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# A polymer electrolyte containing ionic liquid for possible applications in photoelectrochemical solar cells

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**Abstract** Various iodide ion conducting polymer electrolytes have been studied as candidate materials for fabricating photoelectrochemical (PEC) solar cells and energy storage devices. In this study, enhanced ionic conductivity values were obtained for the ionic liquid tetrahexylammonium iodide containing polyethylene oxide (PEO)-based plasticized electrolytes. The analysis of thermal properties revealed the existence of two phases in the electrolyte, and the conductivity measurements showed a marked conductivity enhancement during the melting of the plasticizer-rich phase of the electrolyte. Annealed electrolyte samples showed better conductivity than nonannealed samples, revealing the existence of hysteresis. The optimum conductivity was shown for the electrolytes with PEO:salt= 100:15 mass ratio, and this sample exhibited the minimum glass transition temperature of 72.2 °C. For this optimum PEO to salt ratio, the conductivity of nonannealed electrolyte was $4.4 \times 10^{-4}$ S cm$^{-1}$ and that of the annealed sample was $4.6 \times 10^{-4}$ S cm$^{-1}$ at 30 °C. An all solid PEC solar cell was fabricated using this annealed electrolyte. The short circuit current density ($I_{SC}$), the open circuit voltage ($V_{OC}$), and the power conversion efficiency of the cell are 0.63 mA cm$^{-2}$, 0.76 V, and 0.47% under the irradiation of 600 W m$^{-2}$ light.

**Keywords** PEC solar cells · Polymer electrolyte · Ionic conductivity · Ionic liquid

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## Introduction

Polymer electrolytes are potential candidates for the development of energy conversion and storage devices such as solid-state batteries [1–3] and photoelectrochemical (PEC) solar cells [4–7], and the development of such devices are highly important due to the ever increasing demand for usable energy forms [8]. In addition, polymer electrolytes are attractive materials for electrochromic devices and super capacitors. For the realization of fabricating efficient and durable dye-sensitized PEC solar cells, which have the advantage of a reduced production cost compared to that of conventional junction-type devices, good I$^-$ ion conducting electrolytes are needed [4, 6, 7].

Electrolyte systems containing $I_3^-$/I$^-$ redox couple are suitable for TiO$_2$-based dye-sensitized solar cells [4, 6, 7, 9], and this redox couple has been used in the form of aqueous/organic solutions or gel or solid polymer electrolytes [10–12]. Solid polymer electrolytes are more reliable for PEC solar cells than gel-type or liquid-type electrolytes due to various advantages such as easy handling, possibility of preparing thin films, flexibility, avoiding sealing and leakage problems, and minimum side reactions [7, 10, 11,

13]. However, the main drawbacks of solid polymer electrolytes are their low conductivity and low ionic transference numbers. In this study, it was attempted to improve the conductivity and $I^-$ ion transference number of the solid polymer electrolyte based on polyethylene oxide (PEO) host polymer and ethylene carbonate (EC) plasticizer by adding the ionic liquid tetrahexylammonium iodide ($Hex_4N^+I^-$) as the salt.

Many iodides have been tried out to be used as the salt in polymer electrolytes intended for PEC solar cells. In a previous study, Tennakone et al. [10] used different alkaline metal iodides XI (X = Li, Na, K, Cs) in a polymer electrolyte for PEC solar cells. The short circuit photocurrent ($I_{SC}$) has been shown to increase with increasing cation size for the series Li, Na, K, and Cs. This can be understood because the mobility of the anion ($I^-$ in the present case) depends on the degree of interaction of $X^+$ with the polymer [14]. The larger cations of similar electronic configuration interact more strongly with the polymer because of the viscous forces [10]. In addition, they are liable to higher coordination numbers. Furthermore, the cations in the electrolyte tend to coordinate with heteroatoms in the polymer. The enhancement of anion mobilities in conducting polymers with the immobilization of cations is reported in the literature [14]. In addition to the immobilization of the cation, another advantage of using a bulky cation is the expected higher degree of salt solvation due to reduction of lattice energy of the salt. The ionic radii of the alkyl ions $Li^+$, $Na^+$, $K^+$, $Rb^+$, and $Cs^+$ are 0.60, 0.95, 1.33, 1.48, and 1.69 Å, respectively [15, 16], and corresponding lattice energies are expected to decrease with increasing size of the ion.

