

Polyethyleneoxide (PEO)-based, anion conducting solid polymer electrolyte for PEC solar cells

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Abstract Solid polymer electrolyte membranes were prepared by complexing tetrapropylammoniumiodide ($\text{Pr}_4\text{N}^+\text{I}^-$) salt with polyethylene oxide (PEO) plasticized with ethylene carbonate (EC), and these were used in photoelectrochemical (PEC) solar cells fabricated with the configuration glass/FTO/ TiO_2 /dye/electrolyte/Pt/FTO/glass. The PEO/ $\text{Pr}_4\text{N}^+\text{I}^-$ + I_2 =9:1 ratio gave the best room temperature conductivity for the electrolyte. For this composition, the plasticizer EC was added to increase the conductivity, and a further conductivity enhancement of four orders of magnitude was observed. An abrupt increase in conductivity occurs around 60–70 wt% EC; the room temperature conductivity was $5.4 \times 10^{-7} \text{ S cm}^{-1}$ for 60 wt% EC and $4.9 \times 10^{-5} \text{ S cm}^{-1}$ for the 70 wt% EC. For solar cells with electrolytes containing PEO/ $\text{Pr}_4\text{N}^+\text{I}^-$ + I_2 =9:1

and EC, IV curves and photocurrent action spectra were obtained. The photocurrent also increased with increasing amounts of EC, up to three orders of magnitude. However, the energy conversion efficiency of this cell was rather low.

Keywords Solar cells · Polymer electrolyte · Ionic conductivity · Plasticizers · Dye sensitized

Introduction

As a part of the global research effort to develop low cost solar cells, many investigators have tried out different types of wet photoelectrochemical (PEC) solar cells using various electrodes and electrolytes, as they show a greater potential to convert solar energy to electricity [1–3] or chemical energy [4]. In the recent past, dye-sensitized TiO_2 solar cells using gel electrolytes have gained a considerable attention due to the low preparation cost, non-toxic nature, and improved efficiency [1–3, 5–7]. However, such PEC cells using liquid or gel electrolytes have many drawbacks such as electrode deterioration, cell degradation due to gas formation, dissolution of the electrodes, and electrolyte leakage, etc. which obstruct the practical fabrication of good quality durable PEC solar cells with enhanced stable current and voltage. If the liquid electrolytes in these cells can be replaced by solid polymer electrolytes, most of these drawbacks can be minimized [8, 9], paving the way for the rapid development of PEC solar cells similar to the development of solid-state batteries taking place at present [10, 11].

Many efforts have been made to replace the liquid electrolytes with solid p-type inorganic materials [15–17], organic hole conductors [18, 19], low temperature molten salts or ionic liquids [12, 13], and gel-type polymer

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electrolytes [1–3, 5–7] to overcome above mentioned drawbacks of the wet-type PEC solar cells. In the literature, it is reported that gel-type polyethylene oxide (PEO) or polyacrylonitrile (PAN)-based polymer electrolytes can be used for dye-sensitized TiO_2 PEC solar cells and have attained nearly up to 3% energy conversion efficiency [1–3]. It is also reported that the use of solid polymer electrolytes for Si PEC solar cells [20] and n-CdSe PEC solar cells [21] leads to low currents mainly due to high electrical resistance of the electrolyte which limits the ionic mobility for the redox couple in the solid-state electrolyte system. Therefore, investigation for highly conductive solid-state electrolyte system with better mechanical properties and stability for solar cells is of prime importance.

Although a number of cation conducting polymer electrolytes based on PEO has been investigated [10, 11], much less work has been reported on PEO-based electrolytes intended to be anionic conductors. Iodide ion containing polymer electrolytes are important as redox species in PEC solar cells as well as iodide ion conducting solid-state cells. In this study, we report for the first time the anionic conductivity behavior of solid polymer electrolyte membranes prepared by incorporating tetrapropylammoniumiodide ($\text{Pr}_4\text{N}^+\text{I}^-$) salt with ethylene carbonate (EC) as the plasticizer in the host matrix of PEO and without using propylene carbonate (PC) or any other liquid plasticizer.

