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Efficiency enhancement due to the combined mixed cation effect and TiO₂ nanofiller effect in PEO and ionic liquid-based dye-sensitized solar cells

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Abstract

Dye-sensitized solar cells were fabricated with a polyethylene oxide (PEO)-based quasi-solid (gel) electrolyte consisting of the ionic liquid 1-hexil-3-methylimidazoliym iodide (HMII), and tetrapropyl ammonium iodide ($Pr_4N^+I^-$) as the two iodide salts with two dissimilar cations. Titanium dioxide powder (TiO₂) (P-25) was added to the polymer electrolyte to enhance the iodide ion conductivity further by the nanofiller effect. The electrolyte and the solar cells were characterized by ionic conductivity and impedance measurements, DC polarization test, and current-voltage measurements. The maximum ionic conductivity of 6.95×10^{-3} S cm⁻¹ at 30 °C was exhibited by the electrolyte composition with a 5 wt% TiO₂ nanofiller concentration, and the activation energy of this electrolyte was 0.181 eV. The solar cell with this conductivity-optimized gel electrolyte had the highest short-circuit photocurrent of 8.72 mA cm⁻² and the highest efficiency of 4.04% with an opencircuit voltage of 685.4 V and a fill factor of 67.6%. The addition of TiO₂ nanofiller to the PEO-based gel polymer electrolyte has increased the electron recombination lifetime in the TiO₂ photoanode from 2.23 ms for the TiO₂ nanofiller-free electrolyte to 33.84 ms for the filler-added electrolyte. The enhancement of the solar cell efficiency is attributed to the mixed cation effect and the diffusion-mediated ionic conductivity increase due to the presence of the TiO₂ nanofiller.

Keywords Dye-sensitized solar cells \cdot Polymer gel electrolyte \cdot Mixed cation effect \cdot Ionic conductivity \cdot Nanofiller effect \cdot Efficiency enhancement

Introduction

The development of low-cost and easily accessible alternative energy sources to replace non-renewable energy sources has become one of the world's major problems today. Dyesensitized solar cells (DSSCs) are one of the viable and

Highlights

- Dye-sensitized solar cells were fabricated with polymer gel electrolyte with mixed cation iodide salts and TiO₂ nanofiller.
- The maximum ionic conductivity exhibited by the electrolyte composition with 5 wt% is 6.95×10^{-3} S cm⁻¹ at 30 °C.
- The best solar cell had a short circuit photocurrent of $8.72 J_{sc}/mA \text{ cm}^{-2}$ and an efficiency of 4.04%.
- The addition of TiO₂ nano filler increased the electron recombination lifetime in the TiO₂ photoanode from 2.23 ms for the nanofiller free electrolyte to 33.84 ms.
- The ionic conductivity increase is due to the mixed cation effect and the enhanced diffusion mediated ionic mobility due to TiO₂ nanofiller.

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emerging solutions to address this problem, though they have some drawbacks when manufactured on a large scale. Most of these problems arise due to the use of liquid electrolytes, which cause leakage, electrode corrosion, evaporation of the solvent, and high-temperature instability and flammability [1–4]. Incorporation of ionic liquids into polymer electrolytes is a possible strategy to replace volatile organic solvents widely used as electrolytes in DSSCs and achieve chemical and thermal stability along with high ionic conductivity at room temperature [2-5]. In the electrolyte application for dye-sensitized solar cells, the utilization of ionic liquids is getting the highlights to replace volatile organic solvents thanks to their low volatility, and thermal and electrochemical stability. The iodide/triiodide redox electrolyte is the preferred choice for this application, hence numerous iodide-based ionic liquids have been explored and reported.

On the other hand, ionic liquids can combine with polymer electrolytes and inorganic nanofillers to form polymer nanocomposite gels with low viscosity so that the electrolyte can go into the pores of mesoporous TiO_2 film while retaining an acceptable ionic conductivity from iodide ion transport. When the imidazolium cation-based ionic liquid is incorporated into PEO, the resulting gel polymer electrolyte is expected to possess reasonably high iodide ion conductivity while eliminating many problems associated with solvent-based electrolytes [2].

