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Tetrahexylammonium Iodide Containing Solid and Gel Polymer Electrolytes for Dye Sensitized Solar Cells

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Abstract

TiO_2 dye sensitized solar cells (DSSCs) are emerging as an alternative technology to photovoltaic junction devices. DSSCs conventionally use liquid-type electrolytes but solid and gel polymer electrolytes are more promising due to many advantages. However, their conductivity needs to be enhanced in order to make them useful in practical device applications. In this work, an iodide ion conducting polymer electrolyte was prepared using polyacrylonitrile (PEO), tetrahexylammonium iodide salt with ethylene carbonate and propylene carbonate plasticisers. The salt composition was varied to find the optimum conductivity. The sample containing 120% salt with respect to PEO weight showed the highest conductivity. This optimum electrolyte showed a glass transition at -102.3 °C and an ambient temperature conductivity of 2.1×10^{-3} S cm^{-1} at 30 °C. The optimized gel electrolyte was used in a quasi solid-state DSSC and a I_{SC} of 9.37mA cm^{-2}, a V_{OC} of 696 mV and an efficiency of 2.8 % were achieved under irradiation of 1000 W m^{-2}. In addition, a solid polymer electrolyte was fabricated using the same salt with polyethylene oxide host polymer and ethylene carbonate. The salt composition was varied to obtain the highest conductivity and the best performing sample with composition 65% salt with respect to PEO weight showed a conductivity of 4.7×10^{-4} S cm^{-2} at 30 °C. This electrolyte was used in a DSSC and it showed a I_{SC} of 1.26 mA cm^{-2}, a V_{OC} of 745 mV and efficiency of 0.6 %.

Keywords: Dye sencitized; Solar Cells; Polymer electrolytes; Conductivity

1. Introduction

Solar cells provide an alternative energy source which can produce energy from freely available solar radiation in an environmentally friendly manner. Due to lower manufacturing cost compared to photovoltaic junction devices, TiO_2 dye sensitized solar cells (DSSCs) are emerging as an alternative

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technology for solar energy conversion[1,2,3]. In general, DSSCs consist of three major components: photo-electrode, electrolyte, and counter electrode. The photo-electrode absorbs photons in the visible light creating conduction electrons and holes which drift or diffuse away before recombination. The electrolyte contains a redox couple that facilitates the charge transport process between photo-electrode and counter electrode. Therefore, it is important to have an electrolyte with high conductivity of compatible ionic species such as I^- ion for an efficient redox reaction and subsequent charge transfer.

Wet-type DSSCs that use liquid-type electrolytes have already shown high efficiencies more than 10% [1,2]. However, the wet-type cells have many disadvantages such as, lack of long term stability, difficulty in robust sealing, evaporation and leakage problems and side reactions. To overcome these problems efforts are being made to replace the liquid electrolyte by gel or solid polymer electrolyte [4,5,6,7].

Even though solid polymer electrolytes have many advantages such as long term stability, durability and ease of fabrication, relatively few research reports have been published on DSSCs using solid polymer electrolytes compared to the number of reports on quasi-solid-state (gel-type) and wet-type electrolytes for DSSCs [8,9]. This is evidently due to the low ambient temperature ionic conductivity of solid polymer electrolytes which leads to low energy conversion efficiencies. Therefore, it is very important to develop appropriate solid polymer electrolytes with high ambient temperature conductivity for DSSCs. An alternative is to find an appropriate gel polymer electrolyte which can work as a compromise between solid and liquid electrolytes.

Several different methods have been reported for the preparation of the photo-electrodes for DSSCs [10,11]. However, in this study the attention is focused on fabrication of effective solid or gel polymer electrolyte for DSSCs. So far, the most studied and reported highly efficient redox couple in electrolytes for TiO_2 DSSCs is the I^-/I_3^- system [1,2,6,5]. This redox couple has been used in liquid electrolytes, gel electrolytes and solid electrolytes used for DSSCs [1,2,6,5,8,9].

In the present work two types of polymer electrolytes were fabricated using the ionic liquid tetrahexylammonium iodide ($Hex_4N^+I^-$), which is solid at ambient temperature. For the preparation of the first type, a solid polymer electrolyte, polyethylene oxide (PEO) was used as host polymer matrix with controlled amounts of ethylene carbonate (EC) to produce freestanding solid-polymer electrolyte membranes. The second type or gel polymer electrolyte was fabricated using $Hex_4N^+I^-$, salt, PAN host polymer and EC and propylene carbonate (PC), as co-solvents and plasticizers. Solar cells were fabricated using these two types of electrolytes with optimized compositions with highest ambient temperature conductivity and were characterized by using *I-V* curves.

