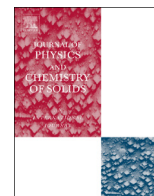




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## Organic dopant added polyvinylidene fluoride based solid polymer electrolytes for dye-sensitized solar cells

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## ABSTRACT

The effect of phenothiazine (PTZ) as dopant on PVDF/KI/I<sub>2</sub> electrolyte was studied for the fabrication of efficient dye-sensitized solar cell (DSSC). The different weight percentage (wt%) ratios (0, 20, 30, 40 and 50%) of PTZ doped PVDF/KI/I<sub>2</sub> electrolyte films were prepared by solution casting method using DMF as a solvent. The following techniques such as Fourier transform infrared (FT-IR), differential scanning calorimetry (DSC), X-ray diffractometer (XRD) and AC-impedance analysis have been employed to characterize the prepared polymer electrolyte films. The FT-IR studies revealed the complex formation between PVDF/KI/I<sub>2</sub> and PTZ. The crystalline and amorphous nature of polymer electrolytes were confirmed by DSC and XRD analysis respectively. The ionic conductivities of polymer electrolyte films were calculated from the AC-impedance analysis. The undoped PVDF/KI/I<sub>2</sub> electrolyte exhibited the ionic conductivity of  $4.68 \times 10^{-6} \text{ S cm}^{-1}$  and this value was increased to  $7.43 \times 10^{-5} \text{ S cm}^{-1}$  when PTZ was added to PVDF/KI/I<sub>2</sub> electrolyte. On comparison with different wt% ratios, the maximum ionic conductivity was observed for 20% PTZ-PVDF/KI/I<sub>2</sub> electrolyte. A DSSC assembled with the optimized wt % of PTZ doped PVDF/KI/I<sub>2</sub> electrolyte exhibited a power conversion efficiency of 2.92%, than the undoped PVDF/KI/I<sub>2</sub> electrolyte (1.41%) at similar conditions. Hence, the 20% PTZ-PVDF/KI/I<sub>2</sub> electrolyte was found to be optimal for DSSC applications.

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## 1. Introduction

The development of renewable energy resources are very important for growing energy demands due to rapid depletion of fossil fuels. Solar energy has a great potential application to fulfill a significant part of sustainable energy demand for future generation. Over the past decades, dye-sensitized solar cells (DSSCs) have gained considerable attention because of their low production cost, eco-friendly, easy fabrication procedure and relatively high power conversion efficiency [1]. The efficiency of DSSCs fabricated with organic liquid based electrolyte containing iodide/triiodide (I<sup>-</sup>/I<sub>3</sub><sup>-</sup>) as a redox couple was found to be higher than the electrolytes dissolved in polymers. This may be due to the high ionic conductivity and very good contact with the electrodes [2,3]. But, this type of electrolyte based DSSC has some disadvantages such as short term stability, sealing problem, evaporation of the solvent, sublimation of iodine and corrosion of counter electrode. Therefore, many researchers have focused on replacing the liquid electrolyte by solid medium such as polymer gel electrolytes, organic hole transport materials and solid polymer electrolytes [4–6].

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Among these the solid polymer electrolyte is a very important type of solid-state electrolytes, because of its reasonable ionic conductivity and also they overcome the sealing and solvent leakage problems. However, the ionic conductivity of these solid polymer electrolytes was found to be still lower than that of liquid electrolytes. Therefore, much effort has been devoted to improve the ionic conductivity. This was made possible by using an amorphous polymeric material possessing good mechanical and thermal properties at room temperature. In order to achieve this, different approaches are employed viz., polymer blending, using copolymer, addition of nanofillers and doping of organic compounds [7–12].

