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Photoelectrochemical Effect of Poly(*N*-vinylcarbazole) as Electrolyte Additive in a N719 Dye Sensitized TiO_2 Solar Cell

Alagar Ramar[1], *Tse-Wei Chen*[2,3], *Shen-Ming Chen*[2,3*], *Devarajan Mutharasu*[1] *and Syang-Peng Rwei*[3,4]

[1] Thermal Management Research Laboratory, School of Physics, Universiti Sains Malaysia, Penang 11800, Malaysia.
[2] Electroanalysis and Bioelectrochemistry Laboratory, Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, No.1, Section 3, Chung-Hsiao East Road, Taipei 106, Taiwan, ROC
[3] Research and Development Center for Smart Textile Technology , National Taipei University of Technology, Taiwan
[4] Institute of Organic and Polymeric Materials, National Taipei University of Technology, Taiwan
[*] E-mail: smchen78@ms15.hinet.net

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Poly(*N*-vinylcarbazole) (PVK) has been used as additive in the I^-/I_3^- redox electrolyte and the photoelectrochemical effect of PVK with various concentration to the photovoltaic performance was studied. Under optimum condition, a maximum efficiency of 6.3% was achieved with a current density of 19.31 mA/cm^2 at the addition of 30 μL THF solution to the electrolyte which is 45 % improved photovoltaic performance compared to that of bare electrolyte. This could be attributed that the electron rich PVK increases the basicity of the electrolyte medium and increases the catalytic reduction of I_3^- ions. So, the increased dye regeneration rate improved photovoltaic performance.

Keywords: Photoelectrochemistry; Poly(*N*-vinylcarbazole); Electrolyte additive; Dye sensitized solar cell; I^-/I_3^- redox electrolyte

1. INTRODUCTION

Dye sensitized solar cells (DSSCs) are considered as one of the emerging solar cell technology which has the potential to reduce the cost of electricity generation. There has been extensive academic and commercial interest on this technology for the last two decades. The seminal paper published by O’Regan and Grätzel1 in 1991 inspired the researchers to take it into a next level [1]. A typical DSSC primarily contains a dye-adsorbed nanocrystalline semiconducting metal oxide, usually TiO_2, as photoanode, an electrolyte typically acetonitrile containing LiI, I_2 and a counter electrode, usually Pt [2]. Among all the components the role of electrolyte is very important since it involves in dye regeneration. Dye regeneration and electron recombination of TiO_2 with dye or electrolyte are vibrant problems in DSSCs [3]. The electron recombination is known as back electron transfer which seriously affects the photovoltaic performance of DSSCs. There have been many strategies developed to reduce the back electron transfer. For example, surface modification of TiO_2 with inorganic metal oxides [4,5] and conducting polymers [6,7], whose conduction edges are higher than that of TiO_2. Also, surface passivation by some organic molecules such as 4-guanidinobutyric acid [8], tris(dodecyloxy) benzoic acid [9], poly(ethylene glycol) based oligomers [10] and citric acid [11] were also reported to assistance in the reduction of charge recombination. Additives have been proposed as another way to improve the photovoltaic performance which primarily have role in dye regeneration and electron recombination [12]. The improved photovoltaic performances are attributed to the modification of redox couple potential, band shift of the semiconducting material, effects of surface blocking and organization of dye at surface. The very first used electrolyte additive is 4-*tert*-butylpyridine (TBP) which demonstrated a remarkable increase in open circuit voltage in LiI based redox electrolyte [13]. Notably, most of the reported additives contain an electron donating nitrogen heterocycle, normally giving results as good as TBP [2]. It has been found from the density functional and perturbation theory levels that the interaction between nitrogen containing additives and iodine are the donor-acceptor type [14,15]. So, it is expected that the nitrogen containing poly(*N*-vinylcarbazole) could be good choice to acts as an additive to I^{-}/I_3^{-} redox electrolyte.

In this paper we report the effect of PVK as additive in the electrolyte on the photovoltaic performance of the DSSCs. A very small amount of PVK was used as electrolyte additive and effect of concentration on the photovoltaic performance was systematically studied. The results demonstrated that the DSSC assembled with PVK added electrolyte showed superior performance compared to that of the bare electrolyte under optimum condition. This was mainly attributed to the increased basicity and hole conducting nature of PVK which aids the I^{-}/I_3^{-} redox process and improve the dye regeneration. Not only PVK cause band shift but also increase the electron life time.