Polyethylene oxide (PEO) is one of the most widely used polymers in dye-sensitized solar cells and many other solidstate devices, including lithium-ion battery electrolytes [6-8]. Incorporating inorganic nanofillers such as TiO₂, SiO₂ Al₂O₃, etc. into the PEO electrolyte can enhance the iodide ion conductivity and hence the energy conversion efficiency of the solar cells made with PEO-based polymer electrolytes [8-12]. Inorganic nanofillers also improve the mechanical, interfacial, and conductive properties of the polymer electrolyte. In the present study, we have added TiO_2 nanoparticles to the electrolyte as the nanofiller which is expected to decrease the crystallinity of PEO and increase the amorphous phase content due to their interactions with the polymer chain [12]. This is because, the iodide ions are expected to migrate in the electrolyte medium by ionic diffusion which is facilitated by the amorphous nature of the electrolyte medium. This would enhance the mobility of I_3^{-}/I^{-} anions in the electrolyte, thereby increasing the short-circuit photocurrent and hence the energy conversion efficiency of the DSSC. In this work, the PEObased nanocomposite gel electrolyte containing 5 wt% of the TiO₂ nanofiller has shown the maximum ionic conductivity at a few selected temperatures.

The studies reported previously by our group on the effect of mixed cations on solar cell efficiency have shown that enhanced solar cell efficiencies can be achieved using mixed-cation iodide salts compared to a single-cation iodide salt [13–15]. In this work, we have selected 1-Hexil-3methylimidazoliym iodide (HMII) and tetrapropyl ammonium iodide (Pr₄NI) as the two iodide salts with dissimilar cations. Due to their bulky cation sizes, they are expected to facilitate the ionic dissociation of the electrolyte providing more iodide ions available for redox reactions [16-18, 20]. The electrolyte composition ratio of PEO: $Pr_{4}N^{+}I^{-}$: HMII was optimized to obtain the highest ionic conductivity to obtain the highest phot current density in the solar cells. The energy conversion efficiency of DSSCs fabricated with this double-cation iodide electrolyte was found to be higher than the efficiencies observed for DSSCs prepared using the single-cation iodide salt PEO: Pr₄N⁺I⁻: HMII evidently due to the higher iodide ion conductivity.

Experimental

Electrolyte preparation

All the chemicals used as starting materials had a purity greater than 98%. Polyethylene oxide (PEO, Mw 4×10^6 ,

Aldrich), tetrapropyl ammonium iodide $(Pr_4N^+I^-)$ (98%, Aldrich), 1-hexil-3-methylimidazoliym iodide (HMII) (Aldrich), iodine (Fluka), glacial acetic acid (99%, Fisher Scientific), Triton-X (Aldrich), and ethanol (BDH) were used as received. Titanium dioxide powder (TiO₂) (P-25) was purchased from Degussa AG. All the chemicals used to prepare the electrolyte except 1-hexil-3-methylimidazoliym iodide and I₂ were vacuum dried at 60 °C for 24 h prior to use.

PEO: $Pr_4N^+I^-$: HMII: $I_2 = 3$: 3: 7: 1 (molar ratios) were kept constant for all the samples [21]. First, PEO polymer and $Pr_4N^+I^-$ salt were stirred in ~ 50 drops of acetonitrile solvent in a closed bottle for 24 h. Next, the lid was opened, and the stirring was continued to allow the acetonitrile to evaporate. After a considerable amount of acetonitrile was evaporated, HMII ionic liquid was added to the mixture and stirred for another 24 h with the lid opened until all the acetonitrile was evaporated. Finally, iodine chips (I_2) were added and stirred overnight with the lid closed to obtain the PEO-based gel electrolyte. TiO₂ nanofiller-added electrolyte samples were prepared separately prior to the addition of I_2 to prepare the polymer nanocomposite electrolyte. The amount of TiO_2 (wt%) was varied in order to obtain the electrolyte composition with maximum solar cell efficiency (Table 1). Two more electrolyte samples containing only one iodide salt in each, sample F containing the ionic liquid only and sample G containing the tetrapropyl ammonium iodide only, were prepared by the same procedure in order to determine the mixed cation effect.

