Optimization of Benzoguanamine doped PVDF/KI/I2 Solid Polymer Electrolytes for Dye-Sensitized Solar Cell Applications

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Research Article

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Abstract

Benzoguanamine doped 0%, 10%, 20%, 30%, 40% and 50% PVDF/KI/I_2 polymer electrolytes were prepared by solution casting technique. The crystallinity, surface morphology, ionic conductivity and photovoltaic performance of polymer electrolytes were analyzed. The PXRD studies have confirmed the decreased and increased crystallinity of benzoguanamine doped polymer electrolytes. The surface morphology of polymer electrolytes is discussed using SEM analysis. From the AC-impedance analysis, ionic conductivity of benzoguanamine doped 0%, 10%, 20%, 30%, 40% and 50% PVDF/KI/I_2 polymer electrolytes were calculated as 5.57×10^{-6} Scm^{-1}, 1.05×10^{-5} Scm^{-1}, 5.95×10^{-5} Scm^{-1}, 3.09×10^{-5} Scm^{-1}, 1.56×10^{-5} Scm^{-1} and 1.48×10^{-5} Scm^{-1}, respectively. The photovoltaic performance of benzoguanamine doped 0%, 10%, 20%, 30%, 40% and 50% PVDF/KI/I_2 polymer electrolytes based DSSCs have achieved 1.5 %, 1.9%, 2.8%, 2.5%, 2.3% and 2.1 % power conversion efficiency, respectively.

Introduction

Ion diffusion and ionic conductivity of the polymer electrolytes are lower than the liquid electrolytes. However, the research is going on to develop a novel polymer electrolyte with higher ion diffusion and ionic conductivity with good stability. Higher ionic conductivity occurs by the creation of an amorphous phase or suppression of the crystallinity of polymer electrolytes. The many efforts are taken to reducing the crystallinity or creating an amorphous phase. This can be achieved by various techniques. They are polymer blending, co-polymerization, addition of nanofillers and the incorporation of organic plasticizers [1–6]. The addition of organic plasticizers decreases both the crystallinity and polymer-polymer chain interactions in polymer electrolytes. It will enhance the segmental motion of the polymer backbone and generate free volume. The ions can easily migrate via the free volume; it will improve ionic conductivity of polymer electrolytes and the performance of DSSCs.

The researchers have fabricated DSSCs with the organic plasticizer doped polymer electrolytes and achieved considerable power conversion efficiency [7–8].

In this present work, one of the organic plasticizer benzoguanamine compound is chosen to prepare the polymer electrolytes with PVDF/KI/I_2. The addition of the benzoguanamine compound in the polymer matrix is one of the routes to create the amorphous phase or decreased crystallinity of polymer electrolytes. This will increase the ionic conductivity of polymer electrolytes. The benzoguanamine compound consists of nitrogen atoms, which will form complex with I_2. This complex formation avoids the sublimation of iodine and it will increase the lifetime of the DSSC [9]. The benzoguanamine compound is of low cost and it is also a new material for the electrolyte preparation in DSSC.

Materials

Titanium dioxide (TiO_2) nanoparticles synthesized by Sol-Gel technique [10]. Fluorine doped tin oxide (FTO) substrates, N719 dye (cis-diisothocyanato-bis (2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium (II) bis(tetrabutylammonium)), and platinum catalyst solution (platisol) were used as purchased from Solaronix, Switzerland. Ethanol and N,N-dimethylformamide (DMF) were used as purchased from Merck. 2-amino-4,6-dimethoxypyrimidine was used as obtained from Alfa Aesar. PVDF (MW ~ 275,000 g/mol), KI and I_2 were used as purchased from Sigma-Aldrich.

Preparation of Benzoguanamine-doped PVDF/KI/I_2 Electrolyte Films

The benzoguanamine-doped PVDF/KI/I_2 electrolytes were prepared by dissolving PVDF (0.3 g), KI (0.03 g), I_2 (0.006 g) and benzoguanamine (different weight percentages of 0%, 10%, 20%, 30%, 40% and 50% with respect to KI) in DMF (20 mL) under continuous stirring at 80°C until the homogeneous polymer electrolyte solutions were obtained. The obtained homogeneous polymer electrolyte solutions were poured into glass petri dishes. The DMF solvent was removed by using a vacuum oven at 60°C for 12 hrs.