2. MATERIALS AND METHODS

2.1. Preparation of Photoanode

TiO_2 colloidal paste was prepared by grinding TiO_2 (6 g) (P25, Sigma-Aldrich), poly(ethylene glycol) (M_n =20,000, Sigma-Aldrich) (0.66 g), 200 µL of acetylacetone (Sigma-Aldrich), 200 µL of Triton X-100 (Sigma-Aldrich) and 12 mL deionized water in an agate mortar for 1 h. Spin coating method was used to coat TiO_2 paste on a pre-cleaned tin-doped indium oxide (ITO) (Merck Display Technologies Ltd., Taiwan) substrate at a speed of 1000 rpm for 10 s and followed by 2000 rpm for 30 s (Delta spin coater, Taiwan). Prior to the coating of TiO_2 paste, ITO coated transparent substrates were ultrasonically cleaned in sequence by Triton X-100, acetone, ethanol and in water for ten minutes and dried in an oven at 80ºC. The TiO_2 coated films were annealed at 450 °C for 1 h after drying at room temperature for 30 min. The coating and annealing procedure were repeated once again to get a 20 µm uniform thick film. The prepared electrodes were soaked in a 0.5 mM ethanolic solution of N719 dye (Sigma-Aldrich) at room temperature for 24 h. Then the films were rinsed by ethanol and dried in air at room temperature. A platinum sputtered ITO substrate was used as counter electrode.

2.2 Preparation of Electrolytes and Fabrication of DSSCs

The liquid electrolyte containing I^-/I_3^- redox couple was prepared by dissolving 0.3 M 4-*tert*-butylpyridine (Sigma-Aldrich), 0.5 M LiI (Sigma-Aldrich), and 0.05 M I_2 (Sigma-Aldrich) in acetonitrile. The electrolyte additive PVK was dissolved in THF (1mg/mL) and added with variable amount (10-50 µL) to the electrolyte solution (1 mL). Hereafter it will be notified as Electrolyte/PVK_x, where x denotes the amount of PVK added to the electrolyte *viz.* 10, 20, 30, 40 and 50 µL respectively. DSSC assembled with N719 dye sensitized TiO_2 as photoanode and sputtered Pt as counter electrodes in a sandwich type cell using 60 µm surlyn film (Solaronix) as spacer. The sealing was accomplished by hot-pressing the sandwich cell at 100 °C. The active area of the cell was 0.25 cm^2. The electrolyte was injected into the space between the electrodes by capillary effect before testing.

2.4. Measurements

FT-IR spectra were recorded using 8400 S Shimadzu FT-IR spectrophotometer in the region of 4000–400 cm^{-1} with a spectral resolution of 2 cm^{-1} using dry KBr at room temperature. Scanning electron microscope (SEM) images of the powder sample was obtained using a JEOL scanning electron microscope (JSSM-6390). Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) patterns were performed using a JEOL 3011 instrument, operating at 300 kV with ultra-high-resolution pole piece. Thermogravimetric analysis (TGA) was performed using a thermogravimetric analyser (TAQ500) at a heating rate of 10 °C/min under nitrogen atmosphere. The current-voltage (I-V) measurements of the assembled DSSCs were obtained by illuminating the cells using a solar simulator (HONG-MING TECH) under one-sun illumination (AM 1.5G, 100 mW/cm^2) connecting with a digital source meter (Keithley Instruments Inc., Model 2400).

