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ORIGINAL PAPER

# Efficiency enhancement in dye-sensitized solar cells fabricated with poly(ethylene oxide) based solid polymer electrolyte mediated by the mixed cation and nano filler effects

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**Abstract**

The use of volatile liquid electrolytes in dye-sensitized solar cells (DSSCs) hinders their large-scale commercialization. In this regard, DSSCs based on solid polymer electrolytes or gel polymer electrolytes have emerged as devices offering improved stability and enhanced efficiency. In this work, solid and gel polymer electrolytes based on poly(ethylene oxide) (PEO) were explored in conjunction with the mixed cation iodide salts (tetrapropylammonium iodide and potassium iodide), and $TiO_2$ nanofillers. DSSCs sensitized with N719 dye were fabricated with these materials, and their performance was evaluated. The PEO-based solid polymer electrolyte containing 15 wt% $Pr_4N^+I^-$ exhibited the highest ionic conductivity of $3.97 \times 10^{-5}$ S·m$^{-1}$ and the DSSC power conversion efficiency (PCE) of 1.08%. The incorporation of 42.5 wt% of the solid plasticizer, ethylene carbonate (EC) increased the amorphous phase content in the PEO electrolyte and improved the iodide ion transport, enhancing the solar cell efficiency to 1.46%. Further enhancement in efficiency to 1.81% was achieved by incorporating two iodide salts with mixed cations ($Pr_4N^+$ and $K^+$), benefiting from the synergistic “mixed cation effect”. Incorporating 2.5 wt% $TiO_2$ nanofiller further boosted the PCE to 3.02% due to the nanofiller effect. $TiCl_4$ surface treatment of the $TiO_2$ photoanode substantially enhanced the DSSC efficiency to 3.41%.

**Keywords** Dye-sensitized solar cells (DSSCs) · Solid polymer electrolyte · Poly(ethylene oxide) (PEO) · Mixed cation effect · $TiO_2$ nanofiller

## Introduction

Modern society’s growing reliance on electricity is primarily met by fossil fuels, hydropower, nuclear power, and geothermal energy. Among these, fossil fuels have become the major contributors to environmental degradation, driven by global warming. As these ecological concerns intensify, the shift toward renewable sources such as solar and wind energy has become increasingly imperative. Solar photovoltaic (PV) technology, in particular, has attracted significant interest from the global community due to its sustainability and scalability. Although first-generation silicon-based solar cells offer high efficiencies (~ 25%), their high production costs have limited widespread adoption. This limitation has prompted the advancement of second-generation thin-film solar cells and, later, third-generation photovoltaics, which offer reduced production costs and incorporate

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environmentally friendly materials. However, they generally exhibit lower efficiencies [1–4].

Among the third-generation photovoltaic technologies, dye-sensitized solar cells (DSSCs), introduced by O'Regan and Grätzel in 1991 [5], have gained considerable attention. DSSCs offer several advantages, including low production costs due to inexpensive materials, simple fabrication processes, and favorable performance under both indoor and outdoor ambient lighting conditions. Additional benefits include design versatility (e.g., transparency, multiple color options), short energy payback times (< 1 year), high performance-to-cost ratio, bifacial light harvesting, and lightweight structure [6, 7]. DSSCs are generally classified as liquid, solid, or quasi-solid-state based on the electrolyte type. Liquid electrolyte-based DSSCs typically exhibit superior efficiency. However, their commercial viability is hindered by challenges related to electrolyte leakage, poor long-term stability, and complex sealing requirements. Consequently, in order to overcome these limitations and to enhance the practical applicability of DSSCs, there is a growing interest in developing solid-state electrolytes, especially with solid polymer electrolytes.

Among the various types of solid polymer electrolytes, poly(ethylene oxide) (PEO)-based polymer electrolytes are the most studied candidates for dye-sensitized solar cells due to their complexing ability, presence of polar groups, chemical stability, and low glass transition temperature [8]. For an efficient DSSC, the ionic conductivity of a polymer electrolyte employed in the device should be in the range of $10^{-3}$ S $cm^{-1}$ or higher at ambient temperature. However, it has been reported that even when used as polymer electrolytes in $Li^+$ ion batteries, the ionic conductivity of pure PEO-salt-based polymer electrolytes at ambient temperature ($10^{-7}$–$10^{-6}$ S $cm^{-1}$) is not high enough [9]. Therefore, to improve the ionic conductivity of PEO-based electrolytes, the addition of plasticizers and/or nanosized oxide fillers to the PEO-salt matrix has been widely used as one of the most common methods [10, 11].

Even though there are numerous research studies on PEO-based polymer electrolytes, most of the reported electrolytes used in the fabrication of $I^-/I_3^-$ redox couple-based DSSCs consist of a single ionic salt such as LiI, KI, or $Pr_4NI$. However, it has been reported that mixed-cation iodide electrolytes containing a small cation and a large cation can enhance solar cell efficiency due to the enhanced iodide ion conductivity caused by the "*mixed-cation effect*" [10–16]. In the present study, we systematically investigated the efficiency enhancement achieved through the sequential incorporation of a solid plasticizer, mixed-cation iodide salts, $TiO_2$ nanofiller, and finally $TiCl_4$ treatment in DSSCs fabricated with a PEO-based solid polymer electrolyte [17].

## Experimental

### Materials

Poly (ethylene oxide*)* (PEO, Mw ~ $4 \times 10^5$, Aldrich), Tetrapropylammonium iodide ($Pr_4N^+I^-$) (Aldrich), Potassium iodide (KI) (99.5%, Fluka), Ethylene carbonate (EC) (purity >99%, Fluka), Titanium dioxide powder ($TiO_2$) (P25 and P90) and Iodine ($I_2$) (Fluka) were used as starting materials. All the chemicals except $I_2$ were vacuum dried at 60 °C for 24 h prior to use. Titanium dioxide powders ($TiO_2$) (P25 and P90) were purchased from Degussa AG. Acetonitrile was used as the common solvent. Triton-X-100 (Aldrich) was used as received. Ruthenium dye N719, purchased from Solatronix, was used as the sensitizer.

## $TiO_2$ electrode reparation

A compact layer of P90 $TiO_2$ was prepared using a $TiO_2$ slurry containing well-ground 0.25 *g* of P90 $TiO_2$ powder with 1 ml of 0.1 M $HNO_3$ in an agate mortar for about 20 min. The paste was then coated on a well-cleaned, F-doped $SnO_2$ glass substrate (FTO) (Nippon Glass with a sheet resistance of 8 Ω/sq) using a spin coater rotating at 3,000 rpm for 60 s. Each of the spin-coated FTO glass electrodes was finally sintered at 450 °C for 30 min.

Another type of $TiO_2$ paste, to be used as the main photoanode active layer, was prepared by grinding 0.25 g of $TiO_2$ (Degussa P-25) with 0.05 g of PEG, one drop of Triton X-100, and 1 ml of 0.1 M nitric acid. The resulting paste was applied *to* the previously prepared, sintered P90 $TiO_2$ layer on FTO glass and on bare FTO glass separately. An active area of 0.25 $cm^2$ was obtained by spreading the paste using the doctor blade technique and then sintering it at 450 °C for 45 min. The resulting $TiO_2$ nanoporous film was allowed to cool completely. Subsequently, the $TiO_2$ electrodes were immersed in an ethanolic dye solution containing 0.3 mM ruthenium dye N719 and left for 24 h to allow dye adsorption.

## Preparation of solid polymer electrolyte for ionic conductivity measurements

A mixture of 0.25 g of PEO, different weight ratios of $Pr_4N^+I^-$ (5, 10, 15, 20, 25 wt%), and $I_2$ were dissolved in acetonitrile and stirred at room temperature overnight until a homogeneou*s* solution was obtained. The weight of iodine was taken by keeping the salt-to-iodine ratio at 10:1. The resultant slurry was cast on a Teflon plate and kept until the solvent was gradually evaporated. This procedure resulted in a visually homogeneous polymer electrolyte film, which was vacuum-dried for 12 h to remove traces of acetonitrile and obtain a thin solid polymer electrolyte film PEO: $Pr_4N^+I^-:I_2$.

For the measurement of ionic conductivity, a polymer solid electrolyte sample was sandwiched between two stainless steel (*SS*) electrodes. The measurements were carried out using a computer-controlled impedance analyzer (Autolab PGSTAT128N with FRA3*2* frequency generator) in the 0.01 Hz to 1 MHz frequency range. The temperature of the electrolyte samples was varied from room temperature (30 °C*)* to 65 °C at approximately 5 °C temperature intervals during heating. The ionic conductivity at each temperature was extracted from the impedance data. The composition exhibiting the highest room temperature ionic conductivity was selected for the fabrication of DSSCs.

## Preparation of plasticized solid polymer electrolytes for DSSC fabrication

Ethylene carbonate (EC) was added as a solid plasticizer to the optimized electrolyte composition obtained from conductivity measurements as described in Sect. 2.3. The amount of EC was varied using different weight ratios of PEO: EC as 0:85, 10:75, 35:50, 40:45, 42.5:42.5, and 75:10 w/w%. Figure 1 shows the inverted bottle test to demonstrate the solid nature of the prepared electrolytes PEO: EC: $Pr_4N^+I^-:I_2$, depending on the above composition ratios. It was found that the solid nature of the electrolyte could be clearly observed for the samples made with a PEO: EC ratio of 42.5:42.5 and 75:10 w/w%. When the EC content exceeded 42.5 wt%, the electrolyte turned into a low-viscosity gel. The PEO-free electrolyte with 85 wt% EC exhibited a liquid nature.