Among these, the doping of organic compounds like ethylene carbonate (EC), propylene carbonate (PC), diethyl carbonate (DEC), ionic liquids (ILs) and organic nitrogenous compound into a polymer electrolyte is found to be the most successful technique for improving the ionic conductivity of the polymer electrolyte at room temperature with high stability [13–17]. The incorporation of organic compound into the polymer electrolyte decreases the crystallinity and polymer–polymer chain interactions, which will in turn improve the segmental motion of the polymer backbone and generate free volume. Therefore, the ions can easily migrate in these free volumes which will turn improve the ionic conductivity as well as the performance of the DSSCs.

Nowadays, polyvinylidene fluoride (PVDF) based solid polymer electrolytes are gaining much attention for the fabrication of highly efficient DSSC because of its semi-crystalline nature of the polymer and its strong electron withdrawing functional group (–C–F) with high dielectric constant ( $\epsilon \approx 8.4$ ) [18–20]. Additionally, PVDF is stable against most corrosive chemicals including acids, alkali and halogens [21]. The fluorine atoms in –C–F possess the smallest ionic radius and very high electronegativity which helps to improve the ionic transport and reduces the recombination rate at the semiconductor/polymer electrolyte interface in DSSCs [22]. Hence, PVDF is chosen as a polymer in the present investigation.

Kusama et al. [23–25] used the nitrogen-containing heterocyclic compounds as dopant in liquid electrolytes based DSSCs and reported that the presence of the lone pair of electrons in the nitrogen atom of the amine group increased the short circuit current ( $I_{sc}$ ) and open circuit voltage ( $V_{oc}$ ) by interacting with  $I^-/I_3^-$  redox couple. Phenothiazine (PTZ) has been chosen as a dopant in the present study because it possesses a lone pair of electrons in both the nitrogen and sulphur atoms and hence it can easily form a charge-transfer complex with iodine ( $I_2$ ). Therefore, the problems such as leakage of electrolytes, solvent evaporation and sublimation of iodine can be prevented.

In the present investigation, the different weight percentage (wt%) ratios of PTZ doped PVDF/KI/ $I_2$  electrolytes are prepared and the optimized composition has been selected for the fabrication of DSSCs.

## 2. Material and methods

### 2.1. Materials

PVDF ( $M_w \sim 275,000$ ), PTZ, chloroplatinic acid hydrate ( $H_2PtCl_6 \cdot H_2O$ ), N3 dye ([cis-dithiocyanato-*N,N*-bis-(2,2-bipyridyl-4,4-dicarboxylic acid) ruthenium(II)] dihydrate) and fluorine-doped tin oxide (FTO) glass substrate with sheet resistance  $10 \Omega/cm^2$  were purchased from Sigma Aldrich. Potassium iodide (KI), iodine ( $I_2$ ), *N,N*-dimethyl formamide (DMF), isopropanol and absolute ethanol were purchased from SDFCL, India. Titanium dioxide ( $TiO_2$ ) powder was a gift sample from Degussa, Germany. All chemicals were used without further purification.

### 2.2. Preparation of polymer electrolyte films

The polymer electrolyte films were prepared by solution casting technique. 0.3 g of PVDF, 0.03 g of KI, 0.006 g of  $I_2$  and different wt% ratios (0, 20, 30, 40 and 50%) of PTZ with respect to KI were dissolved in 20 mL of DMF under continuous stirring for 3 h at  $80^\circ C$  until a homogenous viscous solution was formed. Then, the polymer electrolyte solution was poured into a Teflon petri dish and dried in vacuum oven at  $60^\circ C$  for overnight to aid solvent evaporation. The obtained thin polymer film was used for the further studies. The various compositions of the prepared polymer electrolytes are shown in Table 1.

