Efficiency enhancement of photovoltaic performance of dye sensitized solar cell using conducting polymer electrolyte of different functional group

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Abstract. Dye-sensitized solar cells (DSSCs) which have a polymer electrolyte added to with various function groups were studied to determine the effect of their composition on the efficiency of the solar cell. Four function group polymers got employed, those groups are polymethylmethacrylate (PMMA), polyvinyl acetate (PVA), polyethylene oxide (PEO) and polyacrylonitrile (PAN). The iodine salt cation is caged by the function groups which cause a positive shift in the dye HOMO level and result in a deceleration in the recombination rate more than that of ordinary iodine electrolyte. The polymer electrolyte ionic conductivity improves the rate of the dye regeneration to make it faster than ordinary iodine as well. Adding pyridine to electrolyte solution makes the conduction band of the TiO2 more negative leading to an increase in the open circuit voltage (Voc). The photo generated current (Jsc) is increased by the employed configureuration, subsequently, the solar cell photovoltaic efficiency is enlarged. PVA is with highest efficiency at 8%, unlike the rest of the polymers which show lower efficiencies.

1. Introduction
Photovoltaic (PV) cells meet the challenge of the global energy deficiency, converting sunlight into electricity [1], [2]. Regular dye Sensitized Solar Cell (DSSC) has the configureuration of photo electrode, wide band gap semiconductor, sensitizing dye, electrolyte and counter electrode. Normally, the liquid electrolyte represents a serious challenge due to the solvation problem, on the other side polymer electrolyte presents an attempt to increase the efficiency and the life time of the solar cell[3].Furthermore, polymer red-ox electrolytes provide flexibility and ionic conductivity which enhance the cell efficiency and life time[4]. The addition of low dielectric solvents like acetonitrile (ACN) and plasticizers such as ethylene carbonate (EC) increase the flexibility of the polymer red-ox electrolyte and improves the interfacial contact with the dye and the diffusion of the ions in the cell [5]. In this work we apply four different polymers, polyvinyl acetate (PVA), polyethyleneoxide (PEO), polyacrylonitrile (PAN) and polyacrylonitrile (PAN) and polymethylmethacrylate (PMMA)as a host matrix of the ions for the red-ox process. The molecular structure of these polymers is shown in figure 1 The polymer caging that occurs
as the polymer chain is coordinated to the cations of the iodine salt (K⁺), has two different roles in the electrolyte [6].

First it is the key process for creating the ionic conductivity (I⁻) that increases the redox process and help a faster regeneration rate of the oxidized dye. Second it is caging more cations, hence making the potential more positive which leads to the downward shift of the highest occupied molecular orbital (HOMO) of the dye [7]. This helps to decrease the recombination rate of the electrons in the conduction band of TiO₂ with the holes in the HOMO of the dye. Furthermore, the addition of pyridine as a donating material changes the surface charge of the TiO₂ shifting the conduction band of the TiO₂ upward and increasing the open circuit voltage ($V_{oc}$). This configuration increase the open circuit voltage ($V_{oc}$) and hence increase the photovoltaic efficiency $\eta$ defined as [8].

$$\eta = \frac{P_{max}}{P_{in}} = \frac{V_{m}J_{m}}{P_{in}} = \frac{FFV_{oc}J_{sc}}{P_{in}} \quad (1)$$

where $P_{max}$ is the maximum output power and $V_{m}$, $J_{m}$ are the maximum output voltage and output current density respectively.

$$FF = \frac{V_{m}J_{m}}{V_{oc}J_{sc}} \quad (2)$$

where $FF$ is the fill factor and $V_{oc}$, $J_{sc}$ are the open circuit voltage and short current density respectively.

2. Experimental

2.1. Materials

TiO₂ powder (Degussa, P25) (Sigma Aldrich), FTO slides of resistance of about 7Ω/square (Sigma Aldrich), EC (Sigma Aldrich), (KI) (Sigma Aldrich), iodine (I₂) (Sigma Aldrich), pyridine (Sigma Aldrich), ethanol (Sigma Aldrich), triton X100(Sigma Aldrich), acetylaceton (Alpha,India), acrylonitrile (Alpha,India), cis-bis(isothiocyanato)bis(2,2-bipyridyl-4,4-dicarboxylato)-ruthenium(II) (N719)(Sigma Aldrich), acetonitrile (Alpha,India), potassium iodide (Sigma Aldrich) and ethylene glycol (Alpha,India) were used without any purification.