## Fabrication of DSSCs and their characterization

In order to fabricate the DSSCs, the PEO-based polymer electrolytes with different amounts of EC were prepared using appropriately weighed mixtures of PEO, EC, $Pr_4N^+I^-$, and $I_2$, as shown in Sect. 2.4, and stirring the mixtures overnight until each mixture became a homogeneous solution or a flowing gel. For fabricating the DSSCs, the solution electrolytes (~400 µL) were spread on the surface of dye-adsorbed $TiO_2$ electrodes (FTO/P90/P25 and FTO/P25), following a two-step casting method. Here, first, a dilute solution of the electrolyte (~200 µL) was spread dropwise on an aforementioned porous, dye-adsorbed $TiO_2$ electrode. After allowing sufficient time for the acetonitrile in the electrolyte to evaporate, the remaining amount of the electrolyte (~200 µL) was spread dropwise on the first electrolyte layer on the $TiO_2$ electrode.

Subsequently, the $TiO_2$ electrodes were vacuum-dried for 4 h to ensure that no traces of acetonitrile remained in the electrolyte medium. The DSSC assembly was completed by gently pressing a platinized counter electrode against the above $TiO_2$ electrode, with the solid/gel film of electrolyte sandwiched between them. The photocurrent-voltage (I–V) characteristics of the cells were measured under the illumination of 100 mW cm$^{-2}$ simulated sunlight

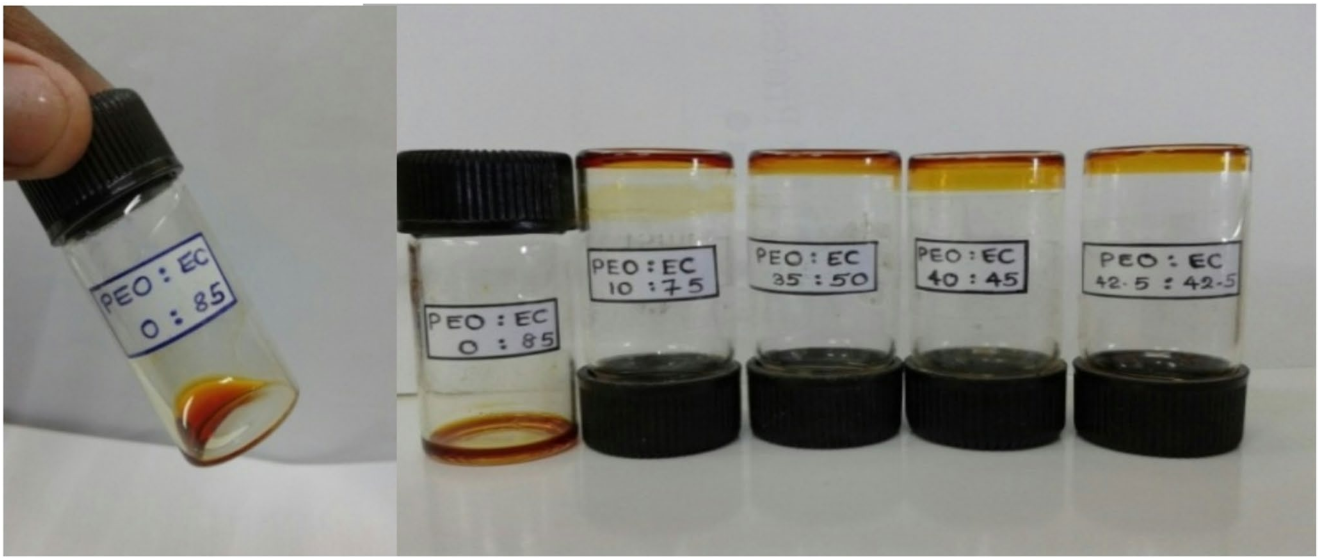

**Fig. 1** The inverted bottle test; The solid nature of the electrolytes PEO: EC: $Pr_4N^+I^-:I_2$ after 4 h of vacuum drying at room temperature. PEO: EC weight ratios 10:75, 35:50, 40:45, 42.5:42.5, and 75:10 w/w% and the liquid nature of PEO: EC = 0:85 w/w% (PEO-free) electrolyte

using a computer-controlled measuring system coupled to a Keithley 2000 multimeter and a galvanostat HA-301. A Xenon 500 lamp was used with an AM 1.5 filter to obtain the simulated sunlight with the above intensity. Figure 2 shows a schematic diagram of the assembled solar cell structure (not to scale).

In order to enhance the efficiency of these DSSCs using the mixed cation effect [10–12], a second iodide salt, KI, was added to the electrolyte system, PEO/EC/$Pr_4N^+I^-$/$I_2$, and the EC composition was optimized as described in the previous section (Sect. 2.4). The optimized electrolyte composition exhibiting the highest ionic conductivity was obtained for the mixed cation salts of $Pr_4N^+I^-$ and KI at a weight ratio of 75:25. The electrolytes were characterized by electrochemical impedance spectroscopy (EIS) analysis.

In order to further enhance the performance of the solar cells, $TiO_2$ photoanodes were slightly modified by dipping the sintered $TiO_2$ electrodes (with both P90 and P25 $TiO_2$ layers, as prepared in the previous case) in a 0.04 M $TiCl_4$ solution for 24 h and sintering them at 450 °C for 45 min. Subsequently, the dye adsorption was carried out as described previously.

To improve the photovoltaic performance further, solid nanocomposite polymer electrolytes were prepared by incorporating nano-titanium dioxide ($TiO_2$) with different weight ratios (1.5, 2.5, 5, and 10 wt%) into the best-optimized DSSC electrolyte system developed as described in the previous sections. The DSSCs were fabricated with the $TiCl_4$-treated $TiO_2$ photoanode and filler-added solid polymer electrolytes, and their performance was measured using I–V characteristics. The electrolytes were independently characterized by electrochemical impedance spectroscopy (EIS) analysis.

## Results and discussion

### Ionic conductivity of solid polymer electrolyte

Figure 3 shows the temperature dependence of ionic conductivity of the solid polymer electrolyte (SPE), PEO: $Pr_4N^+I^-$: $I_2$, comprising with different weight percentages of tetrapropyl ammonium iodide ($Pr_4N^+I^-$) salt. As can be seen from this figure the conductivity of the electrolyte gradually increases with increasing amounts of $Pr_4N^+I^-$ in the electrolyte up to a 15 wt% ratio and then starts to decrease with further addition of the salt.

Figure 3 shows the temperature dependence of ionic conductivity of the solid polymer electrolyte *(*SPE*)*, PEO: $Pr_4N^+I^-$:$I_2$, comprising different weight percentages of tetrapropylammonium iodide *(*$Pr_4N^+I^-$*)* salt. As can be seen from this figure, the conductivity of the electrolyte gradually

