Physics, Chalmers University of Technology, Göteborg, Sweden

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ABSTRACT

Dye-sensitized solar cells are promising candidates as supplementary power sources; the dominance in the photovoltaic field of inorganic solid-state junction devices is in fact now being challenged by the third generation of solar cells based on dye-sensitized, nano-porous photo-electrodes and polymer electrolytes. Polymer electrolytes are actually very favorable for photo-electrochemical solar cells and in this study poly(acrylonitrile)–MgI₂ based complexes are used. As ambient temperature conductivity of poly(acrylonitrile)–salt complexes are in general low, a conductivity enhancement is attained by blending with the plasticizers ethylene carbonate and propylene carbonate. At 20 °C the optimum ionic conductivity of $1.9 \times 10^{-3} \text{ S cm}^{-1}$ is obtained for the (PAN)₁₀(MgI₂)_n(I₂)_{n/10}(EC)₂₀(PC)₂₀ electrolyte where $n = 1.5$. The predominantly ionic nature of the electrolyte is seen from the DC polarization data. Differential scanning calorimetric thermograms of electrolyte samples with different MgI₂ concentrations were studied and glass transition temperatures were determined. Further, in this study, a dye-sensitized solar cell structure was fabricated with the configuration Glass/FTO/TiO₂/Dye/Electrolyte/Pt/FTO/Glass and an overall energy conversion efficiency of 2.5% was achieved under solar irradiation of 600 W m⁻². The *I*–*V* characteristics curves revealed that the short-circuit current, open-circuit voltage and fill factor of the cell are 3.87 mA, 659 mV and 59.0%, respectively.

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1. Introduction

The extensive and freely available energy of the sun is one of the major energy forms that can be harnessed to fulfil future energy requirements. Nano-porous, dye-sensitized solar cells are promising devices to convert solar energy to electrical energy, due to a prospected low cost, environmentally friendly operation and relatively high efficiency [1–5]. The recent development of solid polymer electrolytes for dye-sensitized solar cells is now challenging the dominance in the photovoltaic field of inorganic solid-state junction devices [1,3].

In general, a dye-sensitized PEC solar cell consists of a dye-coated nano-porous TiO₂ photo-electrode, a platinum coated counter electrode and a thin electrolyte layer sandwiched between these two electrodes. It is reported that PEC solar cells containing solvent electrolytes have reached a power conversion efficiency of about 11% [4,5]. However, in general, PEC solar cells with liquid-

type electrolytes has several disadvantages such as poor stability of performance due to the difficulty to control side reactions, risk for leakage and toxicity of inserted organic solvents, etc. [6,7]. Thus, research has been carried out to substitute organic-solvent electrolytes with p-type inorganic semiconductors or hole-conducting materials but currently with mediocre success [8–10]. However, in the recent past, PEC solar cells that employ polymer electrolytes were prepared by adding low molecular weight gelators or polymer materials or ceramic fillers have exhibited good conductivities and efficiencies [11–14].

There are many advantages of using polymer electrolytes in fabricating quasi-solid-state solar cells. Mainly, polymer gel electrolytes have shown relatively high ionic conductivity. In addition, their flexibility provides good interfacial contacts with nano-porous TiO₂ film and counter electrode. The other advantages are simplicity of fabrication procedure and chemical inertness of the host polymer matrix to the electrodes. Thus the search for prominent solid or gel electrolyte to be used in PEC solar cells is highly important. Polyacrylonitrile (PAN) is one of the host polymers widely used as polymer electrolytes in electrochemical power sources and its chemical and physical properties are also suitable to be used as host polymer matrix for dye-sensitized solar cells [15].

* Corresponding author at: Department of Applied Physics, Chalmers University of Technology, Kemivägen 9, SE-412 96 Göteborg, Sweden. Tel.: +46 031 7723354; fax: +46 031 7721236.

E-mail address: awijendr@yahoo.com (T.M.W.J. Bandara).