Preparation of the TiO₂ photoanode

TiO₂ paste was prepared by grinding 0.2 g of TiO₂ with 12 drops (~0.15 g) of glacial acetic acid, 1 drop (~0.02 g) of Triton X-100, and about 2 ml of ethanol. The paste was doctor-bladed on pre-cleaned fluorine-doped conducting tin oxide (FTO) glass (Nippon glass of sheet resistance 10–12 Ω /square) keeping an active cell area of 0.25 cm². The photoanode plates were sintered at 450 °C for 45 min and allowed to cool down to room temperature. They were

Table 1 Weights of TiO_2 nanofiller added to prepare the PEO polymer nanocomposite gel electrolyte

Sample	PEO/g	HMII/g	Pr ₄ N ⁺ I ⁻ /g	TiO ₂ /g	I ₂ /g
A	0.015	0.069	0.029	0.0000	0.0085
В	0.015	0.069	0.029	0.0013	0.0085
С	0.015	0.069	0.029	0.0026	0.0085
D	0.015	0.069	0.029	0.0037	0.0085
Е	0.015	0.069	0.029	0.0053	0.0085
F	0.015	0.069			0.0085
G	0.015		0.098		0.0085

subsequently dipped in an ethanoic dye solution containing Ruthenium N 719 dye purchased from Solaronix [RuL₂ (NCS)₂: 2TBA, where L = "2,2'-bipyridyl-4'-dicorboxylic acid; TBA = tetrabutyl ammonium] and left overnight for dye adsorption prior to use in solar cells.

Characterization of the solar cell

The solar cells were fabricated by sandwiching the gel polymer electrolyte between the TiO₂ photoanode and the Pt counter electrode in the configuration glass/FTO/TiO2/ dye/electrolyte/Pt/FTO/glass. The photocurrent–voltage (*I-V*) characteristics of the cells were measured under the illumination of 1000 mW cm⁻² (AM 1.5) simulated sunlight using a homemade computer-controlled setup coupled to a Keithley 2000 multimeter and a potentiostat/galvanostat HA-301. A Xenon 500 lamp was used with an AM 1.5 filter to obtain the simulated sunlight with the above intensity.

Conductivity measurements of polymer electrolytes

The ionic conductivity of the polymer electrolytes was determined by AC complex impedance spectroscopy using a computer-controlled (Nova software) Autolab (PGSTAT 128N) impedance analyzer in the frequency range of 0.1 Hz to 1 MHz. The electrolytes were sandwiched between two polished stainless steel (SS) electrodes to be used in the impedance measurements. The Thermo Scientific-Lindburg Blue M oven was used to vary the temperature of all the samples from 30–55 °C. The measurements were taken at 5 °C intervals after keeping the sample for about 15 min at the selected temperature for thermal stability. The conductivity values were extracted from the impedance measurements.

Impedance measurements of solar cells

The impedance measurements of the solar cells were determined by AC complex impedance spectroscopy using a computer-controlled (NOVA 1.9 software) AUTOLAB (PGSTAT 128N) impedance analyzer in the frequency range 0.01 Hz–1 MHz with an AC amplitude of 10 mV in steady state settings for the electrolyte samples prepared with filler (Sample C) and without filler (Sample A). The potentiostat controlled the bias potential equal to the open circuit voltage as determined by *I-V* measurements. For the measurements taken under dark conditions, the bias voltage was kept at 0 V. The measurements were taken under the illumination of 1000 mW cm⁻² (AM 1.5) simulated sunlight as well as under dark conditions to determine the recombination lifetime of electrons.

Results and discussion

Characterization of the gel polymer electrolytes

The non-flowing gel nature of the polymer electrolytes prepared according to the compositions given in Table 1 can be confirmed by the "inverted bottle test" shown in Fig. 1 for the two electrolyte samples, one with 0 wt% TiO₂ nanofiller (Fig. 1a) and the other with 5 wt% TiO₂ nanofiller (Fig. 1b). The absence of the characteristic peak of the bond of acetonitrile at 2250 cm⁻¹ FTIR spectra of both samples (not shown) confirmed the absence of acetonitrile in both samples A and C [11, 19]. The ln (σT) vs 1000/*T* variation of ionic conductivity of the gel electrolyte samples A, B, C, D and E (Table 1) are shown in Fig. 2.