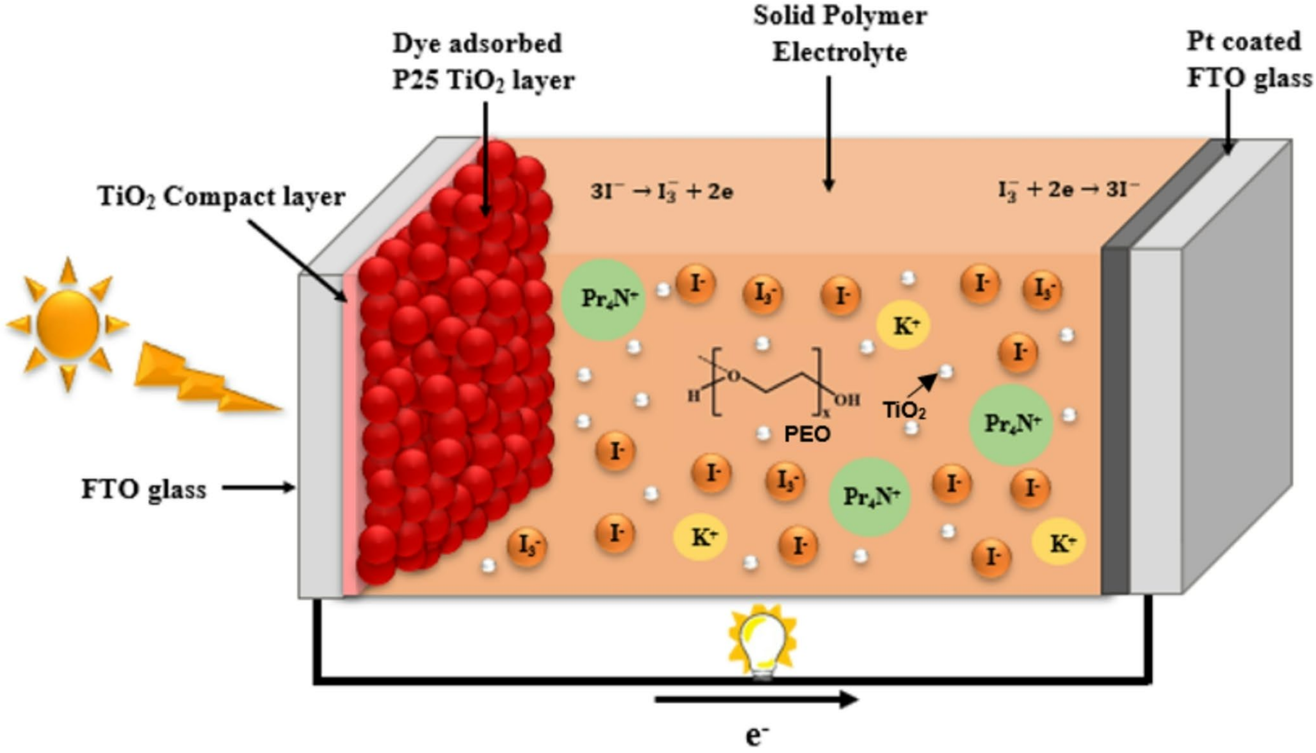

**Fig. 2** Schematic diagram of a DSSC assembly with configuration of FTO glass/$TiO_2$/dye/solid polymer electrolyte/Pt

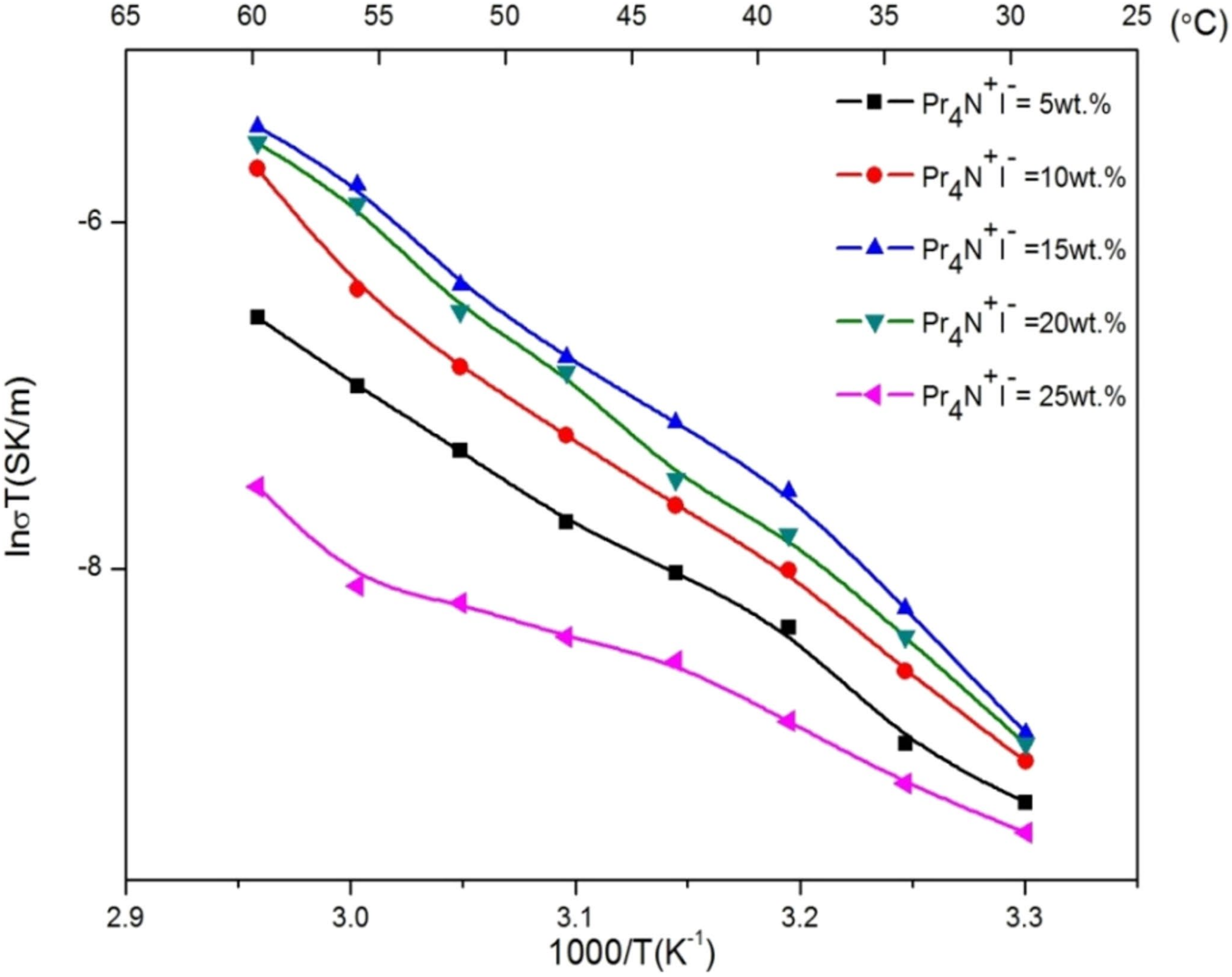

**Fig. 3** Variation of temperature dependence of ionic conductivity for different compositions of $Pr_4N^+I^-$ salt in the solid polymer electrolyte, PEO: $Pr_4N^+I^-$: $I_2$

increases with increasing amounts of $Pr_4N^+I^-$ in the electrolyte up to a 15 wt% ratio, and then starts to decrease with further addition of the salt.

Variation of conductivity with wt% of the $Pr_4N^+I^-$ salt in the solid polymer electrolyte, PEO: $Pr_4N^+I^-$:$I_2$, at different temperatures in the 30–65 °C temperature range is shown in Fig. 4 as conductivity isotherms, and the conductivity values are tabulated in Table 1. The figure also clearly shows that, at all measured temperatures, the ionic conductivity of the electrolyte initially increases with the salt content, reaching a maximum at 15 wt% of $Pr_4N^+I^-$, and subsequently decreases with further increases in salt concentration. The total ionic conductivity of the solid electrolyte is composed of the contributions of the individual conductivities of $Pr_4N^+$, $I^-$, and $I_3^-$ ions in the electrolyte.

As seen from these conductivity isotherms, the composition with 15 wt% $Pr_4N^+I^-$ shows the highest ionic conductivity at all temperatures, with a value of $3.97 \times 10^{-5}$ S cm$^{-1}$ at 30 °C. Above this composition, a conductivity drop can clearly be seen in the electrolyte for higher salt concentrations up to 25 wt% salt. This decrease is quite likely due to the formation of ion pairs and higher ionic aggregates, which reduce the number of free ions available for ionic transport.

In a typical PEO-based polymer electrolyte, the cation movement is primarily facilitated by ionic hopping, which is enabled by the segmental flexibility of the polymer chains. This process involves the cation detaching from one coordinating site (e.g., an oxygen atom in the PEO chain) and reattaching to a nearby site. In contrast, the polymer chain has a weaker interaction with the anions. As a result, the transport of anions, $I^-$ and $I_3^-$, takes place by ionic diffusion through the electrolyte medium, which is also facilitated by the segmental flexibility of the PEO polymer chain [17].

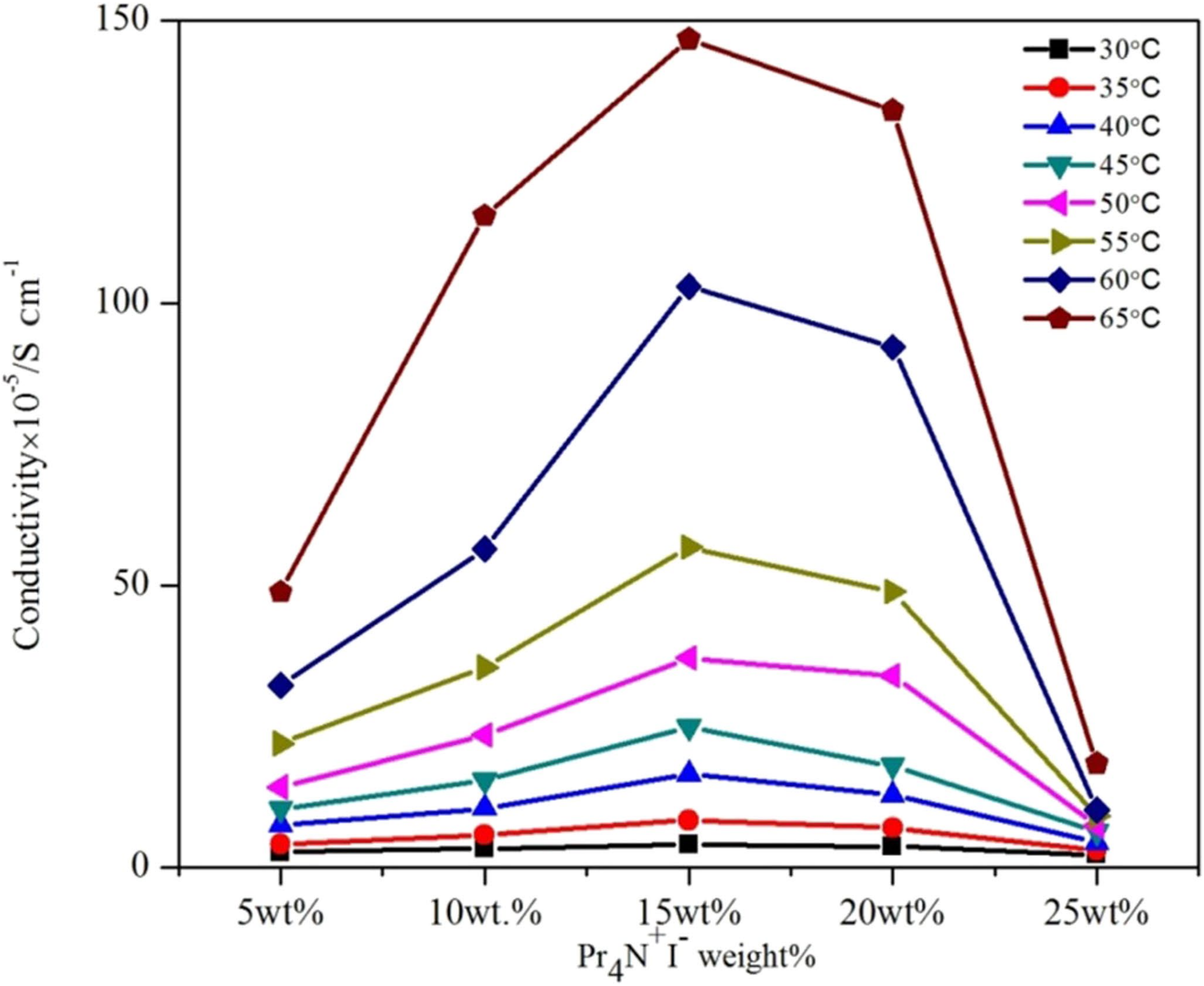

**Fig. 4** Conductivity isotherms of solid polymer electrolyte, PEO: $Pr_4N^+I^-$: $I_2$ in the 30–65 °C temperature range

