



A poly (ethylene oxide), poly (vinylidene fluoride) and polycaprolactone polymer blend doped with an indigenous nitrogen–sulfur based organic compound as a novel electrolyte system for dye-sensitized solar cell applications



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ABSTRACT

The present study reports, for the first time, the strategy of blending three different polymers followed by the doping of an organic nitrogenous compound to develop a solvent-free novel doped multi-polymer blend electrolyte system for dye-sensitized solar cell (DSSC) applications. Precisely, this novel electrolyte consists of poly (ethylene oxide) (PEO) blended with poly (vinylidene fluoride) (PVdF) and poly (caprolactone) (PCL) that is incorporated into the synthesized 2,6-bis (2-thio pyridyl) pyridine (BTPP) along with KI and I₂. The current–voltage (*I*–*V*) characteristics of the nanocrystalline DSSC fabricated using the present electrolyte generates a photocurrent of 15.5 mA/cm², a photo-voltage of 905 mV, a fill factor of 0.53 and yields an overall energy conversion efficiency of 9.3% under a simulated sunlight radiation of 80 mW/cm². The impressive photoelectric performance of the fabricated solar cell is mainly attributed to the synergic effects of the electrolyte composed of the unique blending of three polymers and the electron donicity of BTPP that leads to strongly influence the interaction between the nanocrystalline TiO₂ electrode and I[−]/I₃[−] electrolyte, thereby leading to high conversion efficiency.

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1. Introduction

The clean, renewable, free and readily available solar energy has triggered off a growing research interest on dye-sensitized solar cells (DSSCs). The first DSSC with the highest solar to electric energy conversion efficiency of 11% was reported by Regan and Gratzel (1991). A practical DSSC has three vital components; (1) a ruthenium dye coated TiO₂ working electrode (2) a redox electrolyte comprising of a potassium iodide and iodine mixture in acetonitrile medium and (3) a platinum counter electrode. The use of liquid electrolytes (KI and I₂ in acetonitrile) in DSSCs, in general, are known to cause solvent leakage and iodine sublimation problems. Hence, the efforts on replacing these liquid electrolytes have progressed toward the development of solid-state polymer electrolytes with high ionic conductivities (Meng et al., 2003; Hirata et al., 2006; Wang et al., 2003a,b; Stathotos et al., 2002; Wang et al., 2002; Kang et al., 2007; Wu et al., 2007). Recently, much

attention has been centered on modifying polymer electrolytes by co-polymerization and polymer-blending techniques (Nogueira et al., 2001a,b; Wei et al., 2007; Cao et al., 1995; Wang et al., 2004; Katsaros et al., 2002; Ganesan et al., 2011; Stergiopouls et al., 2002; Durrent et al., 2001). The strategy of polymer-blending is mainly used to develop electrolytes with enhanced electrical, thermal and mechanical properties associated with the polymer components (Ganesan et al., 2011). To the authors' best knowledge, quasi solid-state polymer blend electrolytes based on only two different polymers have been reported until now for DSSC applications. Although the concept of blending can be extended to more than two polymers, such an effort has not been undertaken so far for DSSC applications. Also, it remains that the PEO–PVdF polymer electrolyte system has been one of the most studied systems for DSSC applications. The smaller ionic radii and higher electro negativity of fluorine in PVdF tends to improve the ion transport properties and reduces the recombination rate at the semi-conducting electrode and polymer electrolyte interface in DSSC. However, further enhancements in the polymer electrical conductivity and hence DSSC properties can be expected provided

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another polymer containing a group with characteristics analogous to that of fluorine in PVdF is included. On the one hand, it remains comparatively easy to choose polymers with specific properties since they are commercially available whereas significant challenges exist in developing organic dopants as they need to be lab-synthesized after careful consideration of the starting materials and optimizing the organic reaction conditions. In this regard, we reported that the doping of a nitrogen-based organic compound on a PVdF–PEO polymer electrolyte system that improved its electrical conductivities and thereby led to DSSCs with high photo-conversion efficiencies ($\sim 8.5\%$) (Ganesan et al., 2011). The presence of nitrogen atoms in the organic compound aids in the formation of a charge transfer complex with iodine in the redox couple and thereby improves the electrical property of the polymer electrolyte. It is possible that the inclusion of elements (like sulfur) with electron donating properties in the dopant may improve polymer electrolyte and hence DSSC properties; however, its preparation, optimization and raw materials can be stiffly challenging. Therefore, the strategy of effectively tailoring the electrolyte system by developing a multi-polymer blend electrolyte system incorporated with organic dopants containing electron donating characteristics for the fabrication of DSSCs with higher photo-voltaic efficiencies is worth pursuing.