2.2. Device Preparation

The preparation of the TiO₂ paste was reported in the methods [9],[10]: 1 gm of TiO₂ white powder (Degussa, P25) mixed with 1 ml of dispersing agent (10 % v:v ) acetylaceton solution. 1 ml of distilled
water was added to the previous slurry with continuous grinding. Add few drops of surfactant material like Triton X100 to increase the dispersion of the nanoparticles in the suspension. For future use keep the paste in dropper bottle in darkness. The FTO slides of 7Ω/square resistance were cleaned by sonication in ethanol for 15 minutes at room temperature to remove impurities and then kept in air for drying. Sonication of TiO_2 films was 15 minutes before use. TiO_2 layer was made by doctor blade technique and then kept at room temperature for drying 20 minutes followed by sintering at 450°C for 30 minutes minutes. The adsorption of the dye Di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II)N-719 was dipping overnight in ethanol solution [11]. A carbon counter electrode is prepared by using a flame of candle on the FTO glass for few minutes. For normal Iodine solution, 0.19g of I_2 and 2g of KI dissolved in 25 ml of ethylene glycol and 0.25M of pyridine added[12],Polyvinyleacate prepared by bulk polymerization while AIBN used as initiator of weight 0.046 g stirred with 5 ml of the monomer till complete solubility at temperature70°C for 6 hours with a condenser system. The composition of the polymer red-ox electrolytes was PVA (0.225 g), ACN (0.750 g), EC (0.525 g) whilsts the molar ratio of KI: I_2 was 1.50:0.05 and 0.25M of pyridine. The contents sonicated in 2ml ethanol. Polymethylmethacrylate prepared by bulk polymerization while 0.046 g of the initiator AIBN with 5ml of the monomer with till complete solubility at 60°C for 1 hour with the condenser system. The composition of the polymer red-ox electrolyte was PMMA (0.25 g), ACN (0.35 g), EC (0.4 g) whilsts the molar ratio of KI: I_2 was 1.50:0.05 and 0.25M of pyridine. The contents sonicated in 2ml THF. Polycrylonitrile prepared by reduction oxidation polymerization, while 0.025 g of potassium permanganate stirred with (7%) solution of acrylonitrile, (0.045g) of oxalic acid added after a complete solubility. The solution turned to brown colour then (5.6ml) of H_2SO_4 was added. 24 hours needed for the reaction to be finished. The solution was first filtered and washed by methanol and then dried in air. The composition of the conducting polymer electrolyte was PAN (0.225 g), ACN (0.750 g), EC (0.525 g) whilsts the molar ratio of KI: I_2 was 1.50:0.05 and 0.25M of pyridine. Each of the components added to (2%) polymer electrolyte in dimethylsulphoxide (DMSO). PEO (MW: 20.000) was purchased from Alpha India. The composition of the polymer red-ox electrolyte was PAN (0.225 g), ACN (0.750 g), EC (0.525 g) whilsts the molar ratio of KI: I_2 was 1.50:0.05 and 0.25M of pyridine. The contents sonicated in 2ml distilled water. The polymer electrolyte conductivity was measured through 6517A Electrometer/High Resistance while the FTIR was characterized using Perkin Elmer One-B Spectroscopy.