**Table 1** Variation of temperature dependence of ionic conductivity for different compositions of $Pr_4NI$ salt in the solid polymer electrolyte, PEO: $Pr_4NI$: $I_2$

| Temperature/°C | Conductivity ( × $10^{-5}$ S $cm^{-1}$) | | | | |
|---|---|---|---|---|---|
| | $Pr_4NI$ 5 wt% | $Pr_4NI$ 10 wt% | $Pr_4NI$ 15 wt% | $Pr_4NI$ 20 wt% | $Pr_4NI$ 25 wt% |
| 30 | 3.15 | 3.59 | 3.97 | 3.66 | 2.42 |
| 35 | 4.68 | 6.20 | 8.98 | 7.56 | 3.29 |
| 40 | 7.56 | 10.51 | 16.71 | 13.61 | 4.67 |
| 45 | 10.81 | 15.19 | 25.48 | 17.74 | 6.86 |
| 50 | 14.72 | 23.33 | 36.03 | 33.29 | 7.60 |
| 55 | 22.94 | 35.44 | 56.81 | 49.53 | 9.57 |
| 60 | 32.34 | 57.58 | 102.73 | 91.08 | 10.51 |
| 65 | 51.37 | 116.68 | 146.35 | 133.98 | 20.35 |

When the salt concentration in the electrolyte is increased, both the cationic and anionic conductivity contributions increase up to a certain salt concentration (15 wt% in the present case), due to the optimum number of ions that can freely move through the electrolyte. After this, with higher salt concentrations, the conductivity starts to decrease, evidently due to the formation of ion pairs and higher ionic aggregates, which reduce the total ionic conductivity of the electrolyte due to a decrease in the number of free mobile ions.

## Current density - voltage (*J-V*) measurements

The characterization of the DSSCs fabricated with optimized PEO based solid polymer electrolyte made with composition PEO: 15 wt% $Pr_4N^+I^-$: $I_2$ was carried out with the cell configuration of FTO/$TiO_2$/Dye/electrolyte/Pt/FTO by measuring their *J-V* characteristics (Fig. 5). The fill factor (*FF*%) and the efficiency ($\eta$%) were calculated using the open circuit voltage ($V_{oc}$) and short circuit current density ($J_{sc}$).

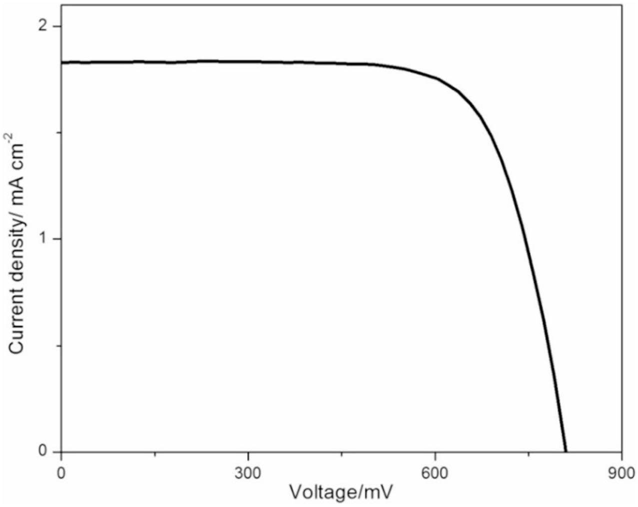

**Fig. 5** The current density – voltage (*J-V*) characteristic curve for solar cell with configuration of FTO/$TiO_2$/Dye/PEO: 15 wt% $Pr_4N^+I^-$: $I_2$ solid electrolyte/Pt

The FF% was calculated by using the relationship,

$$FF\% \ = (J_{max}\ V_{max}) \ / \ (J_{sc}\ V_{oc}) \ \times \ 100\% \tag{1}$$

where, $J_{max}$ and $V_{max}$ are the values of the short circuit current density and the open circuit voltage at maximum power output, respectively. The efficiency of DSSC was calculated according to the equation,

$$n\% \ = \ (J_{sc}\ V_{oc}\ FF) \ / \ (Total\ incident\ power\ density) \ \times \ 100\% \tag{2}$$

Under simulated sunlight with an irradiance of 100 W $m^{-2}$ (AM 1.5), the DSSC fabricated using a solid polymer electrolyte composed of PEO with 15 wt% $Pr_4N^+I^-$ and $I_2$, with the cell configuration FTO/$TiO_2$/dye/PEO:15 wt% $Pr_4N^+I^-$:$I_2$ solid electrolyte/Pt, achieved an open-circuit voltage ($V_{OC}$) of 809.9 mV, a short-circuit current density ($J_{SC}$) of 1.82 mA $cm^{-2}$, and a fill factor (*FF*) of 73.1%. These parameters resulted in a power conversion efficiency ($\eta$) of 1.08%.

## Performance of DSSCs fabricated with plasticized solid polymer electrolytes, PEO: EC: 15 wt% $Pr_4N^+I^-$: $I_2$

### Effect of the solid plasticizer, EC

As the next step in this study, ethylene carbonate (EC) was used as a solid plasticizer to improve the ionic conductivity of the PEO-based polymer electrolyte. The incorporation of a plasticizer increases the ionic conductivity of the PEO-based polymer electrolyte by reducing the crystallinity, albeit at the expense of its mechanical properties. The addition of *a* plasticizer with low molecular weight and high dielectric constant leads to significant modifications in the polymer electrolyte, such as an increase in the content of the amorphous phase, thereby increasing the segmental flexibility of the polymer chains, thus facilitating cation migration by ionic hopping and anion migration by diffusion through the electrolyte [14, 17]. Figure 6 shows the variation *in* efficiency of DSSCs fabricated with different PEO: EC weight ratios of the plasticized electrolyte. Here, the weight of the salts Pr4$N^+I^-$ and $I_2$ *was* kept constant at 15 wt%. As *is* evident from Fig. 6, the overall efficiency of the DSSC increased gradually when the amount of EC *was* increased. However, as shown in this figure, the nature of the polymer electrolyte also changed from a solid state to a gel state, and finally to a liquid state with an increasing amount of the EC solid plasticizer.

According to the results shown in Fig. 6, the DSSC fabricated with the plasticized solid polymer electrolyte with a PEO: EC weight% ratio of 42.5:42.5 shows the highest efficiency of 1.46%. Further addition of EC to the electrolyte changes the nature of the electrolyte from a solid state to a non-flowing "thick" gel state, then to a barely flowing gel state, and finally to a liquid state due to the expansion of the free volume of the polymer matrix caused by the incorporation of the EC plasticizer. The efficiencies of DSSCs corresponding to different PEO: EC wt% ratios obtained from *J–V* measurements are depicted in Fig. 6.

### Mixed cation effect

In the present work, in order to enhance the solar cell efficiency further by using the "*mixed-cation effect*", we have introduced two mixed-cation iodide salts, $Pr_4N^+I^-$ and KI, into the PEO: EC-based plasticized solid polymer electrolyte and studied the effect on the performances of DSSCs [10–17]. For this purpose, PEO: EC-based solid polymer electrolytes with different KI: $Pr_4NI$ weight ratios were prepared, and the DSSCs were fabricated and characterized by *J-V* measurements. The weight ratio of 75 wt% KI:25 wt% $Pr_4N^+I^-$ was found to be the best, resulting in the highest increase in the $J_{sc}$ and efficiency. As tabulated in Table 2, due to the mixed-cation effect, the efficiency of the PEO-based solid-state DSSC increased from 1.46% to 1.81%.

As can be clearly seen from Table 2, the main reason for the efficiency enhancement of the DSSC made with binary salts in the electrolyte is the increase in the short-circuit photocurrent density ($J_{sc}$). Our research group was the first to report that DSSCs with enhanced efficiencies can be achieved using the $Pr_4N^+I^-$ and KI mixed-cation iodide salts in a PAN-based gel electrolyte [13]. Subsequent reports by us and by others have established that the efficiency of dye-sensitized solar cells can be enhanced significantly by using