Electrolytes containing quaternary ammonium iodides have been used successfully in PEC solar cell applications. For instance, tetrapropylammonium iodide ($Pr_4N^+I^-$) has been used with PEO and also with polyacrylonitrile host polymers, and reasonably good cell performance have been reported reaching about 3% overall cell efficiency [7, 9, 11]. Tetrabutylammonium iodide ($Bu_4N^+I^-$) salt has also been reported to show very good cell performance reaching 5.3% cell efficiency [4, 10]. Ionic radii of $Pr_4N^+$ and $Bu_4N^+I^-$ ions are 4.6 and 5.0 Å, respectively, thus, significantly larger than the alkali-metal ions [17, 18]. When the size of the cation increases, it enhances the salt solvation and anion transference number leading to high iodide ion conductivity which is needed for improving the solar cell performance. In this study, we have used $Hex_4N^+I^-$ salt to fabricate the electrolyte intended for PEC solar cells. The selection of this salt was made expecting higher $I^-$ ion conductivity and PEC cell performance than for $Bu_4N^+I^-$ and $Hex_4N^+I^-$ salts due to the larger size of the cation, see Fig 1. In this study, a solid polymer electrolyte was fabricated using $Hex_4N^+I^-$ salt, PEO host polymer, and

plasticizer EC for solar cells expecting higher stability of cell performance, durability, and ease of cell production even though conductivity is less than that of gel or liquid electrolytes.

## Experimental

PEO (Mw. 4,000,000), $Hex_4N^+I^-$, iodine chips ($I_2$), and EC, all with purity greater than 98% purchased from Aldrich, were used as starting materials. PEO and $Hex_4N^+I^-$ were vacuum dried for 24 h in a vacuum oven at 50 °C prior to use. For preparing the electrolyte samples, the weights of PEO (0.5 g) and EC (0.5 g) were kept unchanged, and the weight of $Hex_4N^+I^-$ was varied. In the text and in the figures, $Hex_4N^+I^-$ salt weight fraction $x$% refers to an electrolyte composition of PEO : $Hex_4N^+I^- = 100 : x$. The amount of iodine was kept so that the molar ratio, salt:$I_2$, is 10:1. The samples were prepared using the solvent casting method. The selected compositions of chemicals were dissolved in anhydrous acetonitrile solvent (30 ml) and were magnetically stirred at room temperature for 12 h until a homogeneous viscous solution was obtained. The resulting slurry was cast 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 measurements.

High frequency complex impedance measurements were performed using a HP 4291 A RF impedance analyzer in the frequency range 1 MHz–1 GHz and in the temperature range of 20 to 80 °C. A flow of nitrogen gas was maintained over the sample to prevent contact with atmospheric moisture. In order to determine the conductivity, disk-shaped electrolyte films of diameter 5 mm and thickness 0.1–0.4 mm were sandwiched between two polished stainless steel blocking electrodes, and complex impedance measurements were taken. The thermal properties of the samples were analyzed using a Mettler Toledo DSC 30 differential scanning calorimeter from −120 to 120 °C in the heating cycle, with a heating rate of 10 °C min$^{-1}$.

Nanostructured $TiO_2$ thin films were prepared on fluorine-doped tin oxide (FTO) glass plates using the already published procedure [9]. The $TiO_2$-coated electrode was immersed in ethanolic solution of *cis*-diisothiocyanato-$N,N''$-*bis*(2,2′-bipyridyl–4,4′-dicarboxylicacid)-ruthenium (II) dihydrate [$RuL_2(NCS)_2.2H_2O$] while both were hot (i.e., temperature ~60 °C). After 24-h absorption, the electrode was withdrawn from the dye solution and then washed thoroughly with acetone to remove unabsorbed dyes and loosely bound $TiO_2$ particles from the dye-coated plate.