All the samples exhibit a linear behavior implying that the conductivity variation follows the Arrhenius equation,

$$\sigma T = A \ e^{\frac{-E_g}{kT}}$$

where A is the pre-exponential factor, E_g is the activation energy, and k is the Boltzmann constant. According to Fig. 3, the activation energy for the electrolyte with 5 wt% TiO₂ nanofiller is 0.181 eV. Also, all five nanofiller-added electrolyte samples have essentially similar activation energy values in the range of 0.121 to 0.210 eV. This is evidently because the activation energy largely depends on the electrolyte medium and specifically on the nature of the polymer heteroatom used to prepare the electrolyte by Frech et al. [21, 22]. It does not depend much on the salt (or salt mixtures) used in the system. Since the electrolyte medium is the same for all five samples and only the concentration of



Fig. 1 Two electrolytes samples, **a** 0 wt.\% TiO_2 and **b** 5 wt.\% TiO_2 showing their non-flowing, gel nature



Fig. 2 $\ln (\sigma T)$ vs 1000/*T* graph for the PEO based nanocomposite gel electrolytes as a function of the TiO₂ nanofiller content

 TiO_2 nanofiller is different, one would expect essentially constant activation energy for all five electrolytes.

The variation of the ionic conductivity with wt% of TiO_2 nanofiller for three different temperatures 30 °C, 40 °C, and 50 °C are shown in Fig. 3. According to these conductivity

Fig. 3 Variation of conductivity with x wt% TiO₂ compositions at three different temperatures

isotherms, the nanocomposite electrolyte containing 5 wt% of the TiO_2 nanofiller exhibits the maximum conductivity at the three selected temperatures.

The use of ionic liquid in the electrolyte also increases the anion concentration in the medium because a large amount of ionic liquid can be dissolved in the polymer medium due to improved ionic dissociation. This is because imidazolium cations can interact with the oxygen atoms present in the ethylene oxide units, forming transient bonds and releasing more iodide anions into the electrolyte medium [3].

It is widely accepted that the addition of inorganic nanofillers enhances the ionic conductivity of PEO-based polymer electrolytes by enhancing the amorphous phase content of the polymer matrix [4, 9–11] According to some reported work on similar systems, the titania particles are arranged in a three-dimensional, mechanically stable network, creating free space and voids through which the I^-/I_3^- anions can easily migrate [2].

The addition of TiO2 nano filler to a poly(ethylene oxide) (PEO) based electrolyte in a dye-sensitized solar cell (DSSC) can influence the iodide ion conductivity in several ways:

- (a) Enhanced Polymer Chain Mobility: Incorporating TiO₂ nanoparticles can modify the polymer chain dynamics in the PEO matrix, potentially increasing chain mobility. This increased mobility can facilitate faster ion transport, enhancing the overall conductivity of the electrolyte.
- (b) Surface Functionalities: TiO₂ nanoparticles often possess surface functionalities that can interact with the



polymer matrix, altering its structure or creating favorable sites for ion conduction. These surface interactions can contribute to improved ion conductivity.

- (c) Reduced Crystallinity or Increased Amorphous Phase: TiO₂ nanoparticles can disrupt the crystalline structure of the PEO matrix or induce an amorphous phase, which could enhance ion mobility within the electrolyte.
- (d) Facilitation of Charge Transfer Processes: In DSSCs, efficient ion transport is crucial for redox reactions involved in the conversion of light to electricity. The TiO_2 nanofiller might aid in facilitating these charge transfer processes by improving ion conductivity, leading to better overall device performance.