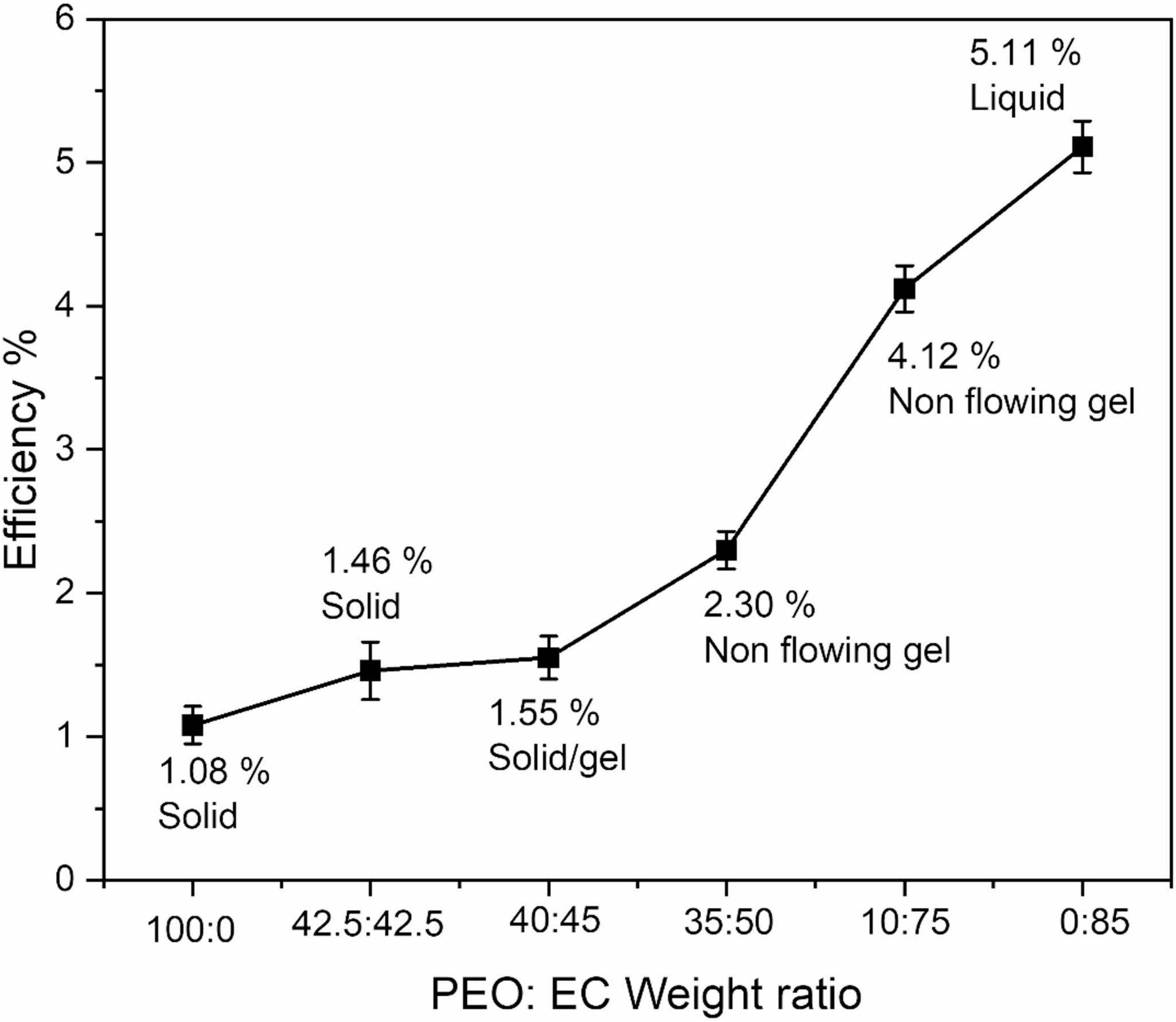

**Fig. 6** The variation of the efficiency of dye sensitized solar cells, fabricated with different PEO: EC weight ratios in the solid electrolyte PEO: EC: 15 wt% $Pr_4N^+I^-$: $I_2$

**Table 2** Comparison of the efficiencies of DSSCs fabricated with PEO - based solid electrolytes using a single iodide salt $Pr_4N^+I^-$ and mixed cation iodide salts with weight ratio, KI: $Pr_4NI = 75:25$ (%)

| Solid Polymer Electrolyte | $J_{sc}$/mA | $V_{oc}$/mV | Fill Factor % | Efficiency % |
|---|---|---|---|---|
| PEO/EC/$Pr_4N^+I^-$/$I_2$ | 2.40 ± 0.90 | 774.4 ± 2.8 | 72.9 ± 1.4 | 1.46 ± 0.09 |
| PEO/EC/$Pr_4N^+I^-$/KI/$I_2$ | 3.86 ± 1.00 | 689.2 ± 2.2 | 68.1 ± 2.1 | 1.81 ± 0.08 |

the "*mixed-cation effect*", where a binary iodide salt system with two differently sized cations is used in the electrolyte instead of the generally used single iodide salt [10–17]. A requirement is that one cation ($Pr_4N^+$) should be bulky, whereas the other cation ($K^+$) should be small. According to these reports, the efficiency enhancement is mainly attributed to the increase in the short-circuit photocurrent density, which is caused by the shifting of the $TiO_2$ conduction band.

The adsorption of cations-in this case, $K^+$ and $Pr_4N^+$ ions-on the surface of nano-$TiO_2$ grains would cause the conduction band edge of $TiO_2$ to move to the positive side (downward shift), regardless of the cation charge density and ionic size, thereby decreasing the $V_{oc}$ value. As a result of this, the short-circuit current density increases while reducing the open-circuit voltage of the DSSC. This effect is expected to be more pronounced for smaller cations like $K^+$ ions (ionic radius, 0.138 nm) than for bulky cations like $Pr_4N^+$ ions (ionic radius, 0.46 nm). This is because the number of adsorbed $K^+$ cations per unit area of the nano-$TiO_2$

grain surface, or the surface charge density of $TiO_2$, would be much greater in comparison with the number of bulky $Pr_4N^+$ cations per unit area adsorbed onto $TiO_2$, mainly due to the difference in their ionic sizes.

## Nano filler effect

The efficiency enhancement in DSSCs due to the nanofiller effect in polymer electrolytes has been reported by several groups [8–14, 17–19]. Our group has also reported earlier that efficiency enhancement in DSSCs can be obtained by incorporating 2.5 wt% $TiO_2$ nanofiller into a gel electrolyte with a mixed-cation composition of 25 wt% $Pr_4N^+I^-$ and 75 wt% KI [10]. In order to see whether the nanofiller effect would also work in the case of DSSCs made with PEO-based solid polymer electrolytes, we studied the performance of DSSCs in the present system by incorporating $TiO_2$ nanofiller into the PEO-based mixed-cation solid polymer electrolyte. It was observed that further improvement in efficiency can be achieved in DSSCs made with PEO-based solid polymer electrolyte by using the nanofiller effect, as depicted in Fig. 7. According to this figure, when the amount of $TiO_2$ nanofiller initially increases, the solar cell efficiency also increases, exhibiting a maximum efficiency of 3.02% at 2.5 wt% $TiO_2$ filler concentration. Further addition of the nanofiller to the electrolyte decreases the cell efficiency. The efficiency enhancement in DSSCs with 2.5 wt% filler can be attributed to the reduction in crystallinity and the increase in the amorphous phase content of the mixed-phase PEO electrolyte. The filler particles with high surface area prevent the recrystallization of the PEO polymer, thereby retaining a higher percentage of the amorphous

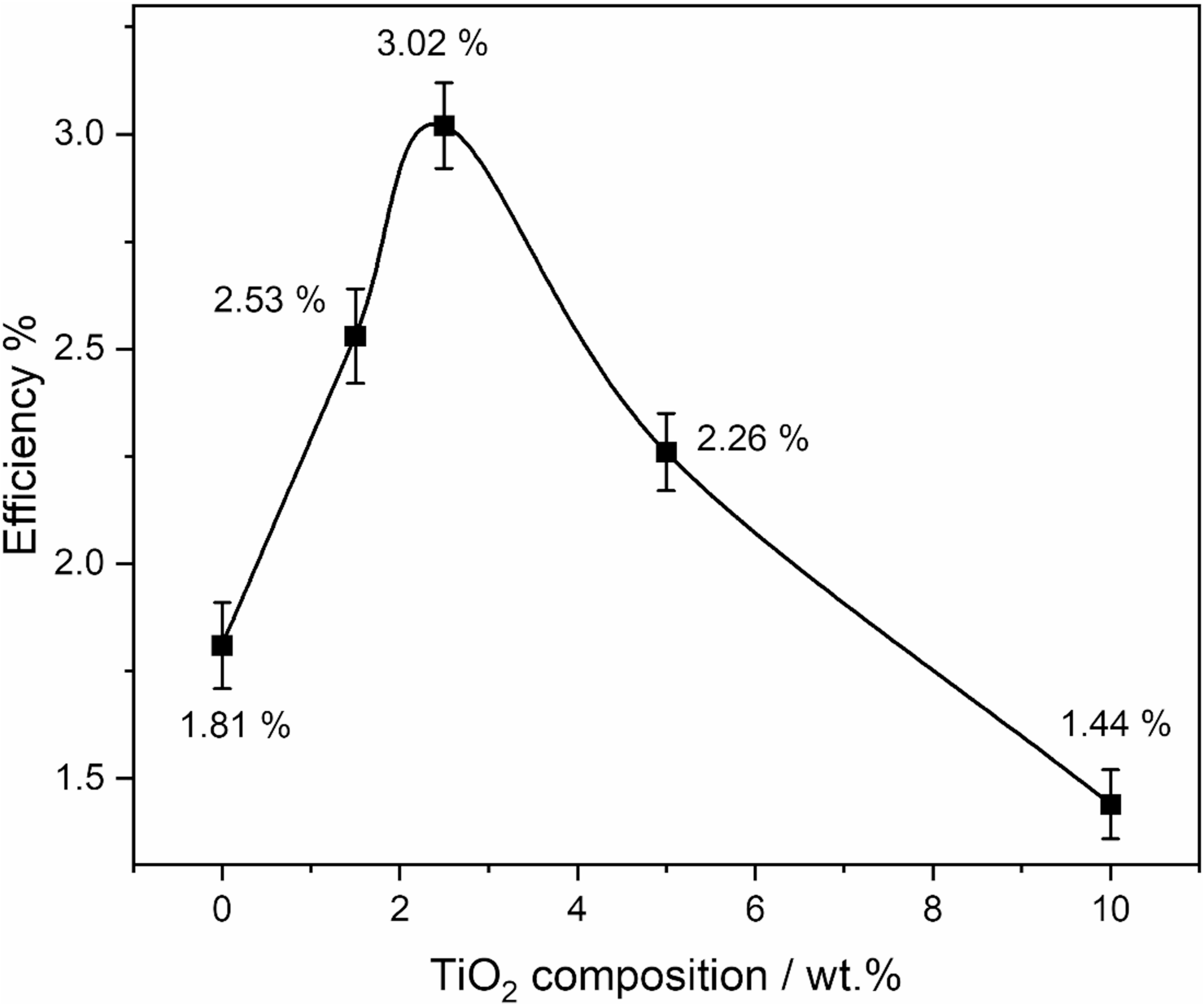

**Fig. 7** The variation of efficiency of dye sensitized solar cell, fabricated with PEO based solid polymer electrolyte containing different weight ratios of the nano filler, $TiO_2$. [PEO: EC: $Pr_4NI$: KI: $I_2+x$ wt% $TiO_2$; $x=0, 1.5, 2.5, 5, 10$]

phase of the electrolyte. This facilitates iodide/triiodide ($I^-$/$I_3^-$) anion migration by diffusion through the electrolyte medium, enhancing iodide ion mobility.