Herein, we report, for the first time, on the strategy of blending three different polymers (PEO with PVdF and PCL) followed by the doping of an indigenously synthesized organic nitrogen–sulfur compound, namely, 2,6-bis (2-thio pyridyl) pyridine (BTPP) to develop a novel doped solid polymer blend electrolyte system for DSSC applications. The presence of the carbonyl group oxygen with smaller ionic radii and higher electro negativity in PCL can improve the ion transport properties and thereby reduce the recombination rate at the electrode/electrolyte interface and enhance the photo-voltaic properties in DSSC applications. Moreover, the organic BTPP dopant or 2,6-bis (2-thio pyridyl) pyridine is a nitrogen–sulfur containing compound lab-synthesized, for the first time, by combining 2-mercapto pyridine and 2,6 dibromo pyridine with a potassium metal catalyst. The fact that this compound contains nitrogen and sulfur atoms implies that they are highly prone to form charge transfer complexes with iodine in the redox couple and reduce iodine sublimation to a large extent and ultimately contribute to improved electrolyte properties. It is worth noting that, although many catalysts including potassium tertiary butoxide and sodium metal were used, only potassium metal catalyst facilitated the completion of the organic reaction and the formation of the final product. Nevertheless, the effect of this novel doped polymer blend electrolyte system on the photovoltaic properties of a fabricated DSSC was also investigated. The conduction behavior of the present PEO–PVdF–PCL polymer blend electrolyte along with KI and I_2 and varying amounts of the organic dopant (BTPP) was investigated to identify the optimized polymer system with relatively sufficient I^-/I_3^- concentration and enhanced photovoltaic properties for stable DSSC applications.

2. Experimental methods

2.1. Chemicals and reagents

The polymers, PEO ($M_w \sim 5 \times 10^6$), poly (vinylidene fluoride) ($M_w \sim 275,000$), and polycaprolactone ($M_w \sim 80,000$), 2-mercapto pyridine, anhydrous 2-methoxy ethyl ether (diglyme), potassium metal, 2,6 dibromo pyridine, Titanium (IV) oxide and the N3 dye is *cis*-bis(iso-thiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) were purchased from Aldrich. The 2-Propanol, acetic acid, Potassium Iodide (KI), Iodine (I_2), Dimethyl formamide (DMF) was procured from Merck.

2.2. Preparation of 2,6-bis (2-thio pyridyl) pyridine (BTPP)

A solution containing 1.8 g of 2-mercapto pyridine (0.0162 mol) in 40 mL anhydrous 2-methoxy ethyl ether medium was stirred with 0.8 g (0.02 mol) of potassium metal at 333 K until the metal dissolved. To this solution was added 1.2 g of 2,6 dibromo pyridine (0.005 mol) in one portion and the resulting mixture was stirred at 353 K for nearly 4–6 h. The solvent was removed completely with the aid of a rotary evaporator. Distilled water followed by chloroform was then added to the resulting compound to separate the organic layer. After chloroform evaporation, the recovered crude sample was further purified by column chromatography using 30% ethyl acetate and 70% n-hexane elution to finally obtain a light brown viscous liquid and the product yield was as high as 90%. The appropriate scheme for the synthesis of 2,6-bis (2-thio pyridyl) pyridine is shown in Fig. 1a. The complex thus obtained was characterized by means of 1H NMR (Fig. 1b) spectroscopy recorded on a BRUKER 300 MHz spectrometer using $CDCl_3$ solvent. The peaks corresponding to BTPP have been assigned as 8.49–8.51 δ (q, 2H), 7.5–7.58 δ (m, 3H), 7.43–7.48 δ (m, 2H) 7.21–7.24 δ (d, $J = 9$ Hz, 2H) 7.12–7.17 δ (m, 2H). The ^{13}C NMR (Fig. 1c) of the above compound showed peaks at 157 δ , 158 δ , 149 δ , 138 δ , 137 δ , 121 δ , 120 δ , 125 δ , 150 δ and 151 δ respectively.

2.3. Preparation of polymer blend electrolytes

The amount of 0.2 g of PEO, 0.05 g PVdF, 0.05 g PCL, 0.03 g of KI and 0.006 g of I_2 were dissolved together in 25 mL of DMF. The resulting solution was stirred well at 360 K for about 3 h and cast on to the dye-coated TiO_2 plate before placing it on a hot plate in order to remove the solvent. This undoped polymer blend electrolyte was tested for DSSC applications and the results were compared with those obtained from the cells utilizing the polymer blend electrolyte system doped with 10, 15 and 20 wt% of BTPP.

2.4. Fabrication of DSSC

The DSSC in this study, were fabricated using a fluorinated tin oxide (FTO) conducting glass cast with nanocrystalline TiO_2 (Degussa) according to the already reported procedure (Srimanne et al., 2002; Kusama and Arakawa, 2004). The TiO_2 nanoparticles were sensitized for 24 h with *cis*-dithiocyanato - N,N-bis (2,2' bipyridyl-4,4' dicarboxylic acid) Ruthenium (II) (N3 dye) solution (4.5×10^{-5} M) and formed the photoelectrode of the DSSC. The active area of DSSC was 1 cm² (1 cm \times 1 cm). The polymer blend electrolyte solution was dropped on to the N3 dye coated TiO_2 film and the solvent was removed using hot plate. Finally, a sandwich type DSSC was fabricated by holding the Pt plate as counter electrode together with alligator clips. All measurements were performed in open air environment.

The cell configurations prepared in the present study are as follows:

- (a) $TiO_2/N3dye/PEO-PVdF-PCL/KI/I_2/Pt$
- (b) $TiO_2/N3dye/PEO-PVdF-PCL/KI/I_2/BTPP$ (10, 15 and 20 wt%)/Pt

2.5. Characterization

The polymer electrolyte films were subjected to thermal, structural, and electrical characterizations for their use in electrochemical devices. Differential Scanning Calorimetry (DSC, NETZSCH DSC 204 model) was used to understand the thermal behavior of the polymer blend electrolytes. The sample was scanned at a heating rate of 10 $^{\circ}C$ min⁻¹ with an appropriate temperature range under a nitrogen atmosphere. Fourier transform infrared (FTIR) spectra

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