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Degradation/ Oxidation Susceptibility of Composite Semiconductor; Organic Photovoltaic cell of ZnO/PEDOT: PSS/Graphite

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Abstract

A criterion of the degradation/oxidation susceptibility of organic photovoltaic (OPV) cells free of any metallic electrodes is considered. This criterion is used to determine the degradation/oxidation of ZnO/PEDOT: PSS/Graphite cells in deionized water and in also polluted water with fine particles of sand. The values of R_p were determined by the electrochemical impedance spectroscopy (EIS) at a low frequency. In addition, results of the criterion of ZnO/PEDOT: PSS/Graphite cells was compared with ZnO/PEDOT: PSS/Silver cells in similar media for a predetermined period of OPV operations. In the meantime, the ZnO/PEDOT: PSS/Graphite cell was found to have good degradation resistance during 1000 hrs of exposure to deionized water and polluted water with respect to the standard plots of $\ln(R_{p_s}/R_{p_{air}})$ versus time of exposure.

Keywords: Degradation/Oxidation, Organic Photovoltaic (OPV) Cells, Power Conversion Efficiency (PCE), Electrochemical Impedance Spectroscopy (EIS), Aqueous Solutions.

Introduction

The Silicon (Si) Photovoltaic (PV) cells, as renewable energy sources, are widely being used as a sole/hybrid system along with the electrical grid [1]. The problem with Si PV cell is that these are very expensive to fabricate. However, advantages of the Si PV cells are that they are stable in the operational surroundings [1]. In contrast, the organic photovoltaic (OPV) cells are cheaper to fabricate, however, the OPV cells are not stable in the typical operational surroundings [2-4]. Despite intensive studies on cause of the failure of organic photovoltaic (OPV) cells, the degradation/oxidation of OPV cells in aqueous solutions have not been well understood [1-3] in order to mitigate the problem. The reason of the intensive studies on improving the power conversion efficiency (PCE) of OPV cells was due to the economic and environmental needs of replacing their inorganic counterparts in the near future[1]. The commercialization of

the OPV cells is dependent on the improvement of the PCE of the cells compared to the inorganic cells, i.e., crystalline silicon solar cells. Nowadays, the crystalline silicon solar cells have by far dominated 99% of photovoltaic markets [4] with a maximum PCE of 24% [5,6]. On the contrary, it has been recently reported [2] that the PCE of the OPV has been gradually improved from 2.5% [7], to 6% [8-13], 6.5% [14], and 10% [15] throughout the years of the development.

Therefore, the development of functional OPV cells with an energy efficient life is more favorable than the inorganic cells, especially in oil producing harsh regions of the world like the gulf co-operative countries(GCC). It became a national policy of GCC to lower the fuel consumption for power generation by 15% by the year of 2030, along with the current status of the oil market of low prices. Instead, the national policy of these countries has encouraged the use of renewable energy sources, i.e., OPV cells, which can be locally manufactured. The materials of the OPV cells consist mainly of a conductive organic materials, i.e, poly (3,4-ethylene dioxythiophene): polystyrene (PEDOT:PSS) that is sandwiched between two electrodes [16,17]. One metallic electrode has a low-workfunction, i.e, silver (Ag). In contrast, the other electrode, has a high-workfunction, i.e. Zinc oxide (ZnO), an inorganic electrode. The electrode with the high-workfunction is usually a transparent/a semi-transparent thin film, in which the light can be harvested directly from a light source, i.e., sun, through the thin film. Then, the light is absorbed by the conductive organic materials. The conductive organic materials has two regions of molecular orbits. One calls highest occupied molecular orbits (HOMO) and the other calls lowest unoccupied molecular orbits (LUMO). So, when the light is absorbed by the conductive organic materials, an electron is promoted from the HOMO to the LUMO, leaving behind a hole in the HOMO. As a result, an exciton is formed.

Subsequently, an exciton disassociation occurs due to the difference between the workfunction, i.e electric field, between