In addition, $TiO_2$ nanoparticles with highly charged surfaces can provide better conductive pathways for the migrating iodide/triiodide ions within the electrolyte. Both these effects enhance the photocurrent density in the solar cell. However, the solar cell efficiency drops with further addition of the nanofiller, quite likely due to the decrease in iodide/triiodide ion mobility caused by the blocking effect resulting from the aggregation of nanoparticles in the electrolyte. Therefore, based on these research findings, it can be concluded that the efficiency of DSSCs made with PEO-based solid polymer electrolyte can be further enhanced up to 3.02% by using the nanofiller effect.

## FTIR analysis

FTIR spectroscopy was used to study the interaction between PEO and $TiO_2$-based solid polymer electrolytes. The Fig. 8 shows the FTIR spectra of the PEO-based solid polymer electrolyte, (a) without $TiO_2$ nanofiller and (b) with $TiO_2$ nanofiller.

According to graph shown in Fig. 8(a), the characteristic peaks of the PEO polymer are observed at 843 $cm^{-1}$ ($CH_2$ wagging mode) and 963 $cm^{-1}$ ($CH_2$ twisting mode). The C–O–C stretching mode appears at 1103 $cm^{-1}$, while $CH_2$ bending vibrations are observed at 1344 $cm^{-1}$. An asymmetric $CH_2$ bending peak is visible at 1467 $cm^{-1}$. Furthermore, the C = O stretching and $CH_2$ stretching modes are detected at 1652 $cm^{-1}$ and 2880 $cm^{-1}$, respectively. These results are consistent with those reported in the literature [20, 21].

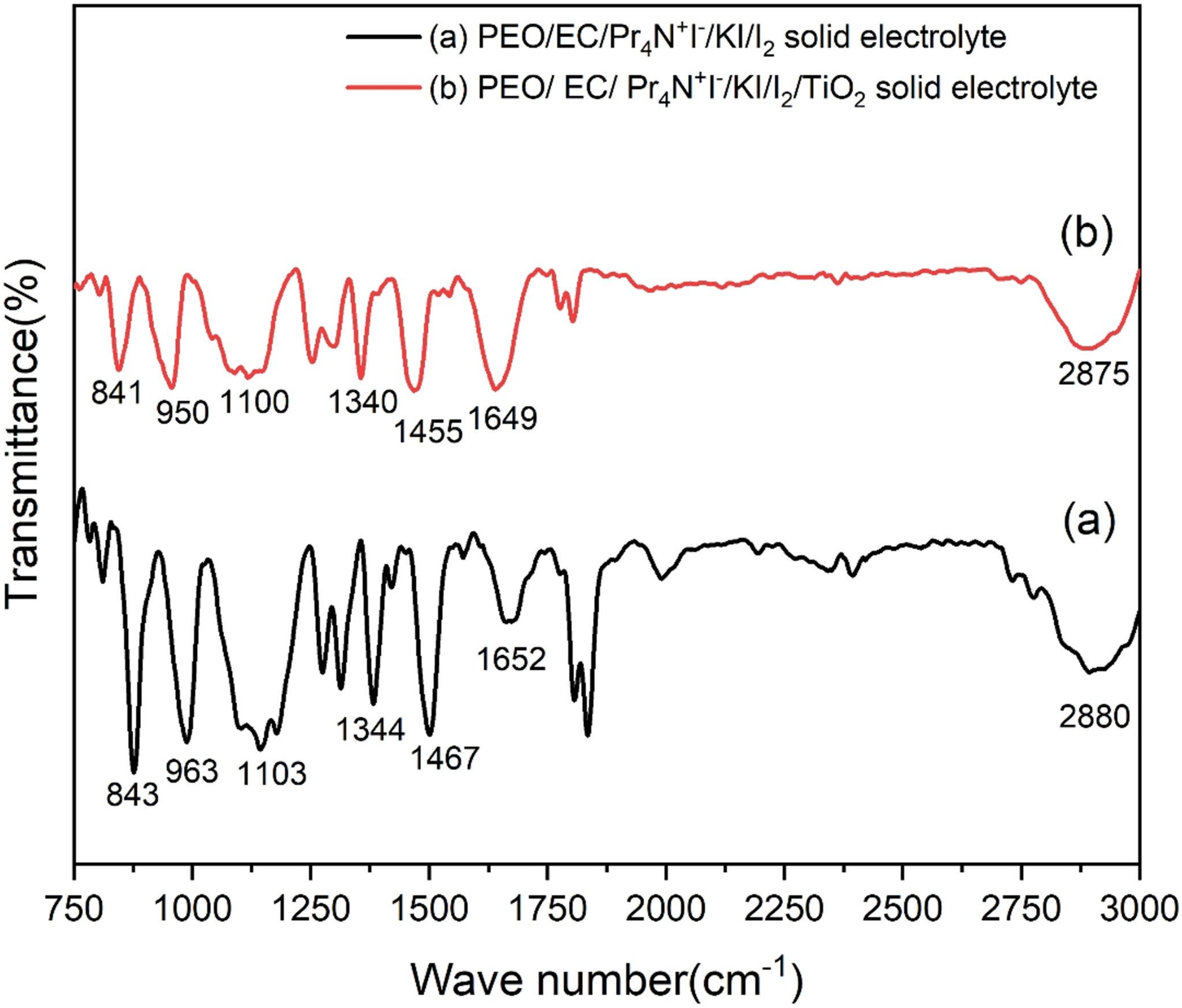

**Fig. 8** Comparison of the FTIR spectra of the filler-free and $TiO_2$ filler added electrolyte samples

Figure 8 (b) shows the FTIR spectrum of the PEO based, solid polymer electrolyte with 2.5 wt% of $TiO_2$ nanofiller. The spectra observed show relatively lower intensities of the vibrational bands of the PEO matrix upon the addition of $TiO_2$ nano filler. The slight shifting of the peaks can be observed after $TiO_2$ nanofiller addition to the polymer matrix. The observed intensity reduction and the slight shifting in peak positions could possibly be due to the polymer-filler interaction caused by the transient coordination bonds formed between the oxygens of the $TiO_2$ and the PEO chain. Similar observations have been reported by Sengwa et al. [21].

## $TiCl_4$ treatment

The effect of $TiCl_4$ treatment in enhancing the efficiency of DSSCs has been reported by many groups [22–24]. However, to the best of our knowledge, this has not been tested for DSSCs made with PEO-based solid polymer electrolytes. Therefore, in order to further enhance the efficiency of the above DSSCs, the $TiO_2$ photoanodes were subjected to the usual $TiCl_4$ treatment using an aqueous solution of titanium tetrachloride ($TiCl_4$). Figure 9 shows the current density-voltage *(J-V)* characteristics of the efficiency-optimized DSSC, fabricated with the optimized solid polymer electrolyte containing PEO: EC: $Pr_4N^+I^-$:KI: $I_2$ + 2.5 wt% $TiO_2$, with and without the $TiCl_4$ treatment. It is clear from Fig. 8 that $TiCl_4$ treatment has enhanced the efficiency of the DSSC from 3.02% to 3.41%.

The $TiCl_4$ treatment is expected to improve the performance of DSSCs by enhancing electron transport, improving light absorption, and increasing the efficiency of charge collection. $TiCl_4$ treatment can improve the adhesion of $TiO_2$ nanoparticles in the photoanode to the conducting glass, facilitating electron transport. The treatment is also expected to promote the formation of necking between $TiO_2$ particles, creating more conductive pathways for electron transport while reducing interparticle resistance. This improved connectivity would lead to faster electron diffusion within the $TiO_2$ photoanode. The suppression of electron recombination due to the $TiCl_4$ treatment can also lead to an increase in $V_{oc}$, which is a key parameter for enhancing DSSC performance [25–27].

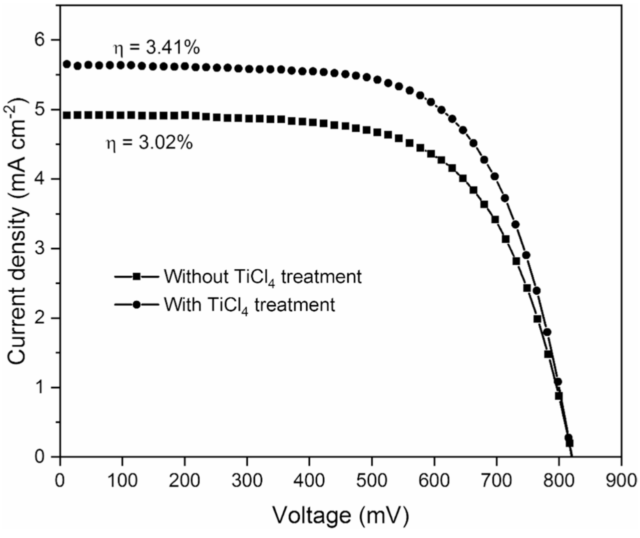

**Fig. 9** Current density - voltage (*J-V*) characteristics of the DSSCs fabricated with solid polymer electrolyte containing PEO: EC: $Pr_4NI$: KI: $I_2$+2.5 wt% $TiO_2$; (**a**) With $TiCl_4$ treated $TiO_2$ photo anode and (**b**) $TiO_2$ photoanode without $TiCl_4$ treatment

The solar cell parameters corresponding to the above two DSSCs are tabulated below (Table 3). According to this table, the efficiency increase after the $TiCl_4$ treatment appears to be related to the increase in the short-circuit photocurrent density.