Fabrication of Dye Sensitized Solar Cell

The solvents (acetone, ethanol and Millipore water) were used to clean the fluorine doped tin oxide (FTO) substrates. The cleaned FTO substrates were treated on $TiCl_4$ treatment (FTO immersed with ice (50 ml), Millipore water (50 ml) and $TiCl_4$ (2 ml) at 70°C for 30 min) after that washed by ethanol and then sintered at 500°C for 30 min. TiO_2 paste (TiO_2 paste was made by adding binder materials such as 2-propanol and triton X-100 with TiO_2 nanoparticles) was deposited on the FTO and then sintered at 500°C for 1 h. $TiCl_4$ treatment is done, followed by sintering at 500°C for 30 min. The photoanode is immersed in N719 dye solution (0.05 mM concentration, absolute ethanol is used as solvent) for 24 h. After that, working electrodes were obtained. The platisol was deposited (doctor blading technique) on FTO substrate and then sintered at 400°C for 30 min. After that, counter electrode was obtained. The semi-solid benzoguanamine doped PVDF/KI/I_2 polymer electrolyte was dropped onto working electrode. It was kept for a few minutes for solvent evaporation and the counter electrode was placed over it. The sandwiched cell was put together with binding clips. The active area of DSSC is 0.5 cm × 0.5 cm. The photovoltaic (J–V) measurements are monitored at air mass (AM) 1.5 illumination using Keithley source meter with a light source of 150 W Xenon arc lamp (Science Tech, Canada) at 100 mW/cm^2.

Characterization Techniques

The powder X-ray diffraction pattern was recorded using Bruker advance D8 powder X-ray diffractometer with CuKα radiation (λ = 1.54 Ǻ). The AC-impedance analysis was taken using an electrochemical workstation (Ametek, V3-500). The scanning electron microscopy images were taken using JEOL 6390 model. The photovoltaic measurements were recorded at air mass (AM) 1.5 illumination using Keithley source meter with a light source of 150 W Xenon arc lamp (Science Tech, Canada) at 100 mW cm^{-2}.

Results And Discussion

Powder X-ray Diffraction Analysis

Figure 1.1 shows the powder X-ray diffraction (PXRD) spectra of benzoguanamine (0%, 10%, 20%, 30%, 40% and 50%) doped PVDF/KI/I_2 electrolyte films. The benzoguanamine (0%, 10%, 20%, 30%, 40% and 50%) doped PVDF/KI/I_2 electrolyte films exhibited X-ray diffraction peaks at 2θ = 20°, 22°, 25°, 36°, 42° and 44°. The peak's intensity of 0% benzoguanamine doped PVDF/KI/I_2 electrolyte film is higher than the benzoguanamine (10%, 20%, 30%, 40% and 50%) doped PVDF/KI/I_2 electrolyte films. These results confirmed the decreased crystallinity of benzoguanamine (10%, 20%, 30%, 40% and 50%) doped PVDF/KI/I_2 electrolyte films. When the benzoguanamine is added, the intensity of peaks was found to be gradually decreased up to 20%. This confirmed the decreased crystallinity of benzoguanamine (10% and 20%) doped PVDF/KI/I_2 electrolyte films. But when the amount of benzoguanamine was increased further, the intensity of peaks was gradually increased. This confirmed the increased crystallinity of benzoguanamine (30%, 40% and 50%) doped PVDF/KI/I_2 electrolyte films. The results obtained from the PXRD measurements confirm the lowest crystallinity of 20% benzoguanamine doped PVDF/KI/I_2 electrolyte film than the other benzoguanamine (0%, 10%, 30%, 40% and 50%) doped PVDF/KI/I_2 electrolyte films.

Ionic Conductivity Studies

The AC-impedance spectra of prepared benzoguanamine (0%, 10%, 20%, 30%, 40% and 50%) doped PVDF/KI/I_2 electrolyte films are presented in Fig. 1.2. The ionic conductivity of benzoguanamine doped PVDF/KI/I_2 electrolyte films was measured from Fig. 1.2, and the obtained values are listed in Table 1.1. The ionic conductivity of benzoguanamine (0%, 10%, 20%, 30%, 40% and 50%) doped PVDF/KI/I_2 electrolyte films are 5.57×10^{-6} Scm^{-1}, 1.05×10^{-5} Scm^{-1}, 5.95×10^{-5} Scm^{-1}, 3.09×10^{-5} Scm^{-1}, 1.56×10^{-5} Scm^{-1} and 1.48×10^{-5} Scm^{-1}, respectively. The benzoguanamine (10%, 20%, 30%, 40% and 50%) doped PVDF/KI/I_2 electrolyte films have higher ionic conductivity than the 0% benzoguanamine doped PVDF/KI/I_2 electrolyte film. The reason for the observed trend is the addition of benzoguanamine. The ionic conductivity was increased with the addition of benzoguanamine up to 20%. This may be due to the increased number of mobile charge carriers and chain mobility of polymer electrolytes [11, 12]. After 20%, the ionic conductivity of benzoguanamine (30%, 40% and 50%) doped electrolyte films was found to be decreased. This is due to the taking up of some free volume, the rapid increase in viscosity and some benzoguanamine may not be dissociated in polymer electrolytes. So, it causes the interrupted mobility of the charge carriers and thereby reduces the ionic conductivity [11]. The highest ionic conductivity was obtained for 20% benzoguanamine doped PVDF/KI/I_2 electrolyte film. This highest ionic conductivity is responsible for the highest power conversion efficiency of DSSC. Figure 1.3 represents the plot of ionic conductivity variations of benzoguanamine doped PVDF/KI/I_2 electrolyte films.