2. Experimental

Polyethyleneoxide (PEO: Mw. 4,000,000), Poly(acrylonitrile), $Hex_4N^+I^-$, iodine and EC, all with purity greater than 98%, purchased from Aldrich, were used as starting materials. PEO, PAN and $Hex_4N^+I^-$ were vacuum dried for 12 h in a vacuum oven at 50 °C prior to use. For preparation of solid polymer electrolyte samples, the weights of PEO (0.5 g) and EC (0.5 g) were kept unchanged, while the weight of $Hex_4N^+I^-$ was varied. In the text and in the figures, $Hex_4N^+I^-$ salt mass fraction x% refers to an electrolyte composition of host polymer (PEO or PAN) : $Hex4N^+I^-$ = 100 : x. The amount of iodine was kept such that the molar ratio of salt to I_2, is 10:1. The selected amounts of chemicals were dissolved in anhydrous acetonitrile and were stirred at room temperature for 12 hours until a homogeneous viscous slurry was obtained. The resulting slurry was casted on to a teflon plate and kept inside a fume box for 24 h in order to gradually drive off the solvent. This procedure yielded visually homogeneous polymer electrolyte films which were vacuum dried for 12 h prior to use for measurements.

For preparing gel polymer electrolyte samples, the weights of PAN (0.1 g), EC (0. 4 g) and PC (0.4 g) were kept unchanged and the weight of $Hex_4N^+I^-$ was varied to determine the composition which was giving the highest conductivity. The weight of iodine in the electrolyte was maintained so that the molar ratio $Hex_4N^+I^-$:I_2 is 10 :1. The selected amounts of chemicals were heated to about 80 °C and stirred for a few minutes until a homogeneous viscous solution was obtained. The resulting slurry was cast on to a glass plate and pressed by another glass plate in order to obtain a polymer electrolyte film for measurements.

Complex impedance measurements were performed using a HP 4192 ARF impedance analyzer in the frequency range of 10 Hz – 10 MHz and in the temperature range of 20 °C to 80 °C. Disc shaped electrolyte films with thickness 0.1-0.4 mm, sandwiched between two polished stainless steel blocking electrodes, were used for impedance measurements. Thermal properties of the samples were analyzed using a Mettler Toledo DSC 30 differential scanning calorimeter (DSC) in consequent heating and cooling cycles, with a rate of 10 °C min^{-1}.

A TiO_2 nano-porous layer was coated on a FTO glass using Degussa P25 powder. For this 0.5 g of Degussa powder (TiO_2) was ground well for ~30 minutes with ~2 ml of HNO_3 (pH = 1) in an agate mortar. The resulting colloidal suspension was diluted to get a 5% (*W/W*) solution and subsequently, it was stirred overnight at 60 °C and 25% (*W/W*) solution was obtained. Then ~0.1 g of carbowax and a few drops of Triton X 100 (surfactant) were added and mixed well. This colloidal suspension was used to prepare a TiO_2 film using doctor blade method and was sintered at 450 °C for 30 min. The TiO_2-coated electrode was immersed in ethanolic solution of the dye, ruthenium 535-bis TBA (Solaronix) while both were hot (~60 °C). After 24 h absorption, the electrode was withdrawn from the dye solution and subsequently washed with acetone to remove unabsorbed dyes from the dye-coated film.

In order to fabricate a PEO based, all solid-state DSSC, a few drops of the PEO based electrolyte slurry were casted on the dye absorbed TiO_2 electrode which was then kept in a fume box to gradually drive off the acetonitrile solvent, and finally vacuum dried for few hours. Subsequently, Pt was painted on the electrolyte using an ethanolic solution of Degussa Pt paste. Finally, this dye-sensitized TiO_2 electrode containing the solid polymer electrolyte and covered by Pt paint was pressed by a Pt coated conducting glass to complete the all-solid DSSC with the configuration glass/FTO/TiO_2/dye/electrolyte/Pt/FTO/glass.

PAN based quasi solid-state PEC solar cells were fabricated by sandwiching a polymer electrolyte film between the dye-coated TiO_2 electrode and a platinized FTO electrode. The cells were characterized by measuring *I–V* curves using an eDAQ EA161 potentiostat with the aid of eDAQ e-corder ED401 under the irradiation of 1000 W m^{-2} (1.5 AM) solar simulator.