Figure 10 shows how the individual effects described so far have contributed to enhancing the efficiency in the DSSCs fabricated with PEO-based solid polymer electrolytes. Figure 11 shows that the ionic conductivity variation by individual effects described earlier which have contributed to the solar cell performance. According to Fig. 11, it can be seen that the improvement of ionic conductivity due to the incorporation of the EC plasticizer, mixed cations and $TiO_2$ nanofiller, greatly contribute to the observed efficiency ienhancement of the DSSC.

## Electrochemical impedance spectroscopy (EIS) measurements

Complex impedance measurements are crucial, especially for understanding the effect of nanofillers on dye-sensitized solar cell (DSSC) electrolytes, because they provide insights into the cell's electrical behavior, including charge transfer kinetics and resistances. Generally, the inclusion of $TiO_2$ nanofillers in a polymer gel electrolyte enhances the diffusion coefficient and reduces the charge transfer resistance at the electrolyte/counter-electrode interface, thereby improving the photovoltaic performance of the corresponding solar cell. Figure 12 shows the complex impedance plots obtained for the aforementioned DSSCs made with PEO-based solid polymer electrolyte, measured in the frequency range from 0.01 Hz to 1 MHz, focusing on the effects of the $TiO_2$ nanofiller in the electrolyte and the $TiCl_4$ treatment in the photoanode.

In an ideal impedance plot of a DSSC, there should be three semicircles, which correspond to (a) charge transfer resistance of the Pt counter electrode/electrolyte interface ($R_{CT1}$), (b) $TiO_2$ electrode/electrolyte interface ($R_{CT2}$), and (c) ion diffusion of the electrolyte ($R_{CT3}$) [18, 25, 26]. However, in the present case, only the first two semicircles are

**Table 3** The solar cell parameters measured for DSSC fabricated with solid polymer electrolyte under the irradiance of 100 W m$^{-2}$ (1.5AM) simulated sunlight with and without $TiCl_4$ treatment of the photo anode

| Solid polymer electrolyte<br>PEO: EC: $Pr_4N^+I^-$ :KI: $I_2$+2.5 wt% $TiO_2$ | $J_{sc}$/mAcm$^{-2}$ | $V_{oc}$/mV | FF % | η % |
|---|---|---|---|---|
| Without $TiCl_4$ treatment | 4.94±0.8 | 809.5±2.5 | 78.5±1.6 | 3.02±0.10 |
| With $TiCl_4$ treatment | 5.63±0.6 | 803.1±3.2 | 75.4±2.0 | 3.41±0.08 |

visible. The third semicircle, which corresponds to ion diffusion in the low-frequency range, is not visible due to the frequency limitation of the instrument in the low-frequency range.

As shown in Table 4, the DSSC fabricated with electrolyte A, without the $TiO_2$ nanofiller, exhibits the highest charge transfer resistance ($R_{CT2}$) at the $TiO_2$ electrode/electrolyte interface compared to the other two DSSCs. It is clear that the charge transfer resistance decreases when the DSSC electrolyte contains 2.5 wt% $TiO_2$ nanofiller, resulting in an efficiency enhancement. The lowest $R_{CT2}$ value is reported for DSSC (C), made with the $TiCl_4$-treated $TiO_2$ electrode, resulting in the highest efficiency of 3.41%.

The charge transfer resistance at the Pt counter electrode/electrolyte interface ($R_{CT1}$) has also decreased as the solar cell efficiency increased, indicating an efficient charge transfer process through the cell, quite likely mediated by the enhanced photocurrent. Therefore, it can be concluded

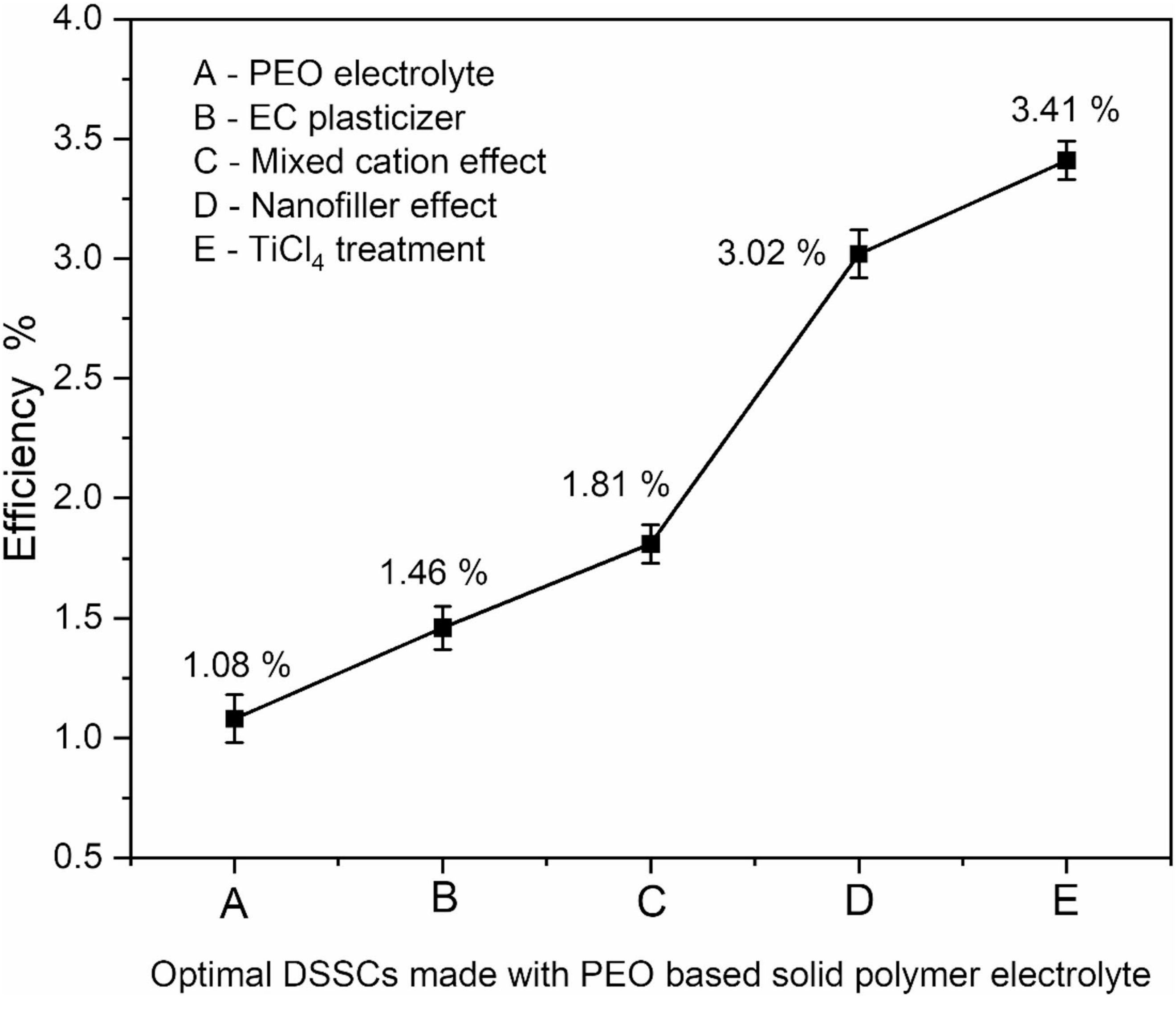

**Fig. 10** Variation of efficiency vs. different "effects" applied to enhance the efficiency of DSSCs based on PEO based solid polymer electrolytes