Table 1.1
Conductivity of benzoguanamine (a) 0%, (b) 10%, (c) 20%, (d) 30%, (e) 40% and (f) 50% doped $PVDF/KI/I_2$ electrolyte films

Electrolyte	Benzoguanamine (%)	Ionic Conductivity (Scm^{-1})
a	0	5.57×10^{-6}
b	10	1.05×10^{-5}
c	20	5.95×10^{-5}
d	30	3.09×10^{-5}
e	40	1.56×10^{-5}
f	50	1.48×10^{-5}

Scanning Electron Microscopy Analysis

The surface morphology of benzoguanamine (0%, 10%, 20%, 30%, 40% and 50%) doped $PVDF/KI/I_2$ electrolyte films is characterized by scanning electron microscopy (SEM) analysis. The SEM images of benzoguanamine (0%, 10%, 20%, 30%, 40% and 50%) doped $PVDF/KI/I_2$ electrolyte films are presented in Fig. 1.4. The surface morphology of benzoguanamine doped $PVDF/KI/I_2$ electrolyte films has shown the spherical particles with voids. The 0% benzoguanamine doped $PVDF/KI/I_2$ electrolyte film has the largest size spherical particles voids than the benzoguanamine (10%, 20%, 30%, 40% and 50%) doped $PVDF/KI/I_2$ electrolyte films. The spherical particle size was gradually decreased with voids up to 20% of benzoguanamine doped $PVDF/KI/I_2$ electrolyte films. In the 30%, 40% and 50% of benzoguanamine doped $PVDF/KI/I_2$ electrolyte films, the spherical particle size was gradually increased with voids. The 20% benzoguanamine doped $PVDF/KI/I_2$ electrolyte film has shown the smallest spherical particles with voids. The benzoguanamine contributes a notable effect in the benzoguanamine doped $PVDF/KI/I_2$ electrolyte films [13, 14].

Photovoltaic Measurements

The DSSCs were fabricated with the prepared benzoguanamine (0%, 10%, 20%, 30%, 40% and 50%) doped $PVDF/KI/I_2$ electrolytes. The current density-voltage (J-V) curves of DSSCs with the benzoguanamine (0%, 10%, 20%, 30%, 40% and 50%) doped $PVDF/KI/I_2$ electrolytes are presented in Fig. 1.5. The photovoltaic parameters of DSSCs with benzoguanamine (0%, 10%, 20%, 30%, 40% and 50%) doped $PVDF/KI/I_2$ electrolytes are exhibited as J_{sc}=5.50 mA/cm^2, V_{oc}=0.72 V, FF = 0.38 and η = 1.5%; J_{sc}=6.28 mA/cm^2, V_{oc}=0.71 V, FF = 0.43 and η = 1.9%; J_{sc}=8.34 mA/cm^2, V_{oc}=0.69 V, FF = 0.49 and η = 2.8%; J_{sc}=7.95 mA/cm^2, V_{oc}=0.70 V, FF = 0.46 and η = 2.5%; J_{sc}=7.48 mA/cm^2, V_{oc}=0.73 V, FF = 0.42 and η = 2.3%; J_{sc}=6.86 mA/cm^2, V_{oc}=0.72 V, FF = 0.42 and η = 2.1%, respectively. The calculated photovoltaic parameters of DSSCs are summarized in Table 1.2. The DSSCs with the benzoguanamine (10%, 20%, 30%, 40% and 50%) doped PVDF/KI/I_2 electrolytes have higher power conversion efficiency than the DSSC with the 0% benzoguanamine doped PVDF/KI/I_2 electrolyte. This is due to the electron donating capability of benzoguanamine. It has nitrogen atoms in its structure. It interacts with I_2 of I_3^- to form charge transfer complex, thereby prevents the sublimation of I_2 [8, 9, 13]. Benzoguanamine decreases I_3^- concentration while it increases I^- concentration [13, 15]. Due to decrease in I_3^-concentration, the reaction decreases between I_3^- at TiO_2 semiconductor electrolyte junction and injected electron, thereby increases the electron concentration [13, 16]. Figure 1.6 shows the power conversion efficiency variations of DSSCs with benzoguanamine doped PVDF/KI/I_2 electrolytes. The interaction between the benzoguanamine and PVDF/KI/I_2 is shown in Fig. 1.7. The DSSC with 20% benzoguanamine doped PVDF/KI/I_2 electrolyte has the highest power conversion efficiency. This may be due to the lowest crystallinity and the highest ionic conductivity of the 20% benzoguanamine doped PVDF/KI/I_2 electrolyte.