The specific mechanism behind the enhanced iodide ion conductivity due to TiO2 addition in a PEO-based electrolyte can depend on various factors like particle size, surface properties, dispersion within the polymer matrix, and the nature of interactions between the nanoparticles and the polymer. Further, the adsorption of imidazolium cations on TiO₂ particles can align the anionic redox couple by electrostatic force, facilitating electron transport by the ion exchange mechanism [4]. The maximum conductivity of the TiO₂ nanofiller-incorporated nanocomposite gel polymer electrolyte (Table 1, Sample C) is found to be 6.95×10^{-3} S cm⁻¹ at 30 °C. Though the ionic conductivity initially increases with the addition of the TiO₂ nanofiller, it starts to decrease after reaching the maximum conductivity point. This phenomenon could be most likely due to the "blocking effect" or "geometrical constrictions" imposed by excess TiO₂ particles, hindering the segmental flexibility of the long PEO chains. The blocking effect can arise due to the excess nanoparticles and also due to particle aggregates.

DC polarization test

Figure 4 shows the DC polarization results obtained for the electrolyte with 5 wt.% TiO₂ filler (sample C, Table 1), which corresponds to the highest solar cell efficiency using the symmetrical cell configuration SS/electrolyte/SS where SS stands for stainless steel electrodes. The decay of the current with time shows that the electronic contribution to the total ionic conductivity is negligible and the electrolyte is predominantly an ionic conductor. This implies that the ionic conductivity is mainly due to the movement of cations and anions in the electrolyte. The ionic radius of the Pr_4N^+ cation is 0.45 nm [23], and the ionic size of the HMIM⁺ ion is assumed to be larger than 0.76 nm [24], while the ionic radius of the iodide ion is 0.22 nm [25].

As both cations in the electrolytes are bulky in size compared to the size of the iodide ions, the ionic conductivity is likely to be mainly due to the diffusion-mediated transport of I_3^-/I^- redox species.



Fig. 4 DC polarization curve for filler-incorporated electrolyte sample C (Table 1) with 5 wt.% TiO_2 filler obtained using SS/electrolyte/SS cell configuration

Solar cell characterization

Current-voltage (*I-V*) characteristics were determined for the solar cells fabricated in the configuration glass/FTO/TiO2/ dye/electrolyte/Pt/FTO/glass. These are shown in Fig. 5 and in Table 2. *I-V* curves for the solar cells fabricated using electrolytes with single iodide salt compositions (samples G and F), double iodide salt compositions without the TiO₂ nanofiller (sample A), and electrolyte samples incorporating the TiO₂ nanofiller (sample C) are shown in Fig. 4. In this figure, only four selected characteristic curves are shown for clarity, although the curves were obtained for all the filler compositions. The efficiency (η) and short-circuit current density (J_{sc}) variations with the TiO₂ filler concentration are shown in Fig. 6. The efficiency of the solar cells is derived from the equation,

$$\eta = \frac{J_{sc}V_{oc}FF}{Total \ incident \ power \ density}$$

where V_{oc} is the open circuit voltage and *FF* is the fill factor which is calculated from the equation,

$$FF = \frac{P_{max}}{J_{sc}V_{oc}}$$

In DSSCs fabricated with mixed cation iodide salts, such as Pr_4NI with a bulky cation and KI with a smaller cation, the cations in the electrolyte are expected to play a dual role in determining the overall efficiency of the solar cell [15]. Iodide salts with bulky cations such as Pr_4N^+ and Hex_4N^+ are expected to facilitate ionic dissociation but minimize the cationic conductivity due to their bulky size,





while enhancing the iodide ion conductivity in the electrolyte. Through increased iodide ion conductivity, they also increase the short circuit photo-current density and charge injection rate at the semiconductor/electrolyte interface.

From Tables 1 and 2, the DSSC efficiency corresponds to the electrolyte with HMII as the only iodide salt is 2.72% while the DSSC efficiency corresponds to the electrolyte with Pr_4NI as the only iodide salt is 2.5%. However, the efficiency of the DSSC made with the filler-free electrolyte with both HMII and Pr_4NI as the binary iodide salt has an efficiency of 3.69%, which is evidently due to the efficiency enhancement caused by the mixed cation effect as has already been reported and explained [15].