3. Results and Discussion

The ionic conductivity of PEO/EC : $Hex_4N^+I^-/I_2$ based solid polymer electrolytes for different PEO: $Hex_4N^+I^-$ =100: *x* mass fractions are shown in Fig. 1-a as a function of inverse temperature. As expected the conductivity increases with increasing temperature however, a sharp conductivity increase can seen for all compositions as the temperature increases from room temperature to ~30 °C. The highest conductivity is observed for the sample with 65% $Hex_4N^+I^-$ mass fraction for all temperatures.

Fig. 1-b shows the conductivity Arrhenius plots for PAN/EC/PC: $Hex_4N^+I^-/I_2$ gel electrolyte samples for different PAN: $Hex_4N^+I^-$ =100: *x* mass fractions up to 140%. Out of these samples, the highest room temperature conductivity is shown for the electrolyte sample containing 120 wt% $Hex_4N^+I^-$ for all the measured temperatures. This optimum salt content is nearly double the amount used for the PEO based solid electrolyte since the gel polymer electrolyte can accommodate more salt as it essentially consist of an electrolyte solution “trapped” within a polymer matrix. Also, a PC in the gel electrolyte has relatively high dielectric constant and hence it helps solvation. All PAN/EC/PC: $Hex_4N^+I^-/I_2$ samples with salt composition higher than 60% showed a conductivity of more than 10^{-3} S cm^{-1}. In general, the conductivity of these PAN based gel polymer electrolytes is higher than that of the PEO based solid electrolyte.

The conductivity isotherms at 30, 40, 50, 60, 70 °C for different $Hex_4N^+I^-$, concentrations are shown in Fig. 2-a for PEO/EC : $Hex_4N^+I^-/I_2$ based solid electrolyte. Two conductivity maxima are clearly visible in these plots. One conductivity maximum occurs at 15% $Hex_4N^+I^-$ mass fraction studied as reported earlier [8]. The other maximum occurs at 65% $Hex_4N^+I^-$ mass fraction, with a measured conductivity value of 4.7×10^{-4} S cm^{-2} at 30 °C and higher than 10^{-3} S cm^{-1} for temperatures above 45 °C. The 1st conductivity increase at low salt concentrations with increasing amount of added salt up to 15% mass fraction may be a result of an increase of the mobile charge carriers with the increase of salt content. The subsequent conductivity decrease observed from 15% to 35% $Hex_4N^+I^-$ salt concentration is possibly due to the blocking effect imposed by non-dissociated and isolated $Hex_4N^+I^-$ species and higher ionic aggregates. This non-dissociated salt can reduce the flexibility of the long PEO chains limiting the ionic mobility. The conductivity increase between 35% and 65% of salt can be due to the effect of interconnected salt grains in the electrolyte, since this salt concentration can be high enough for providing conducting pathways. Thus, the conducting ionic species could travel along and between these interconnected conducting pathways providing a much higher conductivity [12,13]. The subsequent drop in conductivity at more than 65 % salt concentration may be due to a decrease of the number of conducting pathways for ions.

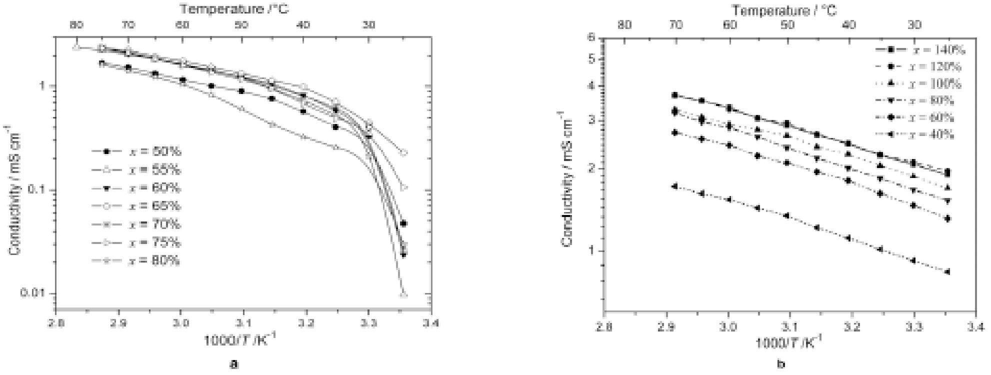

Fig. 1 (a) The conductivity vs. 1000/T for different $Hex_4N^+I^-$:PEO mass fractions (*x* %) in the PEO / EC : $Hex_4N^+I^-/I_2$ electrolyte; (b) The conductivity vs. 1000/T for different $Hex_4N^+I^-$:PAN mass fractions (*x* %) in the PAN / EC/PC:$Hex_4N^+I^-/I_2$ electrolyte.