$$\text{Benzoguanamine} + I_3^- \longleftrightarrow \text{Benzoguanamine} + I^- \qquad (1.1)$$

$$2\,(\text{Benzoguanamine}) + I_3^- \longleftrightarrow (\text{Benzoguanamine})_2\, I^+ + 2I^- \qquad (1.2)$$

Table 1.2 The photovoltaic parameters of DSSCs with benzoguanamine (a) 0%,

(b) 10%, (c) 20%, (d) 30%, (e) 40% and (f) 50% doped PVDF/KI/I_2 electrolytes

DSSC	Benzoguanamine (%)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)
a	0	5.50	0.72	0.38	1.5
b	10	6.28	0.71	0.43	1.9
c	20	8.34	0.69	0.49	2.8
d	30	7.95	0.70	0.46	2.5
e	40	7.48	0.73	0.42	2.3
f	50	6.86	0.72	0.42	2.1

Conclusions

- In the present work, we have prepared benzoguanamine (0%, 10%, 20%, 30%, 40% and 50%) doped PVDF/KI/I_2 electrolytes. The prepared polymer electrolyte films were characterized by PXRD, EIS and SEM studies. The PXRD spectra have proved the lowest crystallinity for 20% benzoguanamine doped PVDF/KI/I_2 electrolyte film. The AC-impedance spectra, revealed that the 20% benzoguanamine doped PVDF/KI/I_2 electrolyte film has the highest ionic conductivity. The 20% benzoguanamine doped PVDF/KI/I_2 electrolyte film has the smallest spherical particles with voids. The DSSCs were fabricated with the benzoguanamine (0%, 10%, 20%, 30%, 40% and 50%) doped PVDF/KI/I_2 electrolytes and measured the photovoltaic performance under the light intensity of 100 mW/cm^2. The DSSC with 20% benzoguanamine doped PVDF/KI/I_2 electrolyte has the highest power conversion efficiency of 2.8%.

Declarations

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Figures

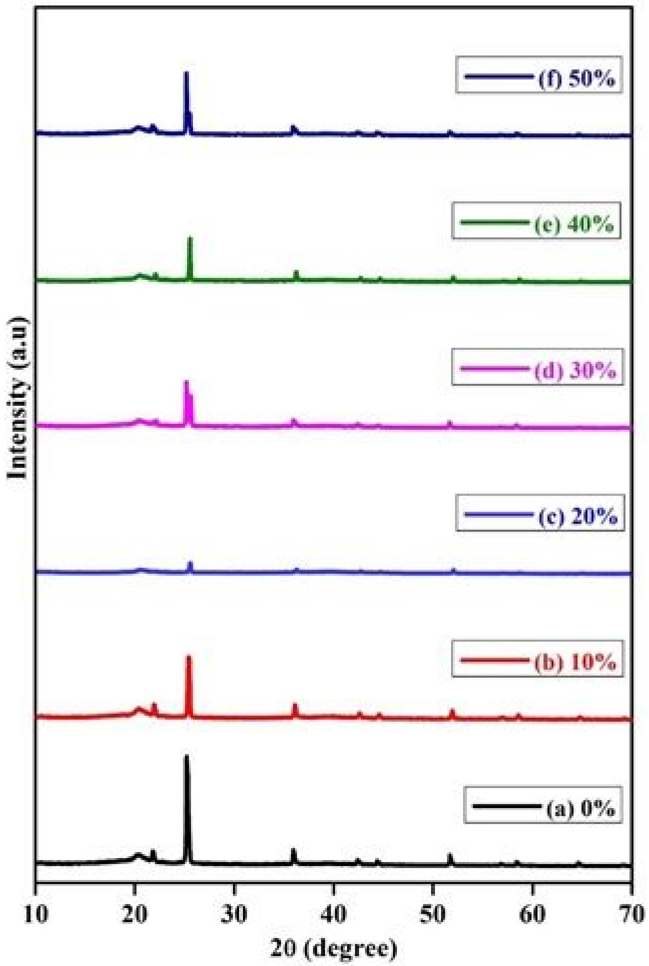

Figure 1

PXRD patterns of benzoguanamine (a) 0%, (b) 10%, (c) 20%, (d) 30%, (e) 40% and (f) 50% doped PVDF/KI/I2 electrolyte films