The energy conversion efficiencies of the solid-state PEC solar cells containing solid polymer electrolytes are less than that of the PEC solar cells containing liquid electrolytes [8, 14] due to the low ionic mobility for the redox couple in the solid-state electrolyte system, low decomposition (ionizing) ability for the salt, and poor mutual contact between semiconductor nanoparticles in the electrode and the electrolyte. To minimize the electrical resistance and to improve the conductivity of the electrolyte system, plasticizers [1–3] or ceramic fillers [10, 11] can be added to the electrolyte, which would facilitate the ion mobility through the solid-state electrolyte system due to change of structural morphology. Further, the relatively high dielectric constant of the plasticizer improves the salt solvating power of the electrolyte [22, 23]. However, the disadvantage of incorporating plasticizers is degradation of the mechanical properties of the electrolyte. More and more addition of plasticizer converts the electrolyte from a solid-type electrolyte to a rubbery type of electrolyte or gel-type electrolyte. Therefore, the amount of plasticizer in the electrolyte should be strictly controlled.

In this work, we demonstrate the possibility of fabricating an all solid PEC solar cell with a conductivity-enhanced PEO-based solid polymer electrolyte and dye sensitized nanoporous TiO_2 photo-electrode. The solid-state PEC cell was fabricated by sandwiching a thin polymer electrolyte film between the TiO_2 photo-electrode and the platinumized

fluorine-doped tin oxide (FTO) glass plate. The photocurrent was improved from less than $0.1 \mu\text{A}$ to almost up to $100 \mu\text{A}$ due to the incorporation of EC to the electrolyte.

Experimental

PEO, $\text{Pr}_4\text{N}^+\text{I}^-$, iodine chips [I_2], and ethylenecarbonate [EC], all with purity greater than 98% purchased from Aldrich, were used as starting materials. All these chemicals, except I_2 , were vacuum-dried for 24 h in a “GALLENKAMP” vacuum oven before use.

For all the electrolyte samples preparations, the amounts 0.066 g of $\text{Pr}_4\text{N}^+\text{I}^-$ and 0.004 g of I_2 were kept constant so that the molar ratio of $\text{I}_2/\text{Pr}_4\text{N}^+\text{I}^-$ was approximately 0.1 as given in [2]. The weight ratio of ($\text{PEO}/\text{Pr}_4\text{N}^+\text{I}^- + \text{I}_2$) was varied to determine the composition giving maximum conductivity without the plasticizer. The samples were prepared using the solvent casting method, i.e., the selected compositions of chemicals were dissolved in anhydrous acetonitrile, and the solution was magnetically stirred at room temperature for 24 h until a homogeneous viscous solution was obtained. The resulting slurry after stirring was cast on to a Teflon plate and kept inside the fume box for 24 h to let the solvent slowly evaporate. This procedure yielded visually homogeneous polymer electrolyte films, and then, the films were vacuum-dried for 24 h in the vacuum oven before use for other measurements.

To optimize the conductivity enhancement of the electrolyte, the amounts 0.066 g of $\text{Pr}_4\text{N}^+\text{I}^-$, 0.004 g of I_2 , and 0.63 g of PEO were kept unchanged, and the EC weight was varied. The samples were prepared using the same solvent casting method. Throughout the process, the molar ratio of the PEO oxygen/EC was maintained less than 1.0 to retain the mechanical properties of the electrolyte.

Complex impedance measurements were performed using a Schlumberger SI-1260 impedance-gain phase analyzer in the frequency range of 10 Hz–10 MHz and in the temperature range of 30 to 100 °C in a temperature-regulated oven (Buchi Model TO-50). Disc-shaped electrolyte films of 13-mm diameter and thickness 0.1–0.3 mm were sandwiched between two polished stainless steel blocking electrodes, and ac impedance measurements were taken to obtain the bulk dc conductivity of the sample.

DC polarization tests were carried out at room temperature by sandwiching disc-shaped electrolyte samples in between two I_2 pellets and two stainless steel (SS) blocking electrodes. The measurements were performed as SS/electrolyte/SS, SS/ I_2 /electrolyte/ I_2 /SS, and SS/ I_2 /electrolyte/SS and vice versa on 1.0 V constant applied voltage. The current through the cell was measured as a function of time for periods up to approximately 30 min using LPS 161A

regulated dc power supply, Keithley model 177 microvolt digital multimeter and CQ 95XYT plotter.

Nanoporous TiO₂ thin films were prepared on FTO glass plates using already published procedure [1]. The TiO₂-coated electrode was immersed in ethanolic solution of *cis*-diisothiocyanato-*N,N''*-bis(2,2'-bipyridyl-4, 4'-dicarboxylic acid)-ruthenium(II) dihydrate [RuL₂(NC-S)₂·2H₂O] 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 TiO₂ particles from the dye-coated plate.