3. RESULTS AND DISCUSSION

3.1. FT-IR Spectral Characterization

Fig. 1 displays the FT-IR spectrum of PVK and it shows its characteristic bands analogous to that of the reported in literature [16,17]. The asymmetric stretching band of aromatic C─H bond appeared at 2964 cm^{-1} whereas the symmetric stretching band appeared at 2927 cm^{-1}. The difference between the C=C stretching in vinylidene and aromatic ring could be clearly observed from its respective bands at 1595 and 1639 cm^{-1}. The ring vibration of N-vinylcarbazole moiety could be observed at 1450 and 1483 cm^{-1}. The band at 1218 cm^{-1} was mainly attributed to the C─H in-plane deformation of aromatic ring whereas the band at 1328 cm^{-1} attributed to that of vinylidene group. One more information about the carbazole ring was obtained by the band at 923 cm^{-1} which indicates the symmetric out-of plane bending mode of carbazole ring. The substituted aromatic ring could be observed from the vibrational band which would appear at 719 cm^{-1}. A band at 418 cm^{-1} is ascribed to the out-of-plane vibration of C─H bond. A more clear information could be obtained from the CH_2 rocking vibration band appeared at 746 cm^{-1} which is due to the tail to tail addition of $(CH_2)_2$ [18].

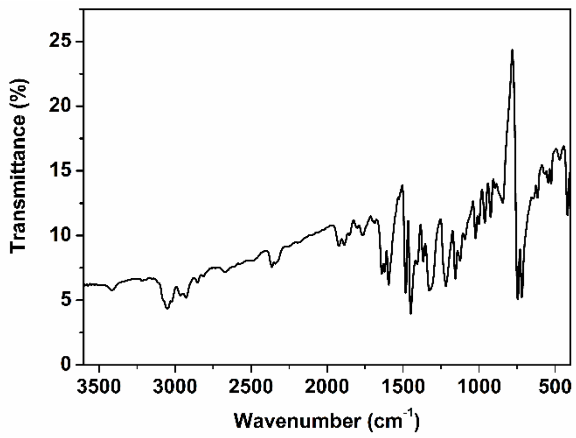


Figure 1. FT-IR spectra of PVK.

3.2. Thermal analysis (TGA)

Thermal stability of the PVK was studied by TGA from 25 to 800 °C. It displayed four-step degradation upon gradual heating of the sample during the entire thermogram. From the Fig.2 it is inferred that there is no weight loss up to 120 °C, 5 % weight loss occurred at 250 °C. A distinguished weight loss about 20% weight loss perceived at 330 °C. A sudden weight loss was observed near to 380 °C and almost all of the samples charred at 399 °C. At 480 °C only 5 % sample was found to left. So it is clear that the PVK additive added electrolyte will not decompose during the illumination under standard conditions.

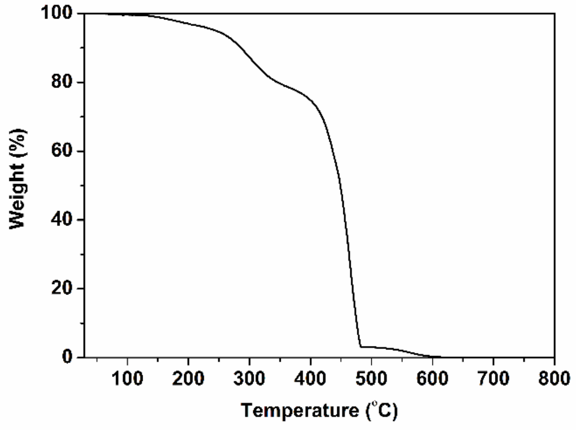


Figure 2. TGA curve of PVK.

3.3 Electron microscopic characterizations (SEM and TEM)

Fig. 3 shows the SEM and TEM images of PVK with SAED pattern. The sub-micro morphological structure of PVK can be seen from the Figs. 3 (A) and (B). It clearly indicates that the presence of a variety of beautiful cavities on the external surface and also shows the existence of differently oriented micro-sized agglomerates with different shape and size. The spherical nanoclusters of PVK could be seen (Figs. 3 C & D) with an average size of 15 nm. SAED pattern used to classify texture and distinguish the crystalline from the amorphous nature of polymer. The amorphous nature of the polymer could be identified from the SAED pattern (Inset of Fig. 3D) which shows the diffused ring pattern.