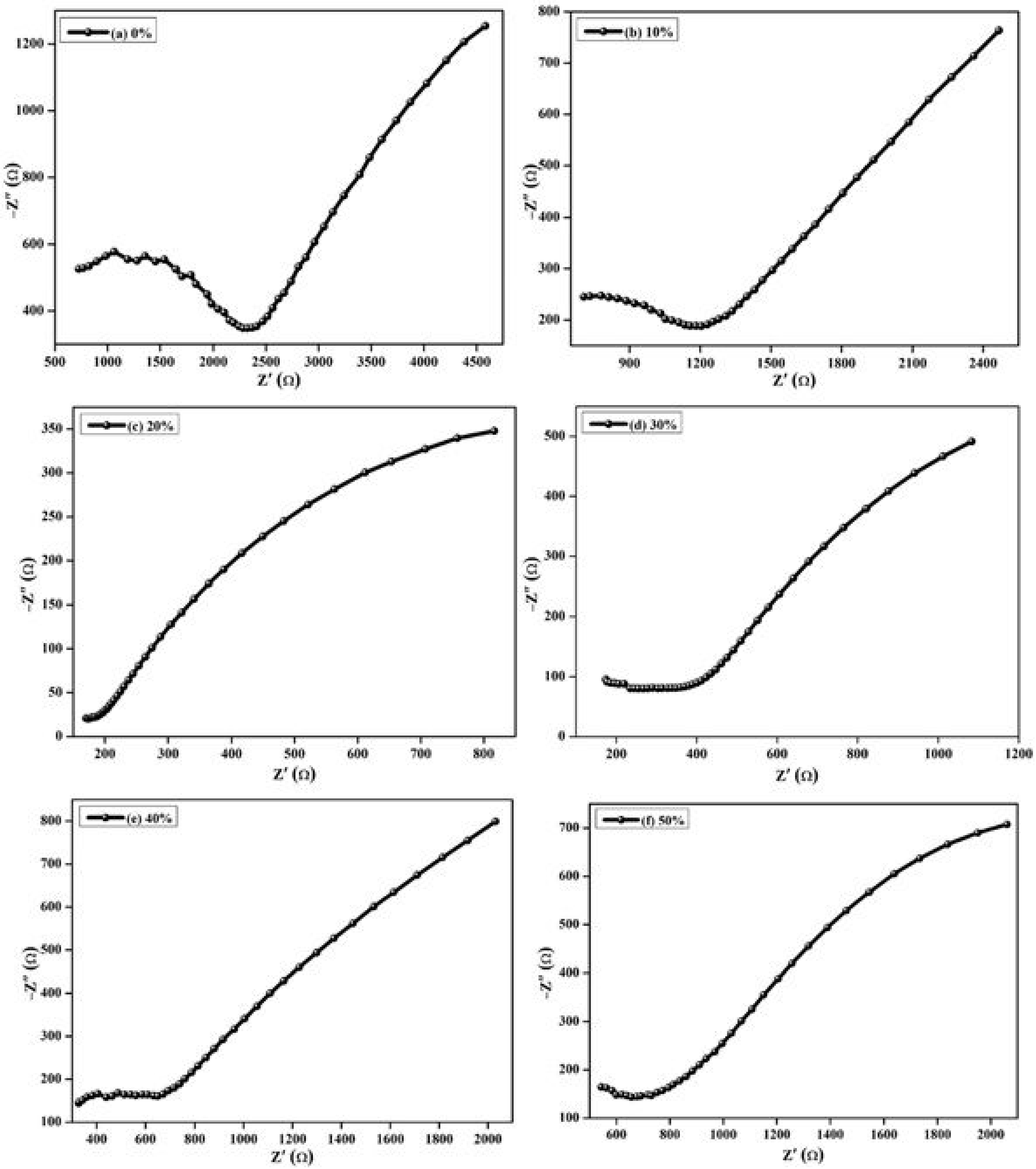

Figure 2

AC-impedance spectra of benzoguanamine (a) 0%, (b) 10%, (c) 20%, (d) 30%, (e) 40% and (f) 50% doped PVDF/KI/I2 electrolyte films