Solid-state PEC solar cells were fabricated by sandwiching polymer electrolyte films of thickness from 100 to 300 μm between the dye-sensitized TiO₂ film and a previously prepared platinized conducting glass plate with the configuration glass/FTO/TiO₂/dye/electrolyte/Pt/FTO/glass. The solar cells were characterized by measuring I-V curves using a computer-controlled potentiostat/galvanostat HA-301 instrument when illuminated by a 1,000-W m⁻² Xenon lamp. The action spectra were recorded using a monochromator-light chopper-lock in amplifier arrangement using a Nikon G 250 monochromator.

Results and discussion

Conductivity vs 1/T plots for different (PEO/Pr₄N⁺I₂) weight ratios are shown in Fig. 1, and those for the plasticized iodide ion conducting electrolyte samples with different weight ratios of PEO with salt are shown in Fig. 2

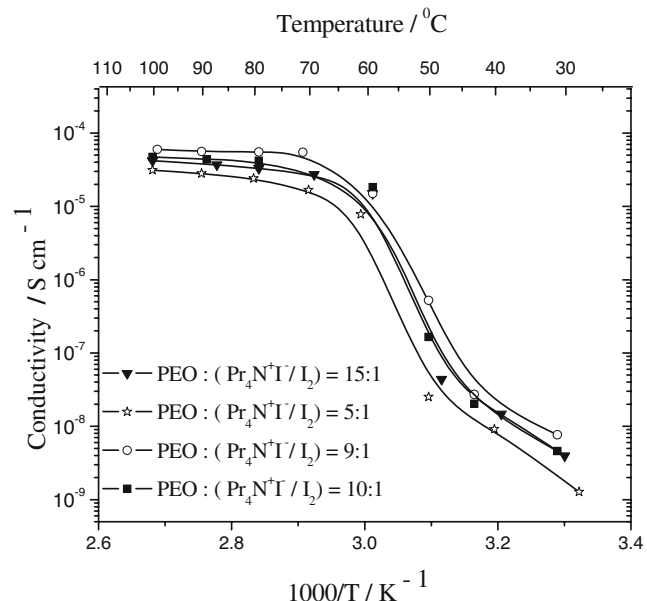


Fig. 1 The conductivity vs 1,000/T plots for different (PEO/Pr₄N⁺I₂) ratios

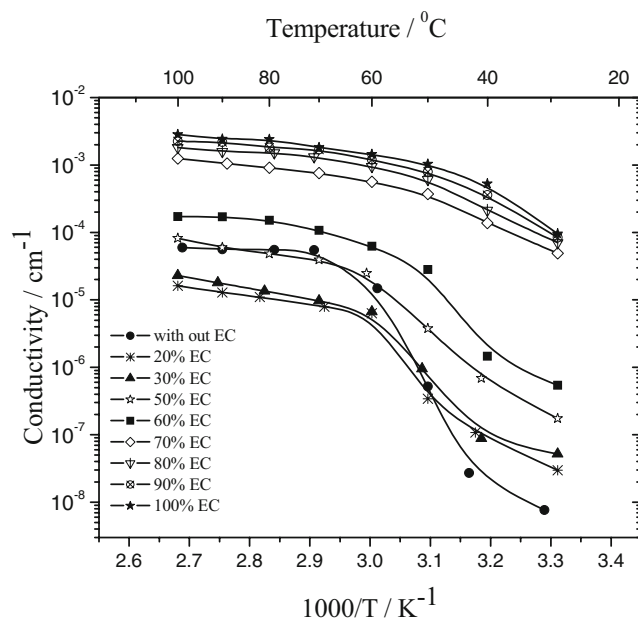


Fig. 2 The conductivity vs 1,000/T plots for different χ values (PEO, Pr₄N⁺I₂/EC ratios)

for different plasticizer (EC) concentrations in the range 0–100% by weight ratio (EC/PEO+Pr₄N⁺I₂). The plot in Fig. 1 shows that a conductivity increase of five orders of magnitude with the temperature increase from 30 to 100 °C mainly due to the crystalline to amorphous phase transition of the PEO near 60 °C [10, 11]. In addition, from these plots, one can observe that the optimum conductivity is obtained for the 9:1 PEO/(salt + iodine) weight ratio. This optimum ratio was selected to use for further conductivity enhancement by incorporating the plasticizer.