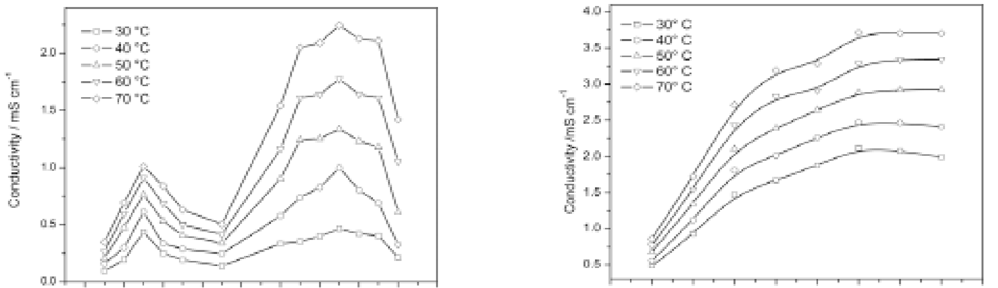

Fig. 2 (a) Conductivity isotherms of PEO / EC : $Hex_4N^+I^-/I_2$ electrolytes for different $Hex_4N^+I^-$ mass fractions for temperatures 30, 40, ..,70 °C; **(b)** Conductivity isotherms of PAN /EC/PC : $Hex_4N^+I^-/I_2$ electrolytes for different $Hex_4N^+I^-$ mass fractions for temperatures 30, 40, ..,70 °C.

The conductivity isotherms at 30, 40, 50, 60, 70 °C for different $Hex_4N^+I^-$, compositions are shown in Fig. 2-b for PAN/EC/PC: $Hex_4N^+I^-$ / I_2 based gel electrolytes. A conductivity increase is shown for the low salt compositions more or less up to 120% salt composition. This conductivity increase with added salt can be attributed basically to an increase of both the number of charge carriers and their mobility with the increasing amount of $Hex_4N^+I^-$. The mobility increase in this region may be due to the disorder imposed by added ions. The low conductivity increase shown for salt mass fractions from 60% to 120% may be the result of a decline of the increasing number of mobile ions due to an increase of ion association. The electrolyte containing 120% salt with respect to the PAN weight shows the highest conductivity at least at high temperatures. The conductivity of the PAN based optimum electrolyte, 2.1×10^{-3} S cm^{-2}, is higher than that of the PEO based optimum electrolyte, 4.7×10^{-4} S cm^{-2} at 30 °C.

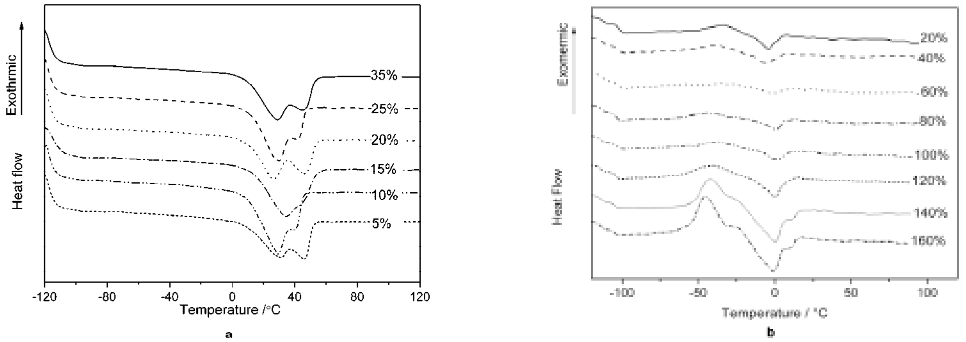

Fig. 3 (a) DSC thermograms of the PEO/EC :$Hex_4N^+I^-/I_2$ electrolyte for 5, 15, ….,35 % $Hex_4N^+I^-$ mass fraction relative to PEO; **(b)** DSC thermograms of the PAN/EC/PC :$Hex_4N^+I^-/I_2$ electrolyte for 20, 40, ….,160 % $Hex_4N^+I^-$ mass fraction relative to PAN.