3. Results and Discussion

The FTIR spectrum to affirm caging process that occurs between the polymer function group on its chain and the iodine salt cation was carried out. Figure 2 shows the FTIR spectrum of the four different polymer electrolytes: PVA, PMMA, PAN and PEO. The interactions of K^+ cation of the iodine salt (KI) and the function groups can be observed through the shifting in the bands of the electrolyte constituents. In Figure 2 (i) to (iv) The FTIR for each of pure polymers, the KI and the mixed polymer electrolyte are shown. In Figure 2 (i) The C-H stretching band in PVA appears at 2881 cm⁻¹ is shifted to 2922 cm⁻¹ in the PVA electrolyte, the C=O stretching band at 1740 cm⁻¹ in PVA is shifted to 1730 cm⁻¹ in the PVA electrolyte, and the C-O-C stretching band at 1386 cm⁻¹ in PVA is shifted to 1372 cm⁻¹ in the PVA electrolyte. The two bands in KI at 1107 cm⁻¹ and 1624 cm⁻¹ are shifted to 1079 cm⁻¹ and 1652 cm⁻¹ in the PVA electrolyte. In Figure.2. (ii) The C=O stretching band at 2876 cm⁻¹ is shifted to 2927cm⁻¹ in the PMMA electrolyte, the C=O stretching bands in PMMA at 1810 cm⁻¹,1777 cm-¹ are shifted to 1800,1768 in the PMMA electrolyte respectively and the C-O-C stretching band in PMMA at 1251 cm⁻¹ is shifted to 1167 cm⁻¹ in the PMMA electrolyte. The two bands in KI at 1107 cm⁻¹ and 1624 cm⁻¹ are shifted at 1079 cm⁻¹ and 1652 cm⁻¹ in the PAN electrolyte. In Figure.2. (iii) the nitrile C≡N stretching band at 2240 cm⁻¹ is shifted to 2246 cm⁻¹ due to the interaction of the N atom in C≡N with K^+. CH2 stretching band in PAN at1453 cm⁻¹ is shifted at 1481 cm⁻¹ in the PAN electrolyte. C-C stretching band at 1186 cm⁻¹ in PAN is shifted at 1175 cm⁻¹ in the PAN electrolyte and the K—I stretching bands appear at 1107 cm⁻¹ and 1624 cm⁻¹.
are shifted at 1078 cm\(^{-1}\) and 1629 cm\(^{-1}\). In Figure 2.(iv) the OH band stretching at 2889 cm\(^{-1}\), the C-O band stretching at 1108 cm\(^{-1}\) in PEO is shifted at 1184 cm\(^{-1}\) in the PEO electrolyte and the \(\text{CH}_2\) bands stretching at 1342 cm\(^{-1}\) and 1468 cm\(^{-1}\) in PEO are shifted to 1350 cm\(^{-1}\) and 1478 cm\(^{-1}\) in the PEO electrolyte.

The K\(\text{I}\) stretching bands at 1107 cm\(^{-1}\) and 1624 cm\(^{-1}\) are shifted to 1078 cm\(^{-1}\) and 1637 cm\(^{-1}\) in the PEO electrolyte. Thus, different shifts due to the function group indicates the caging process of the chain of the polymers and an increasing in the amorphous content in each case polymer because of the increase of its fluidity. Also, the K(I) stretching bands shift is due to the arrest of K\(\text{I}\) through the caging of the conducting polymer chain with the cation of the iodine salt. As an example of the caging complexation, the case of the PAN polymer with the alkali metal cation (K\(^{+}\)) is discussed. PAN polymer has a function group (nitrile group) on its chain which attaches to the cation (K\(^{+}\)) of the iodine salt (KI). This caging helps to free the anion of the iodine salt (I\(^{-}\)) leading to the ionic conductivity. The ionic conductivity in the electrolyte increase the number of anions to be oxidized and to regenerate the excited dye. This increases the current of the cell as shown in Figure 3. Acetonitrile as a dielectric solvent and ethylene carbonate as a plasticizer are used to increase the distance between the chains of the polymer and to increase its flexibility to ease mobility of ions. The difference of function groups of PVA, PMMA, PAN and PEO along their chains affects the ionic conductivity as a result of caging process. PVA and PMMA with the ester group, PAN with cyano group and PEO with ethyl group.

![Figure 2](image_url)

**Figure 2.** i) a) pure PVA, b) KI and c) the PVA electrolyte, ii) a) pure PMMA, b) KI and c) the PMMA electrolyte, iii) a) pure PAN, b) KI and c) the PAN electrolyte and iv) a) pure PEO, b) KI and c) the PEO electrolyte.
The coordination of these function groups influences the caging process which consequently affects the ionic conductivity. Furthermore, in the case of PVA, PMMA ester group complexation is actually stronger because there are two complexation centres in their structure. PVA has two methyl groups while PMMA has one. This makes the complex ability of PVA more than PMMA. The complexation in PAN is more than PEO because of the higher complex ability of the cyano group than the ether oxygen in PEO [16-19]. Table 1 shows the ionic conductivity of the four polymers each with their specific function groups as measured using 6517A Electrometer/High Resistance. The increase of the ionic conductivity in the electrolyte of the solar cell due to the caging process causes an increase in the photovoltaic parameters of the solar cell [13]-[15].