**Fig. 1** Schematic diagram of cations in $Pr_4N^+I^-$, $Bu_4N^+I^-$, and $Hex_4N^+I^-$ salts
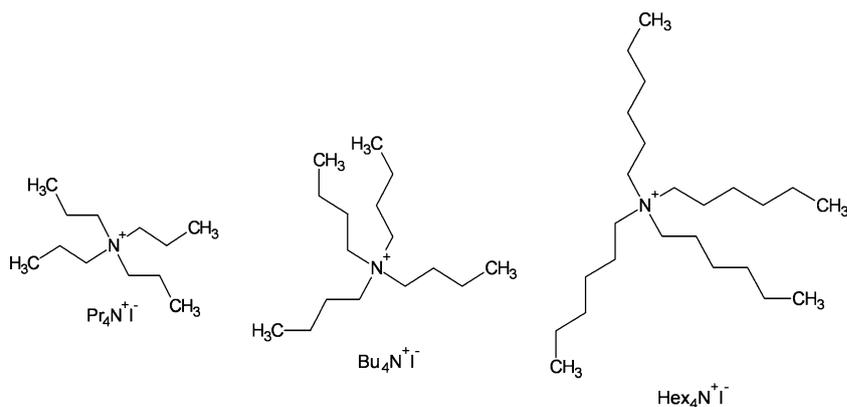


Solid-state PEC solar cells were fabricated by sandwiching polymer electrolyte films of thickness from 0.1 to 0.3 mm between the dye-sensitized $TiO_2$ film and a previously prepared platinized conducting glass plate with the configuration glass/FTO/$TiO_2$/dye/electrolyte/Pt/FTO/glass. The solar cells were characterized by measuring I–V curves using an eDAQ potentiostat EA161 with the aid of eDAQ e-corder ED401 under the irradiation of 600 W m$^{-2}$ light.

## Results and discussion

The ionic conductivity, $\sigma$, of the (PEO):EC:$Hex_4N^+I^-$/$I_2$ solid polymer electrolytes for different $Hex_4N^+I^-$ concentrations ($x\%$) are shown in Fig. 2, as a function of inverse temperature. In general, above 30 °C, the conductivity shows a linear behavior, and an abrupt conductivity increase is also visible just below this temperature. At



**Fig. 2** The conductivity vs $1,000/T$ for (PEO):EC:$Hex_4N^+I^-$/$I_2$ electrolytes containing different mass fractions of $Hex_4N^+I^-$ ($x\%$)

temperatures above ~30 °C, the curves are somewhat curved. However, in order to facilitate the analysis, a fit to the Arrhenius equation,

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

where $B$ is an exponential factor, $E_a$ the activation energy, $k_B$ the Boltzmann constant, and $T$ the absolute temperature, has been made in this temperature range. An advantage of fitting the data to the Arrhenius equation is the possibility of calculating $E_a$ values which have actual physical meaning compared to the fitting parameters obtained using the VTF-type equation. The activation energy values extracted by fitting this equation to the experimental data are shown in Table 1. The sample with the highest conductivity shows the lowest $E_a$ value and vice versa, as expected. However, it is difficult to derive a clear relation between $E_a$ and conductivity since the variation is more or less within the experimental error limit, ±0.03 eV.

The conductivity of the polymer electrolytes annealed at about 80 °C (above the PEO crystallite melting temperature) measured in the second heating run are shown in Fig. 3 as a function of inverse temperature for different $x$ values. Prior to starting the conductivity measurements of annealed samples, they were equilibrated for 12 h at room temperature. As for many polymer electrolytes, there is a distinct hysteresis observed for the conductivity behavior in this case as well, showing a higher conductivity for annealed electrolyte samples. In addition, the abrupt conductivity drop at low temperatures that appears in nonannealed samples has disappeared for annealed samples. However, with prolonged aging of the annealed electrolyte samples, the low temperature conductivity drops gradually, and the abrupt change of the conductivity at about 30 °C reappears.