Even though, research on the use of solid or gel polymer type electrolytes in electrochemical devices like secondary batteries, fuel cells and electro-chromic devices have increased rapidly [15,16], research done on solid-state solar cells with polymer electrolytes is very limited. In particular, it is very difficult to find reports on PEC solar cells with polymer electrolytes containing divalent metal salt, which would enhance the anionic conductivity necessary for PEC cell action. Thus, in this study we focused our attention to fabricate such a PEC solar cell using a polymer electrolyte complexed with a divalent metal salt. The advantage of using a divalent salt like MgI_2 is the possibility of making the cation immobilized via cross linking and to provide an efficient charge transfer mechanism via I^- migration at the interfaces. I^-/I_3^- is the widely used and mutually compatible redox couple for the electrolytes used for TiO_2 based PEC solar cells, where the I^- ion shuttles in between counter electrode and the TiO_2 photo-electrode giving efficient charge transfer mechanism at the interfaces enabling efficient electron transport in the external circuit. However, ambient temperature conductivities of PAN-salt complexes are in general very low and therefore a conductivity enhancement is needed for PEC cell applications. This is attained by blending with plasticizers such as ethylene carbonate (EC) and propylene carbonate (PC) which have relatively high dielectric constants and improve both the ion mobility and salt solvation [15,17].

In this study, conductivity measurements were carried out to determine the optimum salt concentration for maximum conductivity and this sample was used in PEC solar cells. Further, the electrolyte was characterized using differential scanning calorimetry (DSC) and DC polarization. I - V characteristic curves were used to estimate the energy conversion efficiency, fill factor and short-circuit current and open-circuit voltage.

2. Experimental

PAN (Mw. 150,000), MgI_2 , Iodine chips, EC, PC, all with purity greater than 98% purchased from Aldrich were used as starting materials. All these chemicals, except I_2 , EC and PC, were vacuum dried for 24 h in a vacuum oven prior to use. Ruthenium dye was purchased from Solaronix SA.

2.1. Electrolyte preparation

For preparing the electrolyte samples the appropriate weights of PAN, MgI_2 , I_2 , EC and PC were selected according to chemical formula $(PAN)_{10}(MgI_2)_n(I_2)_{n/10}(EC)_{23}(PC)_{20}$ and the “ n ” value was varied. In this formula PAN represents only one monomer of polymer. The selected compositions of MgI_2 , I_2 , EC and PC were mixed in a glass bottle and then PAN was added. The mixture was magnetically stirred at $\sim 80^\circ C$ for a few minutes, until a homogeneous viscous slurry was obtained. Heating was controlled so that iodine will not evaporate. The resulting slurry after stirring was casted on to a glass plate and pressed by another glass plate and finally kept at room temperature until a thin polymer electrolyte film is formed.

2.2. Photo-electrode preparation

Nano-porous TiO_2 thin films with thickness 5–10 μm were prepared on fluorine-doped tin oxide (FTO) glass plates following an already published procedure [18]. The TiO_2 coated electrode was immersed in the ethanolic solution of *cis*-diisothiocyanato- N,N' -bis(2,2'-bipyridyl)-4,4'-dicarboxylic acid)-ruthenium(II) dihydrate $[RuL_2(NCS)_2 \cdot 2H_2O]$ dye while both were hot ($\sim 60^\circ C$). After 24 h absorption, the electrode was withdrawn from the dye

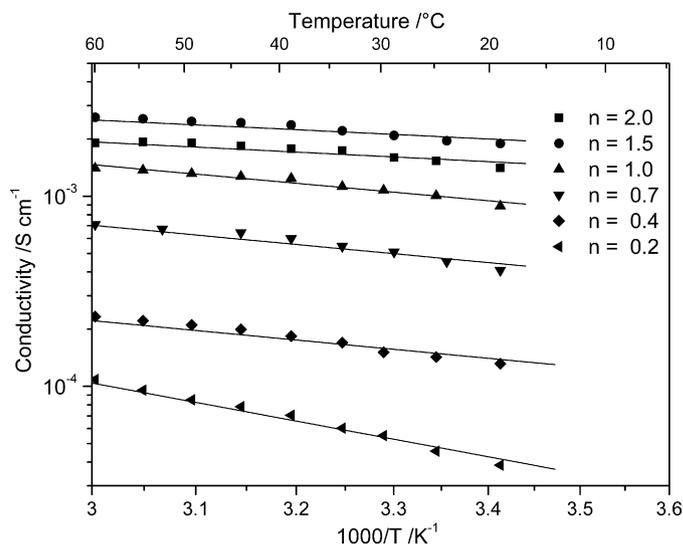


Fig. 1. The conductivity versus $1000/T$ for $(PAN)_{10}(MgI_2)_n(I_2)_{n/10}(EC)_{20}(PC)_{20}$ electrolyte for different “ n ” values.