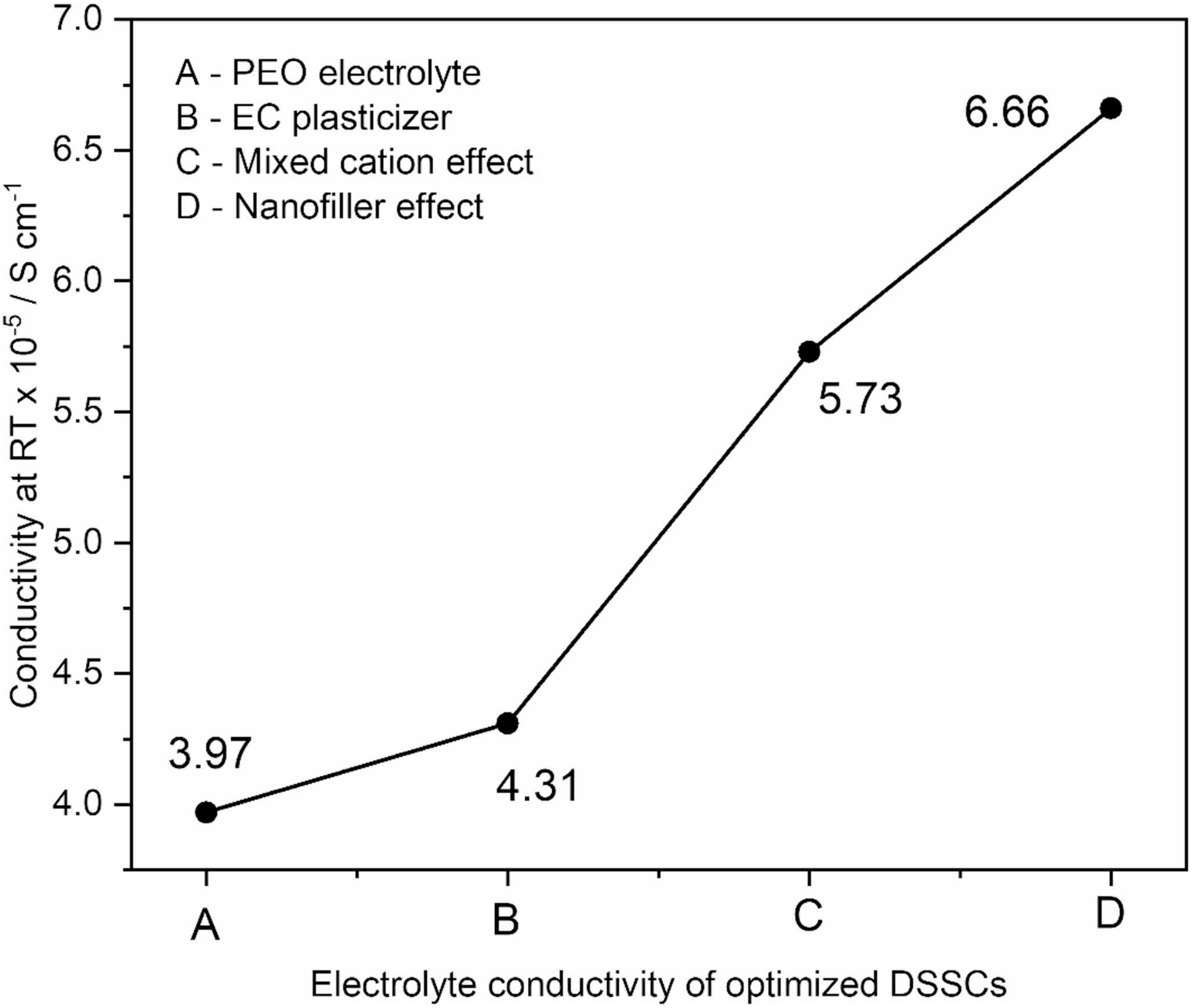

**Fig. 11** Variation of ionic conductivity vs. different "effects" applied on PEO based solid polymer electrolytes

that the efficiency increases in the three DSSCs A, B, and C correlate with the decreased charge transfer resistance at the electrode–electrolyte interfaces, facilitating efficient electron transfer. Table 4 shows the variation of the charge transfer resistance values obtained for the three DSSCs, A, B, and C.

## Conclusion

PEO-based solid polymer electrolytes, PEO: $Pr_4N^+I^-$:$I_2$, containing $Pr_4N^+I^-$ as the iodide salt, were prepared, optimized, and characterized. The highest iodide ion conductivity of $3.97 \times 10^{-5}$ S $m^{-1}$ at 30 °C was obtained for the electrolyte containing PEO:15 wt% $Pr_4N^+I^-$:$I_2$. The optimized DSSC fabricated with this solid polymer electrolyte exhibited an efficiency of 1.08% under an irradiance of 100 W $m^{-2}$. The addition of the solid plasticizer ethylene carbonate (EC) to the electrolyte enhanced the overall efficiency of the DSSC to 1.46%. This corresponds to the optimized electrolyte composition with 42.5 wt% PEO: 42.5 wt% EC: 15 wt% $Pr_4N^+I^-$:$I_2$. The efficiency of the DSSCs was further enhanced to 1.81% through the mixed-cation effect by using the optimized binary iodide salt mixture of 75 wt% KI + 25 wt% $Pr_4N^+I^-$.

The incorporation of 2.5 wt% $TiO_2$ nanofiller into the electrolyte, with a composition of 42.5 wt% PEO: 42.5 wt% EC: 3.75 wt% $Pr_4N^+I^-$: 11.25 wt% KI: $I_2$, further enhanced the overall efficiency of the DSSC to 3.02%, evidently due to the increase in the amorphous phase content of the PEO electrolyte, leading to higher iodide ion mobility. Finally, the $TiO_2$ photoanode surface was modified by $TiCl_4$ treatment to further enhance the solar cell efficiency from 3.02% to 3.41% through improved electron transport in the photoanode.

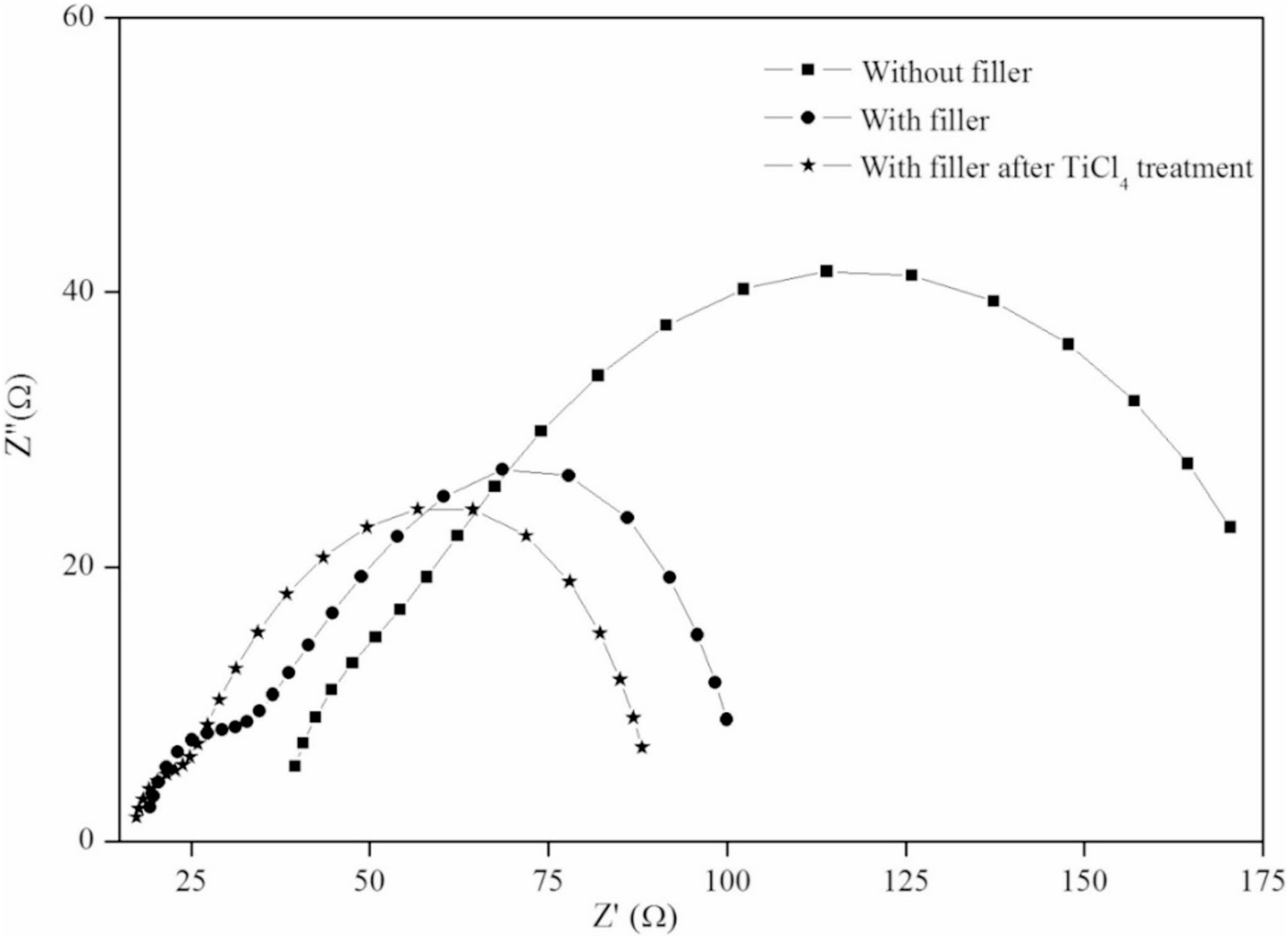

**Fig. 12** Impedance plots obtained for the DSSCs made with three PEO/EC/$Pr_4N^+I^-$/KI/$I_2$ based solid electrolytes (**A**) without $TiO_2$ nano filler, (**B**) with 2.5wt% $TiO_2$ nano filler and (**C**) with 2.5wt% $TiO_2$ filler and $TiCl_4$ treated $TiO_2$ photoanode measured in the frequency range of 0.01 Hz – 1 MHz

**Table 4** Results of the impedance measurements obtained for the three DSSCs made with three PEO/EC/$Pr_4N^+I^-$/KI/$I_2$ based solid electrolytes (A) without $TiO_2$ nano filler, (B) with 2.5wt% $TiO_2$ nano filler and (C) with 2.5wt% $TiO_2$ filler and $TiCl_4$ treated $TiO_2$ photoanode measured in the frequency range of 0.01 Hz – 1 MHz

| DSSC | η% | $R_s$ (Ω) | $R_{CT1}$ (Ω) | $R_{CT2}$ (Ω) | $R_{CT3}$ (Ω) | $V_{oc}$ (mV) |
|---|---|---|---|---|---|---|
| A | 1.81% | 37.0 | 36.1 | 11.9 | 102.0 | 689.2 |
| B | 3.02% | 18.3 | 22.9 | 11.7 | 51.9 | 809.5 |
| C | 3.41% | 16.7 | 6.57 | 10.6 | 57.3 | 803.1 |

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