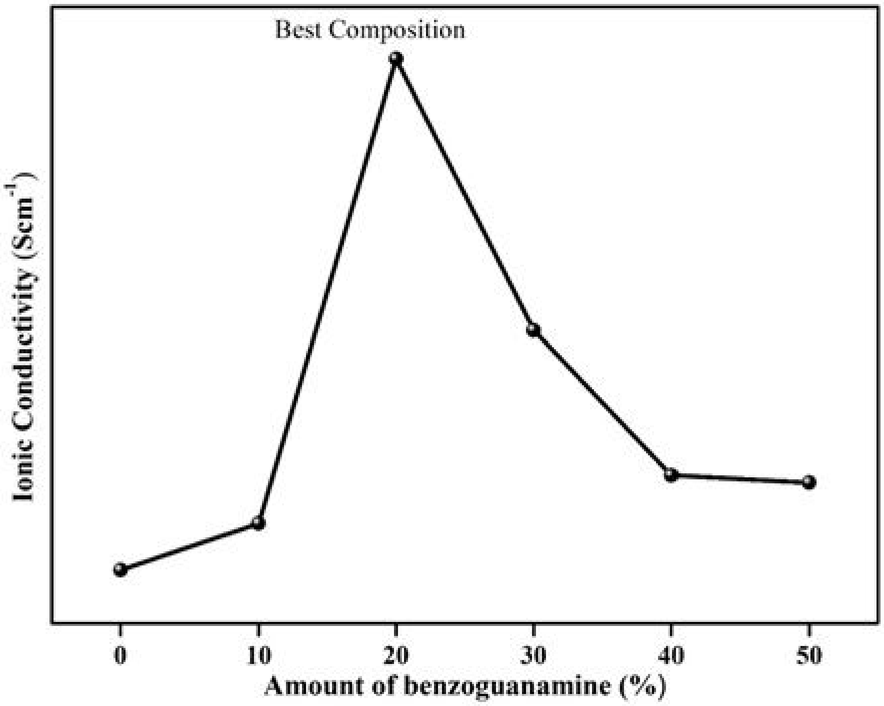

Figure 3

Conductivity variations of benzoguanamine doped PVDF/KI/I2 electrolyte films

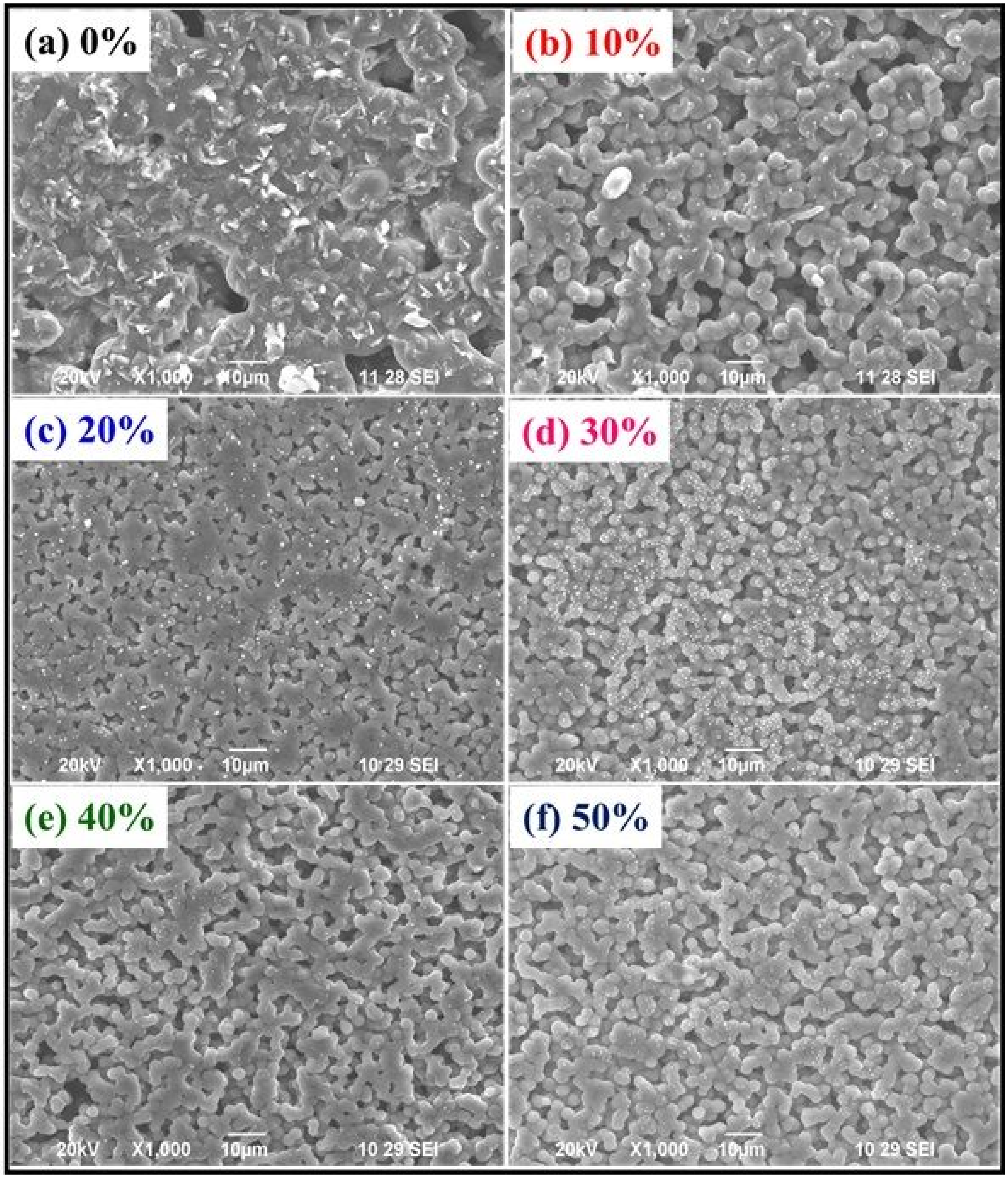

Figure 4

SEM images of benzoguanamine (a) 0%, (b) 10%, (c) 20%, (d) 30%, (e) 