solution and washed thoroughly with acetone to remove unabsorbed dye and loosely bound TiO_2 particles from the dye-coated plate.

2.3. Characterizing the electrolyte

Complex impedance measurements were taken using a HP 4291 ARF impedance analyzer in the frequency range 1 MHz–1 GHz and in the temperature range 20–60 $^\circ C$. Disc shaped electrolyte films of 5 mm diameter and 0.1–0.4 mm thickness were sandwiched between two polished stainless steel blocking electrodes and ac-impedance measurements were performed in order to obtain dielectric data. A flow of nitrogen gas was maintained over the sample to prevent contact with atmospheric moisture. DC polarization tests were carried out by sandwiching a disc shaped electrolyte sample between two stainless steel (SS) blocking electrodes in the SS/Electrolyte/SS configuration and in the SS/ I_2 /Electrolyte/ I_2 /SS symmetrical configuration. Thermograms were taken using a Mettler Toledo DSC 30 differential scanning calorimeter using a heating rate of $10^\circ C min^{-1}$ between -140 and $120^\circ C$ in the heating and cooling cycles.

2.4. Characterizing solar cells

Solid-state PEC solar cells were fabricated by sandwiching polymer electrolyte films of thickness from about 0.2 mm between the dye-sensitized TiO_2 film and a previously prepared platinumized conducting glass plate with the configuration of, Glass/FTO/ TiO_2 /Dye/Electrolyte/Pt/FTO/Glass. Fabricated solar cells were characterized by measuring I - V curves using a computer controlled Potentiostat/Galvanostat HA-301 instrument with $\sim 600 W m^{-2}$ solar irradiation.

3. Results and discussion

Fig. 1 shows the temperature dependence of the conductivity of $(PAN)_{10}(MgI_2)_n(I_2)_{n/10}(EC)_{20}(PC)_{20}$ electrolyte samples for different “ n ” values. The studied gel polymer electrolyte samples with “ n ” value greater than one showed higher conductivities, of the order of $10^{-3} S cm^{-1}$. The highest conductivity is given by the electrolyte sample with “ n ” value 1.5 out of the studied samples. A conductivity enhancement of more than an order of magnitude has thus been observed merely due to the change of salt concentration.

Table 1

Activation energy, E_a , and conductivity (at 20 °C) values of plasticized PAN electrolyte for different MgI_2 contents.

n Value	E_a /eV	$\sigma_{20^\circ C}$ /mS cm ⁻¹
0.2	0.24 ± 0.006	0.04
0.4	0.15 ± 0.005	0.14
0.7	0.14 ± 0.009	0.41
1.0	0.12 ± 0.007	0.89
1.5	0.10 ± 0.005	1.90
2.0	0.10 ± 0.007	1.41

It can be observed that the conductivity variation given in Fig. 1 shows more or less Arrhenius behavior within the measured temperature range. The activation energy, E_a , was calculated fitting the data to the Arrhenius equation.

$$\sigma T = B \exp\left(-\frac{E_a}{k_B T}\right) \quad (1)$$

where, B is an exponential factor, E_a the activation energy, k_B the Boltzmann constant, and T the absolute temperature. The E_a values are shown in Table 1 and these low values corroborate high conductivities of the samples. As expected the lower the activation energy the higher is the conductivity.