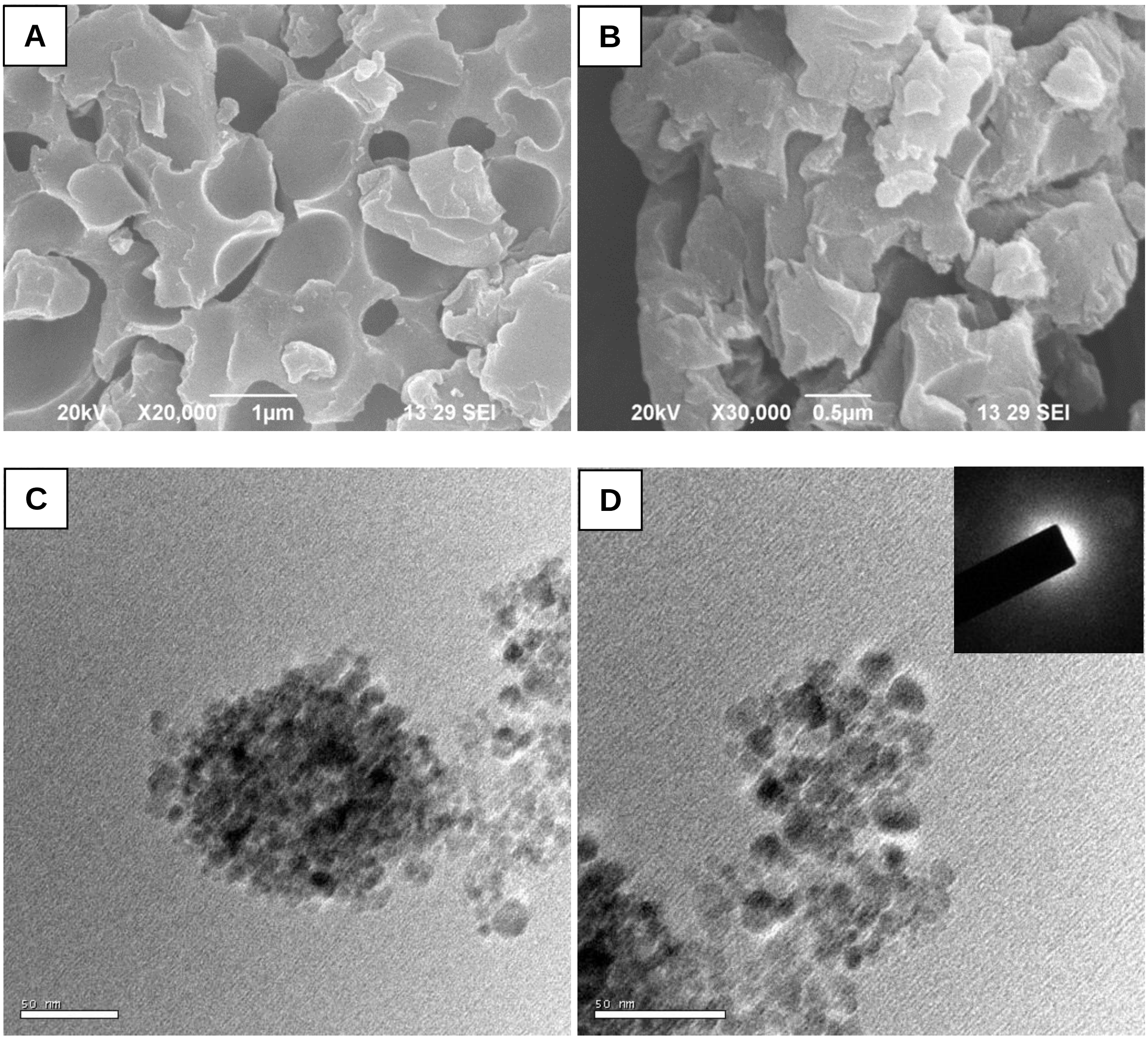


Figure 3. (A) and (B) SEM images of PVK (C) and (D) TEM images of PVK Inset of the (D) is SAED pattern of PVK.