The conductivity isotherms for different salt, $Hex_4N^+I^-$, compositions ($x\%$) are shown in Figs. 4 and 5 for nonannealed and annealed samples, respectively, at 30, 40, 50, 60, and 70 °C. In Fig. 5 also, the conductivity isotherm at 22 °C is included. These plots give a clear idea
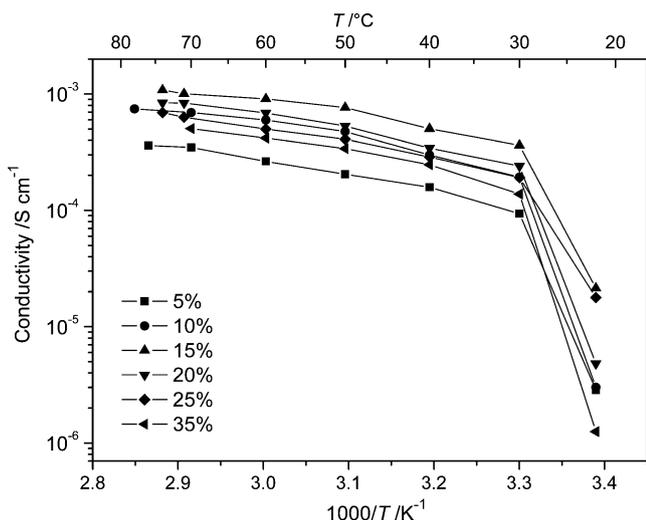
**Table 1** The conductivity of annealed and nonannealed samples at 30 °C for different salt contents ($x\%$) in (PEO):EC: $Hex_4N^+I^-/I_2$ electrolyte

The respective activation energy, $E_a$, and glass transition temperature, $T_g$, are also shown

| $x\%$ | $\sigma_{30}$/Scm$^{-1}$ (nonannealed) | $\sigma_{30}$/Scm$^{-1}$ (annealed) | $E_a$/eV (nonannealed) | $T_g$/°C |
|---|---|---|---|---|
| 5 | $9.37\times10^{-5}$ | $2.13\times10^{-4}$ | 0.26 | −66.5 |
| 10 | $1.93\times10^{-4}$ | $2.48\times10^{-4}$ | 0.26 | −71.8 |
| 15 | $4.36\times10^{-4}$ | $4.55\times10^{-4}$ | 0.22 | −72.2 |
| 20 | $2.40\times10^{-4}$ | $2.44\times10^{-4}$ | 0.26 | −69.8 |
| 25 | $1.92\times10^{-4}$ | $1.99\times10^{-4}$ | 0.26 | −69.0 |
| 35 | $1.38\times10^{-4}$ | $1.65\times10^{-4}$ | 0.28 | −68.5 |

on the conductivity variation with composition. The highest conductivity was obtained for the sample with $x=15\%$ irrespective of temperature and whether the sample was annealed or not. The conductivity increase at lower salt concentrations with increasing amount of added salt is possible due to an increase of the number of mobile charge carriers. The conductivity decrease in the higher salt concentrations may be due to the blocking effect by the nondissociated $Hex_4N^+I^-$ species.

DSC measurements were used to determine the melting temperatures, $T_m$, and the glass transition temperatures, $T_g$, of PEO:EC:$Hex_4N^+I^-/I_2$ electrolyte samples for different $Hex_4N^+I^-$ compositions, see Fig. 6. The $T_m$ of PEO crystallites and EC are ~65 and ~36 °C according to manufacturer's specifications and DSC thermograms, see Fig. 6. Also, the DSC thermograms of the pure ionic liquid are shown in Fig. 6, and it exhibits three endothermic peaks at 72.3, 79.0, and 106.5 °C, indicating a series of phase transitions in this temperature range which is not uncommon for ionic liquids. Two endothermic peaks are observed for all the PEO:EC:$Hex_4N^+I^-/I_2$ electrolyte samples, but in some cases, the two peaks merge. It can be concluded that