The differential scanning calorimetric (DSC) thermograms of plasticized polymer electrolyte samples are shown in Fig. 2 for different MgI_2 contents. A glass transition can clearly be observed for all the samples. The glass transition temperature, T_g , values extracted are also shown in Fig. 2. However, no significant first order phase transition is visible in the DSC in the temperature range -120 to 100 °C. Thus, these amorphous polymer electrolyte samples show good thermal stability in the temperature range where solar cells are operated.

Fig. 3 shows variation of ionic conductivity at temperatures 20, 40 and 60 °C and T_g for different salt contents. As T_g is related to the main chain flexibility of the host polymer and its disordered structure [19,20] the T_g result can be related to a possible change in the flexibility of polymeric chains of the electrolyte due to incorporation of the salt. The T_g values show a very small variation with n , see Fig. 3. This is expected for PAN based electrolytes since the EC/PC part in the electrolyte is trapped in the polymer network and the salt has a limited effect on the PAN [21]. Minimum T_g values, -101.93 and -101.83 °C were observed for the electrolyte with $n = 1$ and 1.5. For other polymer systems the flexibility of the mate-

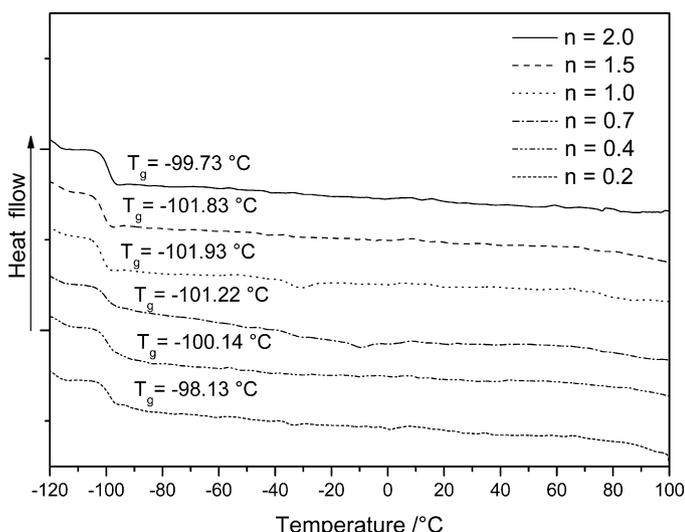


Fig. 2. DSC thermograms for $(PAN)_{10}(MgI_2)_n(I_2)_{n/10}(EC)_{20}(PC)_{20}$ polymer electrolyte for different “ n ” values.

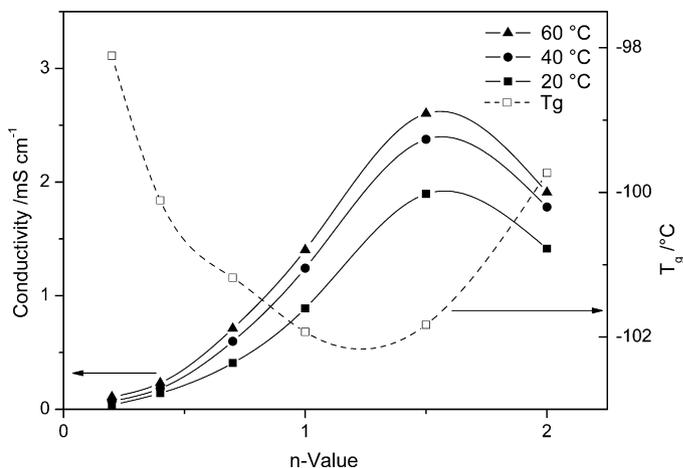


Fig. 3. Relationship between T_g and conductivity as a function of different molar fractions for $(PAN)_{10}(MgI_2)_n(I_2)_{n/10}(EC)_{20}(PC)_{20}$ electrolyte.

rial influences the mobility of charge carriers [22] and also in the present case the minimum T_g seen in Fig. 3 occurs close to the maximum conductivity. However, the conductivity maximum in this case cannot be explained using T_g alone as there can be other contributions like change of number of mobile charge carriers also. The molar conductivity, which can be obtained by dividing the conductivity by the concentration of charge carriers and is a measure of individual contributions of ions to the conductivity, may be a better indicator but, for this purpose a proper estimation of the number of mobile ions is needed. Tentatively, if we assume that all the ions are mobile then the molar conductivity of the $n = 1$ sample is higher than the molar conductivity of the $n = 2$ sample, while the actual conductivity in Fig. 3 shows the opposite. For example, at 20 °C the molar conductivity of the $n = 1$ sample is 4.13 S cm⁻¹ g mol⁻¹ and that of the $n = 2$ sample is 3.50 S cm⁻¹ g mol⁻¹.