3.4. Photovoltaic performance studies

The effect of PVK additive to the I^{-}/I_3^{-} redox electrolyte on the photovoltaic performances of the N719 dye sensitized TiO_2 based solar cells are shown in Fig. 4 and in Table 1. It can be seen that the DSSC tested with the bare electrolyte exhibited a moderate solar conversion efficiency (η) of 4.37 % with a short-circuit current density (J_{sc}) of 10.23 mA/cm^2, an open-circuit voltage (V_{oc}) of 0.758 V and a fill factor (FF) of 56 %. The diagram clearly shows some improvement in short-circuit current density when adding 10 µL solution to the electrolyte and hence the efficiency also enhanced. Further addition of PVK additive solution to the electrolyte causes improved photovoltaic performance. Under optimum condition the DSSC tested with 30 µL PVK added electrolyte showed an open-circuit voltage of 0.653 V, a short-circuit current density of 19.31 mA/cm^2, a fill factor of 50 % and the efficiency of 6.37 %. The efficiency value increased from 4.37 to 6.37 % which is 45 % improvement compared to the bare electrolyte. The J_{sc} value improved still higher *viz.* 88 % higher than that of the bare one. The photovoltaic data clearly indicates that the PVK additive has some interaction with the photoelectrode/electrolyte interface, the redox electrolyte and counter electrode/electrolyte interface which caused the obvious change in the photovoltaic performance. The enhanced performance was mainly attributed to the enhanced basicity of the electrolyte medium by the electron rich PVK since it contains electron donating nitrogen heterocycle (Scheme 1). This will ease the reduction of I_3^{-} ion to I^{-} ions [12]. Once the redox process becomes fast then, the dye regeneration will be very fast [19]. So, the current density has been increased and hence the efficiency also. In addition to that the conduction band edge of PVK is higher than that of TiO_2 and N719 dye. So the back electron transfer from TiO_2 to electrolyte would be minimized considerably. However, further addition of PVK to the electrolyte deteriorates the photovoltaic performance and hence the solar cell parameters of 40 and 50 µL PVK added electrolytes based DSSCs showed poor performance. This might be understood that at higher concentration of polymer in the electrolyte, the iodide diffusion slow and hence the dye regeneration becomes lower compared to the bare electrolyte. So naturally one can expect poor photovoltaic performance [3].

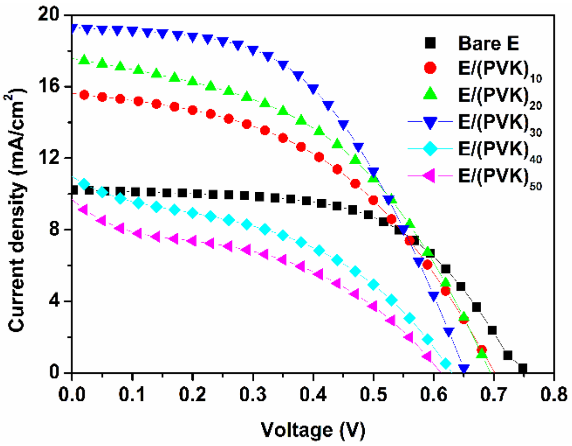
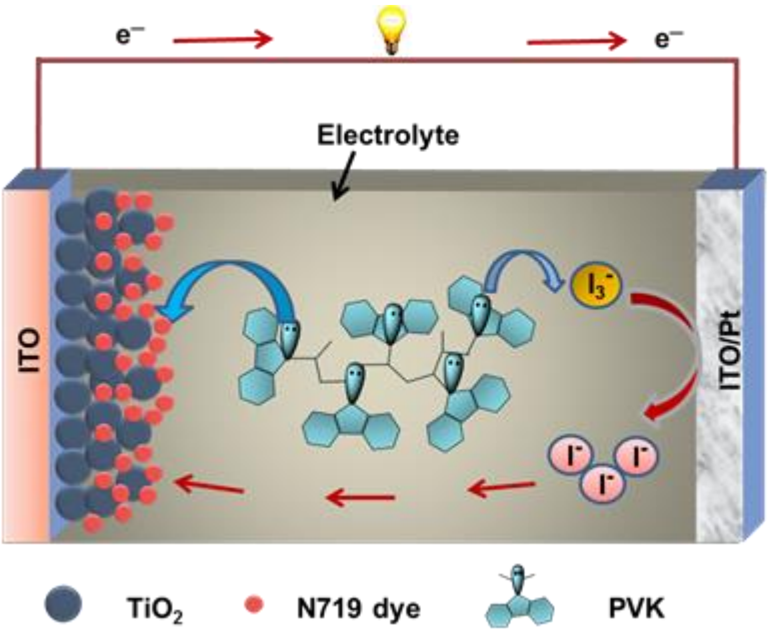


Figure 4. *J-V* curves of DSSCs assembled with bare and PVK additive added electrolytes.