the two electrodes. This leads to the electron collection at the metallic electrode with the low-workfunction, i.e., Ag, and the collection of the holes at the inorganic electrode with the high-workfunction, i.e., ZnO. Even though the OPV cell seems to have a simple structure of a thin film, however the film has a heterostructure that is made of at least three different materials (heterojunction). This sort for heterostructure would be electrochemically active especially when the film operates in the surrounding environment, where access to oxygen, water, and pollutants are present. In other words, a successful operation of OPV cells in the future will be dependent on the integrity assessment of the heterojunction of the film in the surrounding environment. Naturally, the success of the operation of OPV cells can be measured by the produced PCE and also the operational life of the cells. There are a number of investigations on OPV cells that have been conducted in order to determine the cause of the degradation of the organic materials and the oxidation of metallic electrodes of the OPV cells. A review on different methods of investigating the cause of the degradation/oxidation of the cells is given elsewhere [3]. Among the methods, the electrochemical impedance spectroscopy (EIS) was used [16-20] to provide physical/chemical information on the reason of the decrease of the photoelectric current of the cells. It was found that the conductivity of the heterojunction varies between the bulk of the heterojunction and the contact region between the metallic electrodes of organic materials [18,19] in the present of ambient environment. The conductivity of the contact region between the metallic electrodes and the organic materials was found much lower than that in the bulk of the heterojunction. This observation was interpreted due to the corrosion of the Al electrode to Al_2O_3 , in the present of O_2 or a relative humidity, in which that the dielectric constant of the region increases by depletion of the Al materials and consequently, decreases the photoelectronic current [18,19]. In a similar manner, the corrosion of the Ag electrode to Ag_2O , in the present of deionized water and polluted water, in which that the dielectric constant of the region increases by depletion of the Ag materials and consequently, decreases the photoelectronic current [16,17]. Another investigation by EIS has suggested to implement a better design for the heterojunction in order to exhibit a large decrease in the dielectric constant under illumination in ambient environment [20]. In general the degradation/oxidation of OPV cells require a mitigation measure on a frequent basis in actual operational environment. A cleaning is essential due to contaminations of the surrounding environment. Therefore, a detail study on the electrochemical behaviour of a OPV cell free of metallic electrodes in simulated operational environment is essential for understanding the effect of the absence of metallic electrodes on the degradation/oxidation of the OPV cell. In the present study, the EIS will be used to measure parameters such as the alternating current impedance (Z) of the OPV cell, free of metallic electrodes, at a low frequency in deionized water and in polluted water, with fine particles of sand. Then, the polarization resistance of the OPV cell at the open circuit potential of the OPV

cell will be determined from the value of Z in deionized water and polluted water. The polarization resistance is known to be a good indicator of the susceptibility to corrosion of metallic electrodes covered by organic thin films [21-23]. The reason of testing the OPV cells in the deionized water and the polluted water is to simulate the surrounding operational environment of cells for producing a sustainable energy source in an arid/wet climate of Kuwait. Subsequently, the obtained parameters of the EIS tests will be compared with those of the OPV cells in air. As a result, the variation of the Rp of the OPV cells will be determined under different conditions. The PCE will be correlated to Rp based on the variation of the Rp of the OPV cell in different solutions compared to the one in air. In addition, a comparison study will be conducted on the OPV cell free of metallic electrodes with another OPV cell with a metallic electrode in deionized water and in polluted water. This sort of study will definitely reveal the effect of the absent of the metallic electrode on the degradation/oxidation of the OPV cell in the deionized water and in polluted water.

In the present work, an implemented criterion of the degradation/oxidation of the OPV cells was used [16,17]. The proposed criterion; $\lim (R_p_s / R_p_{air}) = 1$ will be correlated to the PCE of the OPV cells in aqueous solutions when R_p_{air} became equal (increased) to R_p_s as a function of time of the exposure of the OPV cell to the aqueous solution. This criterion was plotted based on the obtained Rp values by EIS versus the predetermined operation time of the OPV cells, 1000 hrs. The Rp value of the OPV cells can be measured by the EIS at low frequency, $f=0.16$ Hz, as the following [22,23]:

$$R_p = |Z| = rU/A \tag{1}$$

where,

Z is the alternating current (AC) impedance of the OPV cell, Ohm.

Rp is the direct current (DC) resistance of the OPV cell, Ohm;

A is the exposed surface area of the OPV cell to solution, measured here as 2.83 cm²;

U is the thickness of the OPV cell, 121.1 mm, measured by Eddy current principle [24], based on an average of 10 readings.

r is the electrical resistivity of the OPV cell, Ohm cm;

Therefore, a criterion of the degradation/oxidation of the OPV cell was derived from Eq.1 as follows [16,17]:

$$\lim (R_p_s / R_p_{air}) = 1 \tag{2}$$

$$R_p_{air} \rightarrow R_p_s$$

where,

R_p_s is the polarization resistance of the OPV cell in aqueous solution, Ohm;

R_p_{air} is the polarization resistance of the OPV cell in air, Ohm;

Equation (2) states that when R_p_{air} becomes equal (increases) to

R_p as a function of time of the exposure of the OPV cell to the aqueous solution, the OPV cell is deteriorating by degrading of the organic materials or by oxidizing (corrosion) of the metallic electrodes of the OPV cell by the surrounding environment.