DSC measurements were used to characterize the electrolyte samples. As an example, the DSC thermogram obtained during the heating run for PEO/EC : $Hex_4N^+I^-/I_2$ sample up to 35% $Hex_4N^+I^-$ mass fraction is shown in Fig. 3-a. All the electrolyte samples exhibited two melting peaks, at about 30 °C and 45 °C, which possibly correspond to the melting of the EC rich phase and the PEO rich phase in the electrolyte [8]. However, those peaks appeared at 25.6 and 43.5 °C for the optimum 65% $Hex_4N^+I^-$ composition. The sharp conductivity increase shown in Fig. 1-a at about 30 °C can be related to the melting of EC rich phase which is more polar than the polymer rich phase. The glass transitions were very difficult to detect due to the high crystallinity of the electrolyte samples.

The DSC thermograms obtained from 20% to 160% $Hex_4N^+I^-$ mass fractions are shown in Fig. 3-a for PAN/EC/PC : $Hex_4N^+I^-/I_2$ sample. Since the glass transition temperature, T_g, is related to the segmental flexibility of the host polymer and the disordered structure [14,15], the T_g result can be related to a change in the segmental flexibility of polymeric chains of the electrolyte. Hence, T_g can related to the mobility of charge carriers in the PAN host matrix [16]. The minimum value T_g, -102.3 °C was observed for the electrolyte containing 120 wt% $Hex_4N^+I^-$ with respect to the weight of PAN and as expected this salt concentration gives the maximum conductivity. However, the variation of T_g is very small. For salt concentrations less than 120%, the T_g is higher and with the increase of salt concentration the T_g decreases probably due to structural disorder caused by bulky Hex_4N^+ and I^- ionic species added. This shows the contribution to the ionic conductivity enhancement due to structural modifications caused by the salt added.

The PEO based solid polymer electrolyte with the highest conductivity containing 65% salt was used to fabricate all solid state DSSCs. The voltage-current, *V-I,* characteristics of this PEC solar cell was used to characterize the cell. The short circuit current density (J_{SC}), open circuit voltage (V_{OC}) and fill factor of the cell are 1.26 mA cm^{-2}, 745 mV and 62 % respectively. The overall energy conversion efficiency of

0.6 % was achieved under irradiation of 1000 W m^{-2}. The maximum power density is obtained for this sample when the photo-current and the voltage are 1.04 mA cm^{-2} and 562 mV respectively. The efficiency of the cell, 0.6 %, is rather low due to resistive losses of the solid-state electrolyte; however values are reasonable for an all-solid state configuration.

The optimized, PAN based gel polymer electrolyte, containing 120% salt, was used to fabricate quasi-solid state DSSCs. The, *V-I,* characteristics of this cell is used for the characterization. The J_{SC}, V_{OC} and fill factor of the cell are 9.37 mA cm^{-2}, 696 mV and 43 % respectively. The overall energy conversion efficiency of 2.8 % was achieved under irradiation of 1000 W m^{-2} light. The maximum output power density is obtained when the photo-current and the voltage are 6.66 mA cm^{-2} and 418 mV respectively. The efficiency of the cell, 2.8 %, is considerably higher than that of the cell with an all solid configuration, evidently due to the high conductivity of the gel polymer electrolyte that facilitates charge transport between TiO_2 photo anode and the Pt counter electrode.

4. Conclusions

In this work two types of polymer electrolytes were fabricated and optimized using Hex_4NI salt for DSSCs. The conductivity of the solid polymer electrolyte, (PEO): EC : $Hex_4N^+I^-/I_2$ reached a value of 4.7×10^{-4} S cm^{-1} at 30 °C for samples containing 65 % $Hex_4N^+ I^-$ mass fraction with respect to the PEO mass. However, the PAN/EC/PC: $Hex_4N^+I^-$ / I_2 gel electrolyte showed higher conductivities than the PEO based solid electrolyte. The PAN based optimum electrolyte had a conductivity of 2.1×10^{-3} S cm^{-2} at 30 °C. An all-solid and quasi-solid state DSSCs were fabricated using samples with optimized conductivity with the configuration FTO/TiO_2/Dye/Electrolyte/Pt/FTO. The quasi-solid state DSSCs showed better performance than all-solid state configuration due to high ionic conduction of the electrolyte.

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