Table 1. Comparison of the photovoltaic performance of the DSSCs based on the bare and PVK additive added I^-/I_3^- redox electrolyte.

Electrolyte	V_{oc} **(V)**	J_{sc} **(mA/cm²)**	**FF (%)**	η **(%)**	R_S **(m Ω)**	R_{SH} **(m Ω)**
Bare E	0.758	10.23	56.34	4.37	23.74	982.31
E/(PVK)$_{10}$	0.701	15.63	45.68	5.00	18.95	205.90
E/(PVK)$_{20}$	0.694	17.58	46.02	5.61	15.82	148.78
E/(PVK)$_{30}$	0.653	19.31	50.55	6.37	12.56	142.02
E/(PVK)$_{40}$	0.630	10.99	40.53	2.80	25.29	117.85
E/(PVK)$_{50}$	0.612	9.693	38.15	2.26	31.77	113.10



Scheme 1. The reduction and diffusion processes of PVK added electrolyte in a DSSC

From the photovoltaic data, it could be seen some interesting features which represented separately in Fig. 5. The effect of PVK loading on the photovoltaic parameters such as V_{oc}, J_{sc}, FF and η are separately discussed. Very interestingly, the V_{oc} values of the DSSCs based on PVK added electrolytes are found to be decreased upon the increased addition. V_{oc} is the measure of difference between the Fermi level electrons in the TiO_2 and the redox potential of the electrolyte [20]. It is well-known that dyes containing acidic carboxyl group as anchor such as N719, N712 and N3 upon adsorption transfer its protons to the TiO_2 surface, charging it positively and move down the Fermi level [21-23]. As in the previous case the presence of PVK aids in deprotonate from the dye to TiO_2 surface and hence the fermi level of electrons in TiO_2 is gradually moved down, resulting in lower V_{oc} [6]. The current density and efficiency values are following the same trend, attainment high up to 30 µL addition and decreases upon further addition. This could be attributed to the increased resistance of the electrolyte at higher concentration. The fill factor of the PVK additive electrode based DSSCs are moderate up to 30 µL and low at the higher loading.