the high-temperature (~45 °C) peak is associated with the melting of PEO-rich phase, and the low-temperature (~30 °C) peak corresponds to the EC-rich phase as observed for other electrolytes containing PEO and EC [19]. It can also be observed that the PEO crystallite melting temperature of electrolytes shift to lower temperature when the plasticizer is introduced. The peak temperatures corresponding to the melting of the EC-rich phase also appear close to 30 °C, somewhat lower than the melting temperature of pure EC. The abrupt conductivity increase observed in Fig. 2 around 30 °C is most probably due to the melting of this EC-rich phase of the electrolyte. The conductivity is less affected by the melting of the PEO-rich phase confirming the dominant conductivity contribution by the EC-rich phase which is more polar than the polymer-rich phase. The glass transition temperature, $T_g$, values for this kind of system is important as it correlates with the conductivity, since $T_g$ is a measure of the segmental flexibility of the host polymer chains [2, 8, 20, 21]. The $T_g$ values of the electrolyte samples with different $x$ values are shown in Table 1, and as expected, samples with low $T_g$ values exhibit higher conductivity values.

According to the DSC measurements taken during cooling runs (not shown), the crystallization peaks corresponding to the EC-rich phase lie below 0 °C. Therefore, in annealed electrolyte, the EC-rich phase is



**Fig. 3** The conductivity vs 1,000/$T$ variation for annealed (PEO):EC:$Hex_4N^+I^-/I_2$ electrolytes containing 5%, 10%,..., 35%; mass fractions of $Hex_4N^+I^-$
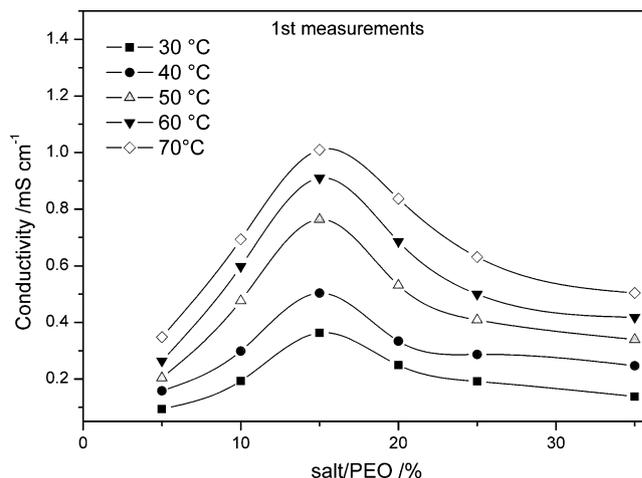


**Fig. 4** The conductivity isotherms of (PEO)/EC:$Hex_4N^+I^-/I_2$ electrolytes for different $Hex_4N^+I^-$ mass fractions ($x\%$), where $x$=salt/PEO
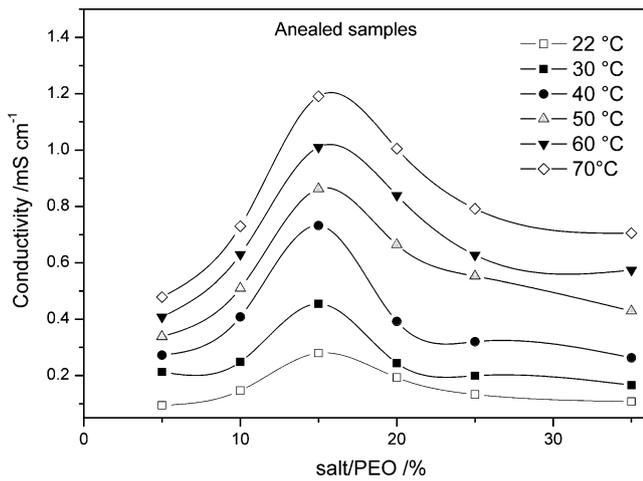
Fig. 5 The conductivity isotherms of annealed (PEO)/EC:$Hex_4N^+I^-$/$I_2$ electrolytes as a function of $Hex_4N^+I^-$ mass fractions ($x\%$), where $x$=salt/PEO