**Table 1**  
The different compositions of prepared PVDF/KI/ $I_2$  based polymer electrolytes.

Electrolyte	PVDF (g)	KI (g)	$I_2$ (g)	PTZ (wt%)
P0	0.3	0.03	0.006	0
P1	0.3	0.03	0.006	20
P2	0.3	0.03	0.006	30
P3	0.3	0.03	0.006	40
P4	0.3	0.03	0.006	50

### 2.3. Characterization techniques

The FT-IR spectra of prepared polymer electrolyte films were scanned in the wave number between  $4000$  and  $400 \text{ cm}^{-1}$  using a Shimadzu IR Affinity-1 FT-IR spectrometer. DSC thermograms of the polymer electrolyte films were performed using a Mettler Toledo DSC 822e equipment at a heating rate of  $10^\circ C/min$  from  $30$  to  $250^\circ C$  under nitrogen atmosphere. The XRD spectra of the polymer electrolyte films were recorded using a Bruker-advance D8 X-ray diffraction meter in the range  $2\theta \sim 10\text{--}70^\circ$  with Cu-K $\alpha$  radiation. The impedance spectra of the polymer electrolyte films were measured by AC-impedance technique using an electrochemical workstation, CH instrument Inc., USA (model CHI-608E) in the frequency range of  $20 \text{ Hz}$  to  $1 \text{ MHz}$  at room temperature ( $303 \text{ K}$ ). The bulk resistance of polymer electrolytes was determined from the impedance spectra. The ionic conductivity of the polymer electrolyte was calculated using the following equation.

$$\sigma = \frac{t}{R_b A} \quad (1)$$

where,  $t$  is the thickness of the electrolyte film which is in the range of  $0.08\text{--}0.09 \text{ mm}$ ,  $R_b$  is the bulk resistance of electrolyte films and  $A$  is the area of the stainless steel electrode containing polymer electrolyte and the area of stainless steel electrode is  $0.785 \text{ cm}^2$ .

### 2.4. Fabrication of dye-sensitized solar cells (DSSCs)

Dye sensitized solar cell with an active area of  $0.4 \text{ cm}^2$  was fabricated as follows: the  $TiO_2$  paste was prepared by grinding  $0.20 \text{ g}$  of  $TiO_2$  with  $145 \mu\text{L}$  of glacial acetic acid,  $20 \mu\text{L}$  of Triton X 100 and  $2 \text{ ml}$  of ethanol. After that, the prepared  $TiO_2$  paste was coated on a well cleaned FTO plate by spreading the paste using doctor plate method followed by heat treatment at  $450^\circ C$  for  $45 \text{ min}$  [26,27]. The resulting  $TiO_2$  film was immersed in absolute ethanol solution containing  $5 \times 10^{-4} \text{ M}$  of N3 dye for about  $24 \text{ h}$  in dark condition to allow sufficient dye adsorption. Then, the dye sensitized  $TiO_2$  film was thoroughly washed with anhydrous ethanol and dried in moisture-free air. The Pt counter electrode was prepared by  $200 \mu\text{L}$  of  $50 \text{ mM } H_2PtCl_6 \cdot H_2O$  in isopropanol solution coated on a well cleaned FTO plate by spin-coating method. This was followed by heat treatment at  $395^\circ C$  for  $15 \text{ min}$  [28].

The DSSCs were fabricated by adding  $250 \mu\text{L}$  of homogeneous polymer electrolyte solution onto dye-sensitized  $TiO_2$  working electrode and the solvent was removed using hot plate maintained at  $353 \text{ K}$ . Then the Pt counter electrode was placed over the polymer electrolyte to make a sandwich structure. Finally, the sandwiched cell was put together with alligator clips without any sealing. All photovoltaic measurements were performed in an open atmosphere.

The photocurrent density–voltage ( $J$ – $V$ ) characteristics were performed using CHI608-E model electrochemical workstation coupled with a light source of  $250 \text{ W}$  tungsten halogen lamp (OSRAM, Germany) at an illumination intensity of  $60 \text{ mW/cm}^2$ . The fill factor (FF) and the power conversion efficiency of DSSCs were calculated using the following equations.

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

$$\eta(\%) = \frac{V_{oc} \times J_{sc} \times FF}{P_{in}} \times 100 \quad (3)$$

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