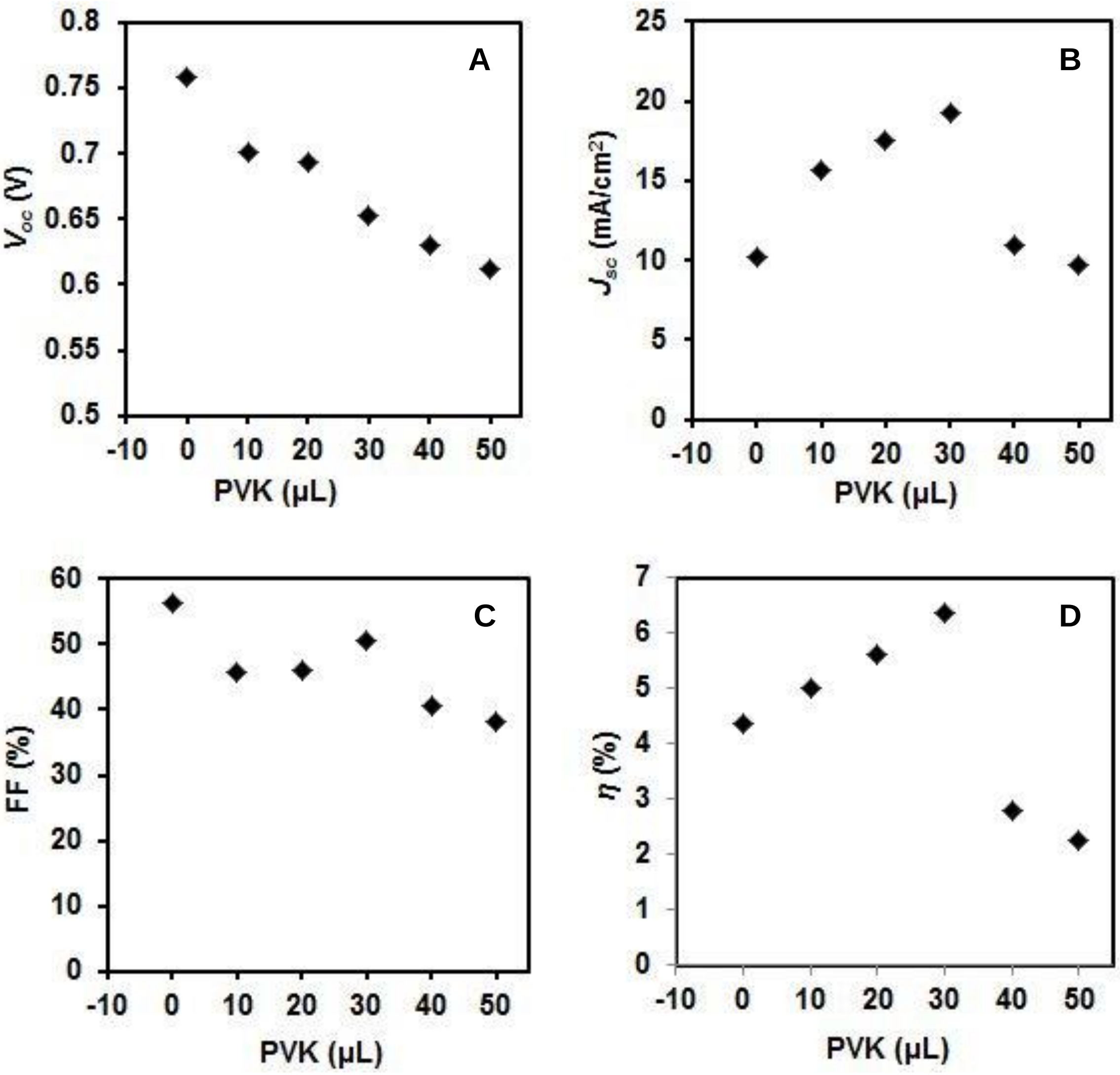


Figure 5. Effects of PVK loading to the I^-/I_3^- redox electrolyte on (A) V_{oc} (B) J_{sc} (C) FF and (D) η in the DSSCs.

The series resistance (R_S) and shunt resistance (R_{SH}) have also influenced on the shape of I-V curve and gives the information about the solar cell performances. The inverse slope near to the V_{oc} is equal to R_S while R_{SH} derived from the inverse slope near to short-circuit current. The R_S is the sum of sheet resistance (R_H), charge transfer resistance at the counter electrode (R_1) and resistance (R_2) related to the diffusion of iodide and triiodide ions within the electrolyte [24, 25]. It was expected that the sheet resistance would not be changed for all cells because the ITO, TiO_2 and dye are same and and also in all cases the Pt counter electrode is same. So it is clear that the charge transfer resistance will not change. From the table 1 one can easily understand that the addition of PVK has facilitated the diffusion process up to 30 µL and detracts upon further addition. It is mainly because of the increased resistance for the diffusion at higher concentration of polymer. There is a linear relationship between R_{SH} and V_{oc}. In this case the V_{oc} decreases as the concentration of PVK increases. At the same time R_{SH} also decreased. A low R_{SH} provides substitute path for the light generated current which affects negatively the power output and fill factor [24]. Compare to bare electrolyte system all PVK added electrolyte showed reduced R_{SH} and hence the fill factor was reduced.

4. CONCLUSION

In summary, poly(*N*-vinylcarbazole) used as additive in the I^-/I_3^- redox electrolyte and the effect of PVK with various loading to the photovoltaic performance was studied. The polymer was added in a very small quantity and it was found to be effective in improving the photovoltaic performance. As a result, the solar energy conversion efficiency was improved dramatically from 4.37 % to 6.37% which is 45 % enhanced value compared to that of bare electrolyte. The change in the photovoltaic performance of PVK additive added electrolytes confirming that there is interaction with photoanode/electrolyte interface, redox electrolyte and counter electrode/electrolyte interface. The additive not only increase rate of the dye regeneration process but also reduce the back electron transfer.

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