40% and (f) 50% doped PVDF/KI/I2 electrolyte films

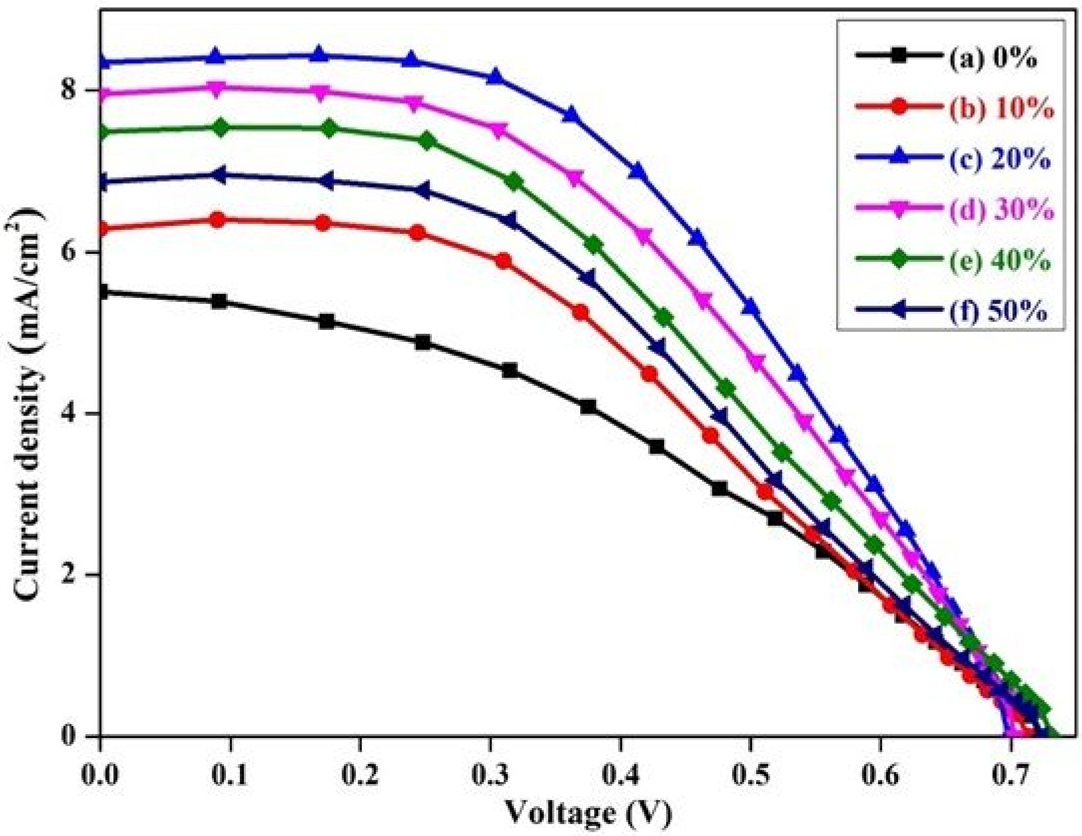

Figure 5

The photovoltaic (J-V) curves of DSSCs with benzoguanamine (a) 0%, (b) 10%, (c) 20%, (d) 30%, (e) 40% and (f) 50% doped PVDF/KI/I2 electrolytes