Experimental Work

In this investigation, Eq. (2) was used to determine the susceptibility of OPV cells to degradation/oxidation by the deionized water and polluted water with fine particles of sand. The pH of the deionized water and the polluted water were measured as 6.2 and 9.2, respectively. The pH values of the deionized water and the polluted water were determined based on an average of five measurements. The chemical composition of OPV cell is ZnO/ PEDOT:PSS/Graphite, free of a metallic electrode. The transparent ZnO was the high-workfunction electrode, facing the light source. The PEDOT:PSS was the active organic materials. The Graphite was the low-workfunction electrode, in which the R_p of the pure Graphite in air will be calculated and the R_p of the Graphite, of the OPV cell, in a deionized water and in polluted water will be measured by the EIS. The thickness of the cell was measured as 121.1mm, in a thin film form. The corrosion was not expected to take place at the contact region between the active organic materials (PEDOT:PSS) and the Graphite electrode in the present of water in aerated environment. The OPV cell was a newly developed and supplied by National Laboratory for Sustainable Energy, Technical University of Denmark, Frederiksborgvej 399, DK-4000 Roskilde, Denmark [25].

EIS measurements were performed against a saturated Calomel electrode (SCE) according to standard procedures described elsewhere [26-28]. A standard electrochemical cell of three electrodes was used. The cell made of a 1000 cm³ flask, a reference electrode (the SCE), a counter electrode (made of high density graphite bar) and a working electrode of the OPV cell. The exposed surface area of all samples was measured as 2.82 cm². In addition, EIS measurements were conducted using a potentiostat/Galvanostat, the Iviumstat brand made by IVIUM

Technologies, in Eindhoven, The Netherland. The Iviumstat was used in order to obtain impedance spectra of the OPV cell in aqueous solution. The EIS spectra of all investigated samples were determined in deionized water and a polluted water, saturated with fine particles of sand. The chemical composition of the sand is a typical of that of Silicon dioxide (SiO₂). The reason of testing the OPV cells in the deionized water and the polluted water is to simulate the surrounding environment of cells during the operation in arid/wet climate of Kuwait. A typical light intensity of 80 W/m² was used during the EIS tests.

The EIS spectra [26-28] were basically the complex plane plots (Nyquist plots) and the Bode plots. The complex plane plots (Nyquist plots) are basically the imaginary impedance (Z_{imag}) versus the real impedance (Z_{real}). Also, values of the AC impedance were obtained from Bode plots at a low frequency for all investigated samples. Values of the AC impedance were obtained at the low frequency based on the extrapolation of the intersection line at a frequency equal to 0.16 Hz from the x-coordinate in Bode plots, to the y-coordinate in Bode plot. Bode plots are basically the logarithm of impedance (Z) (Y-coordinate) and the phase (θ) (Y-coordinate) plotted versus the logarithm of the frequency (X-coordinate). All electrochemical parameters of the OPV cell were determined by using the IviumSoft Electrochemistry Software, using an equivalent circuit model of a painted sample [26-28]. Also, in order to plot the complex plane (Nyquist) and Bode plots, the frequency range was chosen to range between 0.01 to 100000 Hz with amplitude of + 5 mV. The AC impedance (Z) values of the samples were determined from Bode plots (26-28) at a frequency is equal to $f = 0.16$ Hz (at angular velocity $\omega = 1$ rad/s), where $\omega = 2\pi f$. From Eq.(2), the values of ($R_p / R_{p_{air}}$) were calculated based on the obtained data of |Z| from the EIS tests of the OPV cells in the deionized water and the polluted water. The value of $R_{p_{air}}$ of the OPV cell in air for the pure Graphite was obtained elsewhere [29].

Figures 1a and 1b are examples of a Bode plot (a), and a complex plane plot (b) (Nyquist plot) of the ZnO/PEDOT: PSS/Graphite

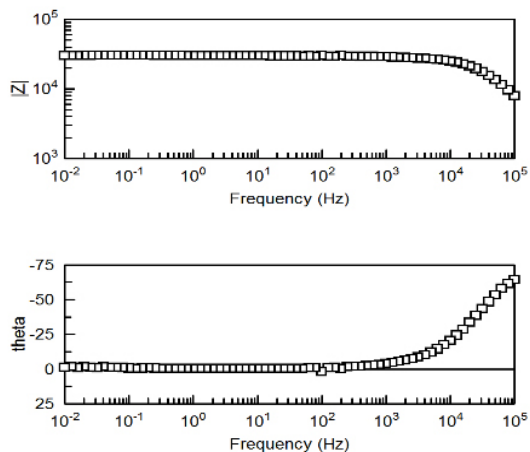


Figure 1a: The Bode plot of the ZnO/PEDOT: PSS/Graphite cell in deionized water. The upper plot is the logarithm of impedance (Z) versus the logarithm of frequency and the lower plot is the phase angle (θ) versus the logarithm of frequency.