As shown in Fig. 4, initially, the addition of TiO_2 nanoparticles up to 5 wt% enhances the J_{sc} which leads to an

Table 2 Solar cell parameters obtained for polymer electrolytes as a function of TiO_2 wt %

Sample	TiO ₂ wt% w.r.t. solid chemicals	$J_{\rm sc}/{\rm mA~cm^{-2}}$	V _{oc} /mV	FF %	η %
A	0.0	8.172	666.9	67.8	3.69
В	2.5	8.304	669.4	68.7	3.82
С	5.0	8.724	685.4	67.6	4.04
D	7.0	8.168	684.2	64.7	3.62
E	10.0	7.228	633.4	67.6	3.09
F	0.0	6.812	618.7	64.6	2.72
G	0.0	5.241	705.8	69.6	2.57

enhancement of the conversion efficiency. By comparing Figs. 3 and 4, we can conclude that the efficiency enhancement is due to the increase in ionic conductivity due to the incorporation of the TiO_2 nanofiller. As discussed earlier, the addition of the nanofiller enhances the amorphous phase content of the PEO polymer, which has enhanced the diffusion-mediated iodide ion conductivity and hence the iodide ion mobility [4, 9–11] The increase in the mobility of I_3^-/I^- redox species has evidently led to an enhancement of the photocurrent density and hence the conversion efficiency of the solar cells.

As seen in Fig. 5, the highest conductivity among the nano titania filler added composite polymer electrolytes was obtained for the sample H (PEO: PC: 25 wt% Pr4N+I+75 wt.% KI) containing 2.5 wt% TiO₂ (with respect to the total weight of the filler-free electrolyte sample). It is well known that in PEO-based solid or gel electrolytes, the addition of nano-fillers decreases the crystallinity of PEO and increases the amorphous phase content [26]. This would favor the ionic mobility and enhance the ionic conductivity because the iodide ions are expected to migrate in the electrolyte medium by ionic diffusion which is facilitated by the amorphous nature of the electrolyte medium.

According to already published reports on the effects of nano-fillers in polymer electrolytes used in DSSCs [8, 9], several effects are possible for the improvement of the iodide ion conductivity and interfacial kinetics at the electrode–electrolyte interfaces. These include (a) increasing the **Fig. 6** Variation of solar cell efficiency and short circuit current density with TiO_2 wt % composition TiO_2 weight percentages are w.r.t. other solid chemicals used for the preparation of the electrolyte samples.



amorphous phase content of the polymer and decreasing the crystallinity, (b) forming an additional channels for migration of the redox couples, (c) increasing ionic mobility and ion diffusivity, (d) reducing the charge recombination resistance at the photoanode/electrolyte interface (R_{ct}), and (e) decreasing the charge transfer resistance at the Pt counter electrode/electrolyte interface (R_{pt}).

It would be easier to interpret the results shown in Table 2 in two steps; Out of the three TiO₂ filler-free electrolyte samples A, F and G, sample A contains both iodide salts (IL and $Pr_4N^+I^-$) and the corresponding DSSC has shown an efficiency of 3.69%, whereas the DSSCs made with IL only and $Pr_4N^+I^-$ only have shown efficiencies of 2.72% and 2.57%, respectively. These efficiency enhancements of about 36% and 44% in these two cases is clearly due to the "mixed cation effect", as cited and explained in detail by several references [12–14, 26]. Out of these two DSSCs, the one made with the IL electrolyte shows a somewhat higher efficiency, evidently due to the liquid nature of the IL iodide salt, which facilitates the diffusion-mediated iodide ion migration in the low-viscous electrolyte medium. The second efficiency enhancement, from 3.69 to 4.04% by about 9.5% is caused by the nano-filler effect due to the presence of the TiO_2 filler. As has been reported and discussed by several groups [9–12], the incorporation of inorganic nanofillers has the effect of increasing the amorphous phase content of PEO-based polymer electrolytes which would also increase the iodide ion mobility contributing to the enhancement of short-circuit photocurrent density and hence the solar cell efficiency.