For low salt concentrations T_g is higher but decreases with increasing salt concentration probably due to structural disorder caused by Mg^{2+} and I^- ionic species. When the salt concentration is increased further, the T_g shows an increase. This could possibly be due to the “geometrical constrictions” imposed by MgI_2 species, making the long PAN chains “immobilized”. In addition, flexibility of long polymer chains can also be reduced due to cross linking by divalent Mg^{2+} ions. The conductivity increase shown in Fig. 3 may come from increasing amount of mobile ions as well as segmental flexibility facilitated by the increasing amount of ionic species. Then the conductivity drop given for higher salt concentration seems to be due to “blocking effect” of the non-dissociated MgI_2 species and reduction of the segmental flexibility substantiated by the increase of T_g .

The results of the DC polarization measurements on the electrolyte sample with the best conductivity taken using stainless steel blocking electrodes and non-blocking iodine electrodes and under +2.0V DC bias voltages at 30 °C are shown in Fig. 4. The predominantly ionic nature of the electrolyte is seen from the DC polarization data obtained with SS blocking electrodes. The ionic and electronic transference numbers estimated from these data are $t_{ion} = 0.96$ and $t_e = 0.04$, respectively [23,24]. Thus the conductivity of the electrolyte is dominated by ions. From DC polarization data shown in Fig. 4 with iodine non-blocking electrodes reveals that ionic conductivity is dominated by iodide ions.

The photocurrent versus photo-voltage curves for the cell fabricated from PAN electrolyte system with $n = 1.5$ is shown in Fig. 5. The short-circuit photocurrent density (J_{SC}) and open-circuit voltage (V_{OC}) of the cell for solar light irradiation of 600 W m⁻² for PAN electrolyte are found to be 3.87 mA cm⁻² and 659 mV, respectively.

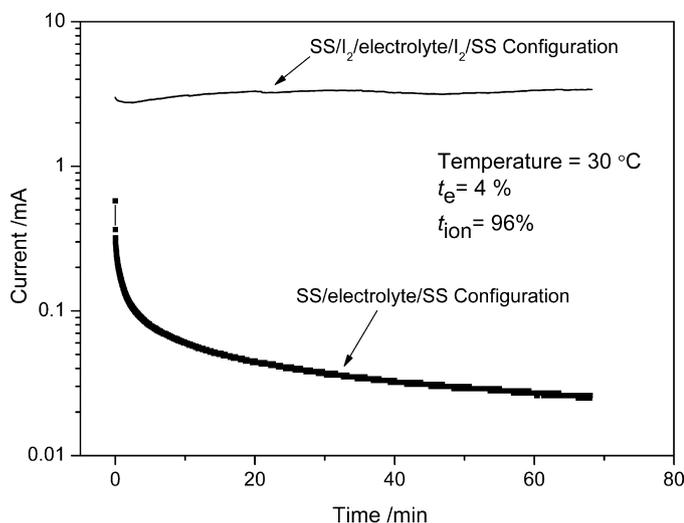


Fig. 4. Current versus time plot for the $(\text{PAN})_{10}(\text{MgI}_2)_n(\text{I}_2)_{n/10}(\text{EC})_{20}(\text{PC})_{20}$ electrolyte sample with $n=1.5$ taken from DC polarization measurements at 30°C .

The fill factor calculated using Eq. (2) for the fabricated quasi-solid-state dye-sensitized solar cell is 59.0%.

The fill factor is given by the equation,

$$ff = \frac{J_{\text{opt}} V_{\text{opt}}}{J_{\text{sc}} V_{\text{oc}}} \quad (2)$$

where J_{opt} is the current density at maximum power output and V_{opt} is the voltage at maximum power output.