In the text and in the figures, χ % EC refers to an electrolyte composition of (PEO + Pr₄N⁺I₂) total weight/weight of EC=100:χ. Figure 2 shows the conductivity enhancement with temperature and with χ value. It is assumed that incorporation of EC causes a decoupling of the ionic motion from the polymer chain and an increase of the ionic mobility by lowering the viscosity of the ionic environment. EC has high relative dielectric constant, which implies that an enhancement of the dissociation of the salt is likely as for solvents in general [22, 23]. At 30 °C, the conductivity increases with increasing χ value most probably due to the electrolyte becoming more amorphous while also increasing the ionization of the salt.

As shown in Fig. 3, there is a significant conductivity enhancement at room temperature when the value of χ changes from 60 to 70% from, 5.4 × 10⁻⁷ S cm⁻¹ at 60 wt% EC to 4.9 × 10⁻⁵ S cm⁻¹ at 70 wt% EC. However, further addition of EC shows only a moderate increase. The polymer electrolyte has apparently become more amorphous with high EC concentrations or χ values. All the electrolyte films used with EC concentrations of greater

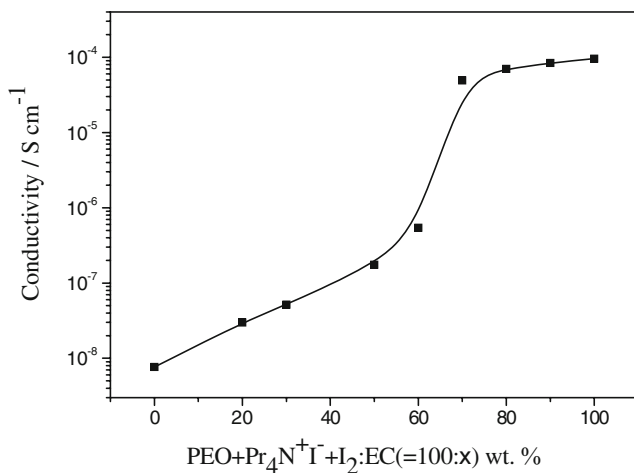


Fig. 3 The variation of room temperature conductivity of electrolyte with χ % EC

than 60 wt% (χ value) and less than 100 wt% were freestanding solid films with significantly high ionic conductivity.

The DC polarization measurements showed a rapidly decreasing current when the electrolyte was sandwiched directly in between the blocking stainless steel electrodes, while the measurements where I_2 pellets were used no appreciable decrease in current was detected. Measurements were also performed on asymmetric cells with corresponding results. It was concluded that more than 90% of the current is due to ionic conductivity, with iodide ions being the likely mobile species.

I-V characteristic curves for fabricated PEC solar cells with different electrolyte samples prepared by changing χ values are shown in Fig. 4. With increasing EC content, the photocurrent increases most probably due to the enhance-

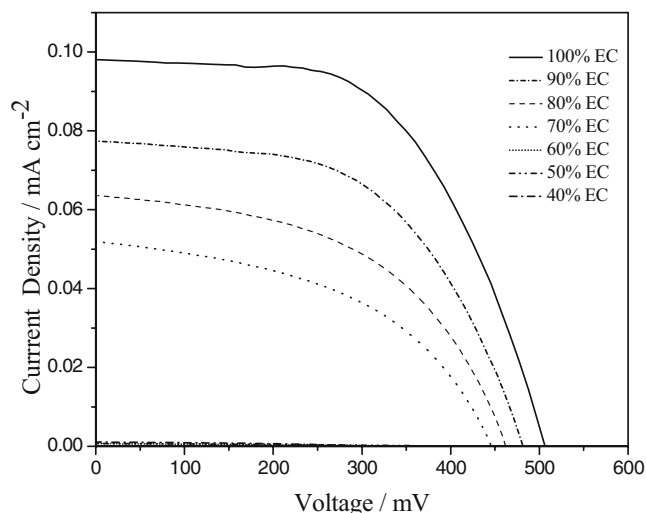


Fig. 4 I-V characteristics of PEC solar cells for different χ values under irradiation of a $1,000\text{-Wm}^{-2}$ Xenon lamp

Table 1 Characteristics of PEC solar cells using electrolytes with different EC content

| EC content (χ value %) | Open circuit voltage (V_{oc} ; V) | Short circuit current (J_{sc} ; $\mu\text{A cm}^{-2}$) | Fill factor (ff; %) | Efficiency (η ; %) |
|------------------------------|--------------------------------------|--|---------------------|--------------------------|
| 40 | 284 | 1 | 38.9 | 0.0001 |
| 50 | 354 | 1 | 38.4 | 0.0001 |
| 60 | 371 | 1 | 36.3 | 0.0001 |
| 70 | 443 | 51 | 47.5 | 0.011 |
| 80 | 461 | 62 | 51.0 | 0.015 |
| 90 | 492 | 77 | 53.3 | 0.020 |
| 100 | 510 | 98 | 56.0 | 0.028 |

ment of the conductivity of the solid polymer electrolyte. Open circuit voltage (V_{oc}), short circuit current density (J_{sc}), fill factor (ff), and energy conversion efficiency (η) are given in percent in Table 1 where the values are estimated from plots in Fig. 4.