Fig. 7 $I–V$ characteristic curve and power output for the solid-state solar cell fabricated using annealed (PEO):EC:$Hex_4N^+I^-$/$I_2$ electrolyte under irradiation of 600 W $m^{-2}$ light

not crystallized, whereas the polymer-rich phase is crystallized during the cooling up to about 20 °C. Thus, annealed electrolytes show higher conductivity due to the presence of molten EC-rich phase. In addition, the abrupt conductivity increase shown for nonannealed electrolytes in Fig. 2 is not visible in Fig. 3 as the EC phase has been already molten for annealed samples. However, a higher conductivity increase can be observed for low temperatures (below 45 °C) possibly due to the melting of polymer-rich phase in the annealed samples.

The photocurrent vs photovoltage curves for the solid-state PEC solar cell which was fabricated using the optimum conducting electrolyte are shown in Fig. 7. The short-circuit photocurrent ($J_{SC}$) and open-circuit voltage ($V_{OC}$) of the cell for solar light irradiation of 600 W $m^{-2}$ for (PEO)/EC:$Hex_4N^+I^-$/$I_2$ electrolyte are found to be

0.63 mA $cm^{-2}$ and 760 mV, respectively. The fill factor, $ff$, was calculated using

$$ff = \frac{J_{opt}V_{opt}}{J_{SC}V_{OC}} \quad (1)$$

where $J_{opt}$ is the current density at maximum power output, and $V_{opt}$ is the voltage at maximum power output. The calculated fill factor for the quasisolid state dye-sensitized solar cell is 59.2%.

The power conversion efficiency, $\eta$, of the all-solid PEC cell was calculated using

$$\eta = \frac{J_{SC}\ V_{OC}\ ff}{\text{Total incident power density}} \quad (2)$$

The power density of the solar cell, plotted against voltage, is also shown in Fig. 7. The photocurrent and voltage at the maximum power point is 0.49 mA $cm^{-2}$ and 564 mV, respectively. The maximum power output of the cell is 2.8 W $m^{-2}$, and the power conversion efficiency of the cell is 0.47% under irradiation of 600 W $m^{-2}$ light.

As usual, the energy conversion efficiency of the all-solid PEC solar cell fabricated is lower than that of quasisolid-state solar cells that use gel electrolytes or wet cells which use liquid type electrolytes. However, in this study, an iodide ion conducting solid polymer electrolyte with good mechanical strength and conductivity is fabricated, and work is still progressing to improve the efficiency of this type of PEC solar cells.



Fig. 6 DSC thermograms of the (PEO):EC:$Hex_4N^+I^-$/$I_2$ polymer electrolyte samples for different EC mass fractions ($x\%$). DSC thermograms of the pure PEO, EC, and salt are also shown

## Conclusion

The conductivity of the plasticized iodide ion ($I^-$) conducting electrolyte (PEO):EC:$Hex_4N^+I^-$/$I_2$ reached the conductivity values of $4.4\times10^{-4}$ S $cm^{-1}$ and $4.56\times10^{-4}$ S $cm^{-1}$ at 30 °C

for nonannealed and annealed electrolyte samples, respectively. The activation energy values of nonannealed electrolytes were calculated for temperatures above 30 °C, and the minimum activation energy of 0.22 eV was obtained for the highest conducting nonannealed electrolyte.

An all-solid-state PEC solar cell was fabricated with the configuration FTO/TiO$_2$/dye/electrolyte/Pt/FTO using the optimum conducting annealed electrolyte. The $J_{SC}$ and $V_{OC}$ of the cell are 0.63 mA cm$^{-2}$ and 0.76 V under the irradiation of 600 W m$^{-2}$ light. The energy conversion efficiency of the cell, 0.47%, is rather low compared to cells with gel or liquid polymer electrolytes due to poor ionic conductivity in the solid polymer electrolyte. However, an all-solid-state configuration has a number of advantages regarding mechanical and chemical stability, and work is progressing on improvement of the efficiency for the solar cell.

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