The power conversion efficiency, η , of the PEC cell was calculated using (3)

$$\eta = \frac{J_{\text{sc}} V_{\text{oc}} ff}{\text{total incident power density}} \quad (3)$$

The result, $\eta=2.51\%$ is a reasonably good value compared to the overall energy conversion efficiency of PEC solar cells reported with similar intensity of irradiated light and fabricated using similar methods but with conventional liquid electrolyte [1,11,25]. However, the efficiency of present cell is quite lower than that of the reported energy conversion efficiency with liquid electrolytes [4,5] using somewhat different cells fabrication methods. Anyhow, the results are comparable with the reported efficiency of the analogous quasi-solid-state PEC solar cell with similar light irradiation

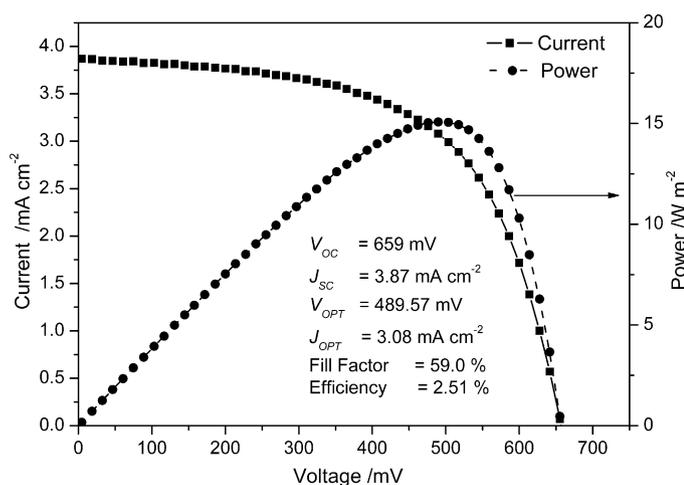


Fig. 5. Photocurrent versus voltage curve for the solar cell with $(\text{PAN})_{10}(\text{MgI}_2)_n(\text{I}_2)_{n/10}(\text{EC})_{20}(\text{PC})_{20}$ electrolyte with $n=1.5$ under irradiation of a 600 W m^{-2} light. The values of calculated parameters are also shown.

intensity and using tetrapropylammonium iodide ($\text{Pr}_4\text{N}^+\text{I}$) salt and PAN host polymer with EC and PC [1,11,25]. The efficiency of the present cell is higher than the reported 0.47% for an all-solid PEC solar cell fabricated using similar method but with tetrahexylammonium iodide salt and PEO host polymer under the irradiation of 600 W m^{-2} light [26]. The dominant iodide ion conductivity of the electrolyte is evident from the performance of this PEC cell. The power density of the solar cell, against voltage is also, shown in Fig. 5. The photocurrent and voltage at the maximum power point is 3.08 mA and 490 mV . The maximum power output of the cell is 15.08 W m^{-2} .

4. Conclusion

PAN based gel type polymer electrolytes, containing MgI_2 salt have been prepared by incorporating the plasticizers EC and PC for PEC solar cell applications. Conductivity enhancement of more than an order of magnitude is obtained only by optimizing the salt concentration. The highest conductivity is observed for the $(\text{PAN})_{10}(\text{MgI}_2)_n(\text{I}_2)_{n/10}(\text{EC})_{20}(\text{PC})_{20}$ electrolyte with $n=1.5$ and the measured values are $1.9 \times 10^{-3}\text{ S cm}^{-1}$ at 20°C and $2.6 \times 10^{-3}\text{ S cm}^{-1}$ at 60°C . The predominantly ionic nature, dominated by iodide ions, of the electrolyte is seen from the DC polarization data. The glass transition temperature of the best conducting electrolyte is -101.8°C . The PEC solar cell fabricated using this electrolyte has shown an open-circuit voltage of 659 mV and a short-circuit current of 3.87 mA cm^{-2} for an incident light intensity of 600 W m^{-2} . The overall efficiency of the cell is 2.5%.

Acknowledgements

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