Solar cell characterization using impedance spectroscopy

The impedance was measured for the solar cells in the frequency range 1×10^{-2} - 1×10^{6} Hz, assembled with filler-free electrolyte sample A and with electrolyte sample C made with 5 wt.% TiO₂ filler, corresponding to the best efficiency solar cell, to determine the electron recombination lifetimes. The determination of physical parameters from EIS spectra of a DSSC is generally done by fitting the spectra to an equivalent circuit. The most widely used equivalent circuit of the complete DSSCs is a transmission line model. Figure 7(a)shows the impedance spectra obtained for these two solar cells in the configuration glass/FTO/TiO₂/dye/electrolyte/Pt/ FTO/glass with electrolyte samples A and C. Figure 7(b) and (c) shows the corresponding equivalent circuits with resistance values obtained from fitting the curves using NOVA 1.9 software which has come with the AutoLab PGSTAT EIS workstation coupled to the Frequency Response Analyzer.

According to Adachi et al. [Ref Adachi], the EIS spectra of DSSCs do not necessarily exhibit three distinct arcs in the complex plane plot or three peaks in the Bode plot; however, proper analysis of the experimental data may help to extract the important physical parameters correctly.

In an ideal impedance spectrum, three semicircles can generally be seen, which correspond to the resistance of the Pt counter electrode/electrolyte interface (R_{1CT}), the TiO₂ electrode/electrolyte interface (R_{2CT}), and the ion diffusion of the electrolyte (R_s), respectively [29, 30]. R_{2CT} is strictly

Fig. 7 a The graph of (-Z'') vs Z' obtained for the solar cells assembled with electrolyte samples A and C, b The equivalent circuit for the solar cell with electrolyte samples C, and c The equivalent circuit for the solar cell with electrolyte sample A



connected to the charge transfer resistance as well as to the reaction mechanism. However, in the present case, only two arcs can be seen in the impedance spectrum. The third arc that corresponds to the ion diffusion cannot be seen in the spectra since the low frequencies needed to obtain the arc are outside the available frequency range of the instrument. Therefore, the R_s value shown here corresponds to the series resistance that appears due to the resistance of the external circuit (Table 3).

The Constant Phase Element (CPE) is used to describe the capacitive process that presents certain frequency dispersion. The impedance of CPE is given by,

$$Z_Q = \frac{1}{Y_O (j\omega)^n}$$

where Y_0 is the value of the argument of the constant phase element (also referred to as a *Q* element) and *n* is the value

Table 3 Resistance values of series resistance (R_s) , the resistance of the Pt counter electrode/electrolyte interface (R_{1CT}) and the resistance of the TiO₂ electrode/electrolyte interface (R_{2CT}) obtained from the solar cell impedance measurements

Sample	R_s/Ω	$R_{1{ m CT}}\Omega$	$R_{2{ m CT}}\Omega$	Electron recombination life time, τ_{t}/ms
A	31.8	14.8	23.2	2.23
С	15.8	13.2	17.6	33.84

of the exponent of the constant phase element. This situation arises when the CPE index n departs from 1 [29]. This can be due to various reasons:

- Non-Ideal Behavior: The ideal case in a Nyquist plot would result in a perfect semicircle with a magnitude of 1 for the complex impedance. Deviations from this ideal behavior can occur due to non-idealities in the system, such as imperfect interfaces, variations in experimental conditions, or deviations from idealized circuit models used to fit the data.
- 2. Heterogeneity or Variations in Interfaces: DSSCs often have complex interfaces with heterogeneous characteristics. This can lead to deviations in the impedance modulus from 1, indicating variations in charge transfer resistances or other complexities in the system.
- 3. Influence of Frequency: At different frequencies applied during EIS measurements, the impedance modulus can vary from 1 due to the kinetics of charge transfer processes occurring at those frequencies. This deviation provides insight into the frequency dependence of charge transfer or relaxation processes.
- 4. Experimental Artifacts: Sometimes, instrumental or measurement artifacts can cause deviations in the impedance spectrum, affecting the impedance modulus values.