**Table 1:** The ionic conductivity of different polymers

| Polymer | Conductivity |
|---------|--------------|
| PVA     | 160 mS/m     |
| PMMA    | 16 mS/m      |
| PAN     | 6 mS/m       |
| PEO     | 2 mS/m       |

Figure 4 shows the photovoltaic parameters of the four different polymer electrolyte solar cells in addition to the regular iodine in the configuration FTO/TiO2/N719/ Polymer electrolyte or regular iodine /FTO. The photovoltaic performances of the four function groups follow the above closely discussion. Furthermore, the effect of pyridine addition is discussed in the following paragraph.
3.1. Effect of pyridine

The addition of pyridine to the Iodine electrolyte shifts the conduction band of the TiO₂ upward (more negative) as it is a donating material. This affects the injection of electrons from the LUMO of the dye to the conduction band (CB) of the TiO₂. Therefore, the $J_{sc}$ decrease sharply with the regular iodine electrolyte accompanied with an increase in the $V_{oc}$ which is the difference between the redox potential and the Fermi-level of the TiO₂. This process is presented in the schematics shown in figure 5 a) and c). On the other hand, the addition of pyridine to the polymer electrolyte as shown in figure 5. b) and d) results in much less decrease in current. The caging process of the polymer with the cation of the iodine salt increases the potential positively shifting the HOMO of the dye downwards (more positive). This results in fast regeneration of the excited dye through the deceleration of the recombination rate than that of the regular iodine, leading to an increase in the current($I_{sc}$) [7]. The difference in the measured photovoltaic parameters results from the varieties of the strength of the caging ability to the cation of the iodine salt. PVA which has the highest complexation, gives the highest efficiency of 8%. The other polymers with decreasing complexation order give decreasing efficiency, PMMA, with lower complexation, has an efficiency of 5.6%, PAN with an efficiency of (2.4%), PEO with an efficiency of (1.57%). It is to be record that the iodine electrolyte comes with an efficiency of 0.55%. Table 2 gives the four photovoltaic parameters $J_{sc}$, $V_{oc}$, FF and $\eta$ of the different polymer electrolytes.

| Polymer Electrolyte | $J_{sc}$ (mA/cm²) | $V_{oc}$ (V) | FF | $\eta$ % |
|----------------------|-------------------|--------------|----|--------|
| PVA                  | 5.18±0.01         | 0.739±0.05   | 08506±0.01 | 8.00±0.01 |
| PMMA                 | 5.14±0.01         | 0.753±0.05   | 05160±0.01 | 5.60±0.01 |
| PAN                  | 4.82±0.01         | 0.616±0.05   | 03459±0.01 | 2.40±0.01 |
| PEO                  | 1.97±0.01         | 0.656±0.05   | 0.4318±0.01| 1.57±0.01 |
| Iodine               | 1.03±0.01         | 0.720±0.05   | 0.7612±0.01| 0.55±0.01 |
Figure 5. The energetic alignments diagram of LUMO and HOMO bands of the dye N719 with respect to those of titania valence and conduction bands (VB and CB) of TiO2 (all data vs. vacuum): a) case for Iodine electrolyte b) case for polymer electrolyte c) case for Iodine electrolyte with pyridine d) case for polymer electrolyte with pyridine.

4. Conclusions
Four polymer electrolyte Polymer electrolytes PMMA, PVA, PEO and PAN had been employed in DSSC with different function groups. Polymer electrolyte increased the efficiency of the solar cell an order of magnitude higher than that of regular iodine electrolyte. Photovoltaic efficiency of the cell is a function of the strength of the caging of the polymer function group. The caging process causing a positive shift of the HOMO of the dye which accelerates the electrons to regenerate the excited dye faster than that of the regular iodine. Also, the caging process decreases the recombination rate increasing both the current $J_{sc}$ and the efficiency $\eta$ of the solar cell. Furthermore, the addition of pyridine shifts of the conduction band of the TiO2 is more negative, increasing the open circuit voltage of the cell. The presented configuration gives an enlarged efficiency that is needed in polymer photovoltaic solar cell.
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