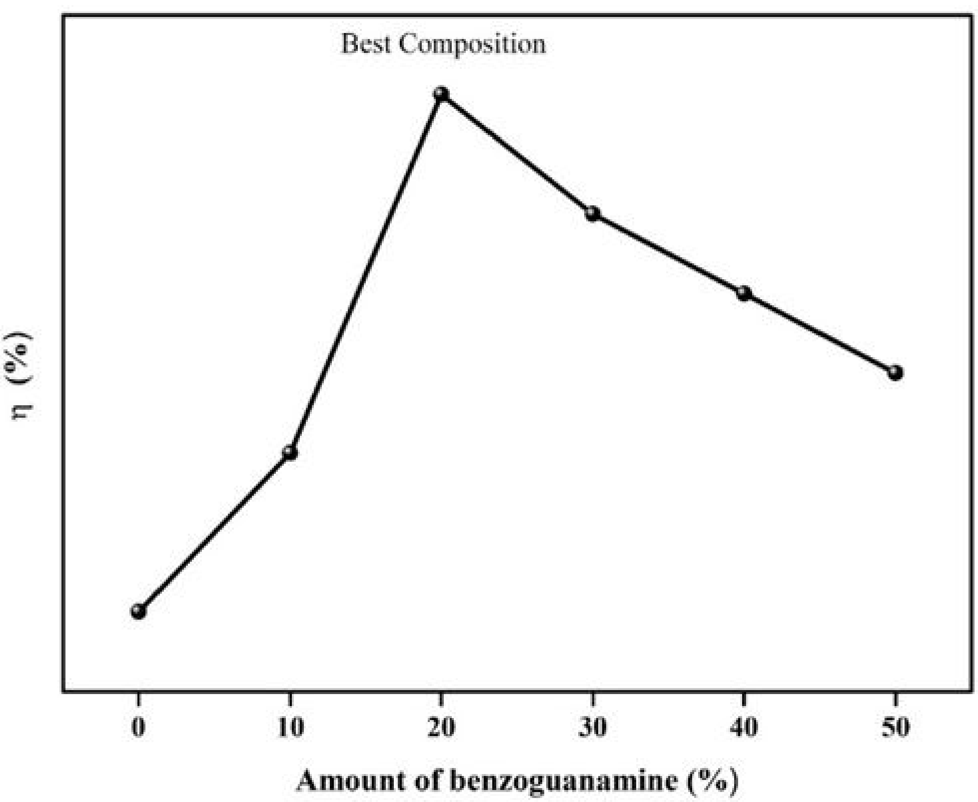

Figure 6

Efficiency variations of DSSCs with benzoguanamine doped PVDF/KI/I2 electrolytes

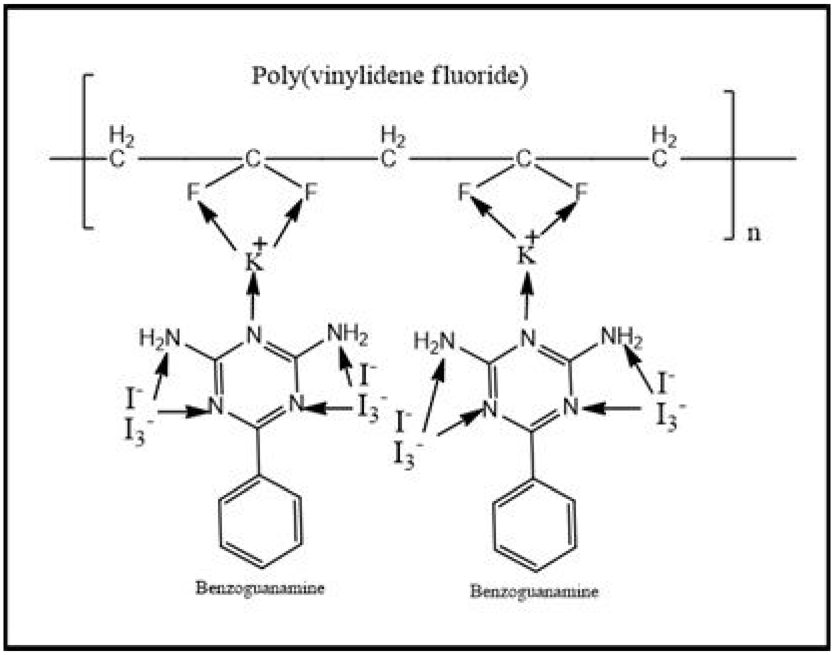

Figure 7

Molecular interaction of benzoguanamine with PVDF/KI/I2