The electron lifetime τ_r in TiO₂ electrode is determined primarily by the recombination of electrons with TiO₂ traps, with the electrolyte, and with the oxidized dye at the





photoanode/electrolyte interface. τ_r can be determined from the data corresponding to the second arc of the impedance spectrum using the relationship,

$$\tau_r = \frac{1}{\omega} = \frac{1}{RC}$$

A higher electron recombination lifetime implies that the electrons get sufficient time to go through the TiO_2 semiconducting layer in the photoanode. In the present study, the addition of TiO_2 nano-filler to the electrolyte has increased the recombination lifetime of electrons from 2.23 ms for the DSSC with filler-free electrolyte to 33.84 ms for the DSSC with filler-incorporated electrolyte, allowing more time for transport of photogenerated electrons within the photoanode [27–29]. Therefore, the DSSC made with TiO_2 nanofiller incorporated polymer electrolyte exhibits the best charge transfer properties at the photoanode/electrolyte interface, evidently due to the increased amorphous nature of the polymer electrolyte caused by the presence of the filler.

Therefore, the DSSC fabricated the hybrid gel polymer electrolyte containing 5 wt% of TiO₂ nanofiller has the highest electron recombination lifetime of 33.84 ms and the best charge transfer properties. These results can be correlated with the effectiveness of the TiO₂ nanofiller in increasing the amorphous phase content of the PEO-based polymer gel electrolyte to promote iodide ion transfer. Similar results have been reported for the solid state DSSC made with hybrid polymer electrolyte composite with SiO₂ nanofiber filler [31].

Figure 8 shows the impedance spectra observed under the dark conditions for the solar cells fabricated with electrolyte samples A and C. As seen in the figure, the solar cell assembled using electrolyte sample C shows a higher resistance compared to the solar cell made with electrolyte sample A. In the dark, the solar cell works as a leaky capacitor. Therefore, under forward bias, electrons are transported through TiO₂ layer which eventually reduces I_3^- to I^- . In the meantime, I^- is oxidized to I_3^- at the counter electrode. In this case, the bigger the middle semicircle, the lesser the recombination at the dyed TiO₂ electrode/electrolyte interface. This is caused by the conduction band electrons in mesoporous TiO₂ electrode captured by the reduction of I_3^- ions. This is very likely due to the improved charge transport in the electrolyte due to the addition of TiO₂ nano filler as described earlier [4, 31–33]. In the impedance spectra (Fig. 8), only the second arc is significant. Here, the first arc is combined with the second one so that their separation cannot be clearly seen in the figure and the third semicircle does not appear at all due to the insufficient frequency range in the impedance meter as described earlier.

Conclusion

Synergistic Enhancement: The combination of mixed cations and nanofillers often produces a synergistic effect that surpasses the individual benefits of each enhancement strategy alone. Mixed cations can optimize the iodide ion concentration in the electrolyte material, while nanofillers can improve the iodide ion mobility and charge transport, and reduce recombination losses. Together, they create a more efficient and stable device than what either method achieves independently.

Improved Stability and Performance: DSSCs face challenges related to stability and efficiency. The introduction of mixed cations in the gel electrolyte can enhance the short circuit photocurrent density while simultaneously, nanofillers can contribute to more robust gel electrolyte structure and improved charge carrier dynamics, leading to higher efficiency and longer device lifetimes.

Tailored Device Properties: The combination of mixed cations and nanofillers allows for the fine-tuning of device properties. Different cation compositions can modify the energy bandgap of the photoanode and optimize light absorption characteristics. Nanofillers further enable control over electrolyte morphology and electron transport properties, allowing for customized optimization of DSSC performance.

Novel Material Combinations: Researchers continually explore new combinations of mixed cations and nanofillers to discover optimal synergies. The exploration of diverse mixed cation electrolyte compositions combined with various nanofillers creates a vast design space for novel materials with enhanced efficiency and stability, driving innovation in DSSC technology.

Challenges in Implementation: Despite the promise, integrating mixed cations and nanofillers in DSSCs involves complex material synthesis, optimization, and fabrication processes. Overcoming these challenges while maintaining scalability and cost-effectiveness is an ongoing focus of research in the field.

Declarations

Conflict of interest The authors declare no competing interests.

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