The fill factor, ff of the device is defined as

$$ff = \frac{J_{opt}V_{opt}}{J_{sc}V_{oc}} \quad (1)$$

where J_{opt} = current density for maximum power output, and V_{opt} = voltage for maximum power output.

The power conversion efficiency of the PEC cell was calculated using

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

All the parameters in Table 1 are high when the χ value is above 60%. J_{sc} and energy conversion efficiency increase drastically when χ exceeds 60%. This enhancement correlates with the conductivity enhancement shown in Fig. 3. The

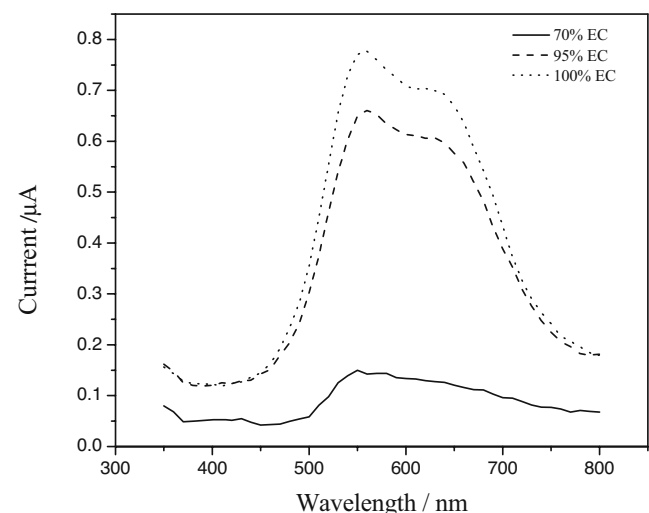


Fig. 5 Action spectra for PEC solar cells for different EC contents

measured photocurrent of the cell using an electrolyte without EC is less than 0.1 μA . Therefore, a three-order increase of photocurrent has been observed merely due to the addition of the plasticizer EC. However, the energy conversion efficiency of these PEC solar cells is still very low mainly due to relatively high resistance of the solid-state electrolyte.

The photocurrent action spectra for 100, 95, and 70% χ value are shown in Fig. 5. The peaks observed are consistent with literature data obtained for the ruthenium-based dye used showing the maximum light absorption in the 500–700 nm wavelength range.

Conclusion

A conductivity enhancement of more than four orders of magnitude at room temperature was observed in the polymer (PEO), salt ($\text{Pr}_4\text{N}^+\text{I}_2^-$) complex electrolyte only due to the addition of the plasticizer EC. The room temperature conductivity was $5.4 \times 10^{-7} \text{ S cm}^{-1}$ for 60 wt% EC sample and $4.9 \times 10^{-5} \text{ S cm}^{-1}$ for the 70 wt% EC sample. Thus, abrupt increase in conductivity occurs around 60–70% EC. This could possibly be associated with microstructural and morphological changes in the host polymer at these compositions, causing enhanced ionic dissociation and increased amorphous nature of the electrolyte.

The energy conversion efficiency of the fabricated PEC solar cell is less than that of the liquid-type or the gel-type PEC solar cells. The maximum energy conversion efficiency (0.028%) was obtained for the electrolyte with 100% EC sample, and for that cell, the short circuit current density is $98.1 \mu\text{A cm}^{-2}$, and the open circuit voltage is 510 mV. However, when the EC content is less than 60%, the photocurrent is approximately 1 μA , and open circuit voltage is less than or equal to 371 mV. An abrupt increase of both the photocurrent of the cell and conductivity of the electrolyte is observed when the EC content exceeds 60% weight ratio. The electrolytes used are solid-state freestanding films, which facilitate fabrication of large area PEC solar cell with minimum deterioration of the electrode.

Although the efficiency of this system is rather low, we believe that our observation that a sharp increase in conductivity of the electrolyte and the PEC cell efficiency around 60–70% EC content is a significant finding for PEO-based PEC cells. The work is in progress to investigate

improving the properties of photo-electrode and electrolyte to enhance the energy conversion efficiency.

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