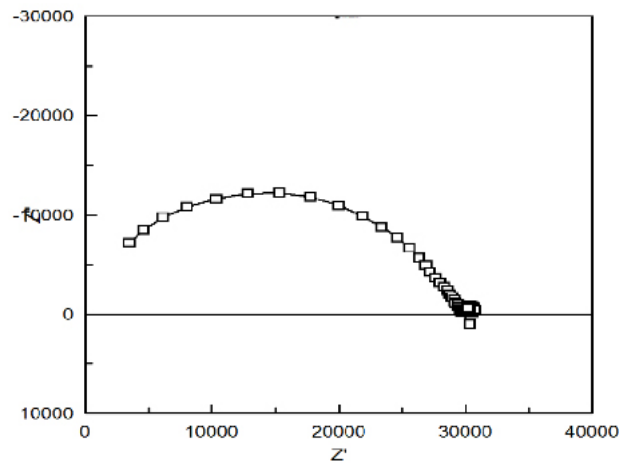


Figure 1b: The complex plane plot (Nyquist plot) of the ZnO/PEDOT: PSS/Graphite cell in the deionized water. The plot is basically the imaginary impedance (Z_{imag}), Y-axis versus the real impedance (Z_{real}), X-axis

cell in deionized water. Furthermore, Figure 2a and 2b is an example of a Bode plot(a) and a complex plane plot(b) (Nyquist plot) of the ZnO/PEDOT: PSS/Graphite cell in polluted water.

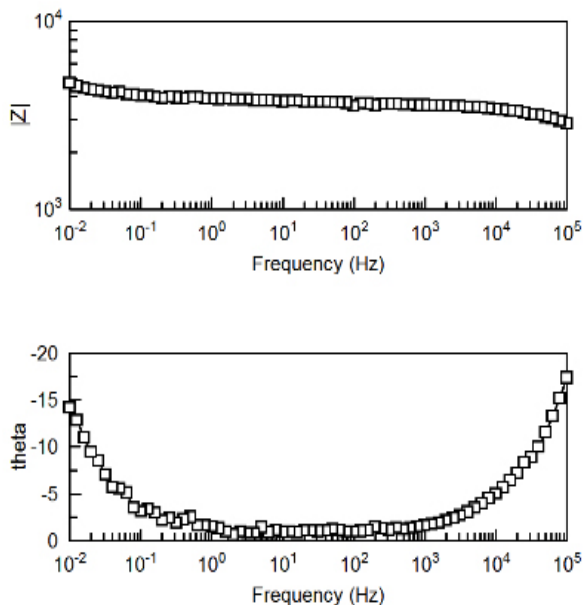


Figure 2a: The Bode plot of the ZnO/PEDOT: PSS/Graphite cell in polluted water. The upper plot is the logarithm of impedance (Z) versus the logarithm of frequency and the lower plot is the phase angle (θ) versus the logarithm of frequency

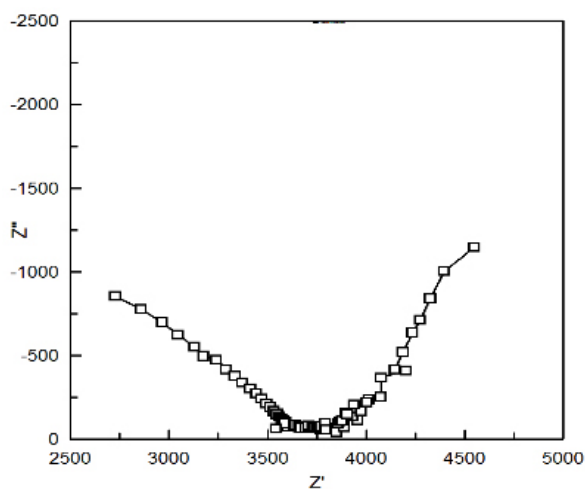


Figure 2b: The complex plane plot (Nyquist plot) of the ZnO/PEDOT: PSS/Graphite cell in the polluted water. The plot is basically the imaginary impedance (Z_{imag}), Y-axis versus the real impedance (Z_{real}), X-axis

The obtained data of $|Z|$ were based on an average of two readings with a standard deviation of ± 1.2 and an error bar of 2.4%. The value of $R_{p_{air}}$ of OPV cell in air was considered as a standard value with respect to the rest of the obtained data in this investigation. Also, the value of $R_{p_{air}}$ of a pure Graphite [29] was calculated in air for a comparison with the other values of Graphite samples in the deionized water and the polluted water. The calculation of $R_{p_{air}}$ for the pure Graphite was based on the resistivity value of Graphite ($\rho=1.0 \times 10^{-8} \text{ Ohm.m}$) [29] by using equ.(1) with $A=2.83 \text{ cm}^2$ and $U=121.1 \text{ mm}$. In other words, the values of $R_{p_{air}}$, and $(R_{p_s}/R_{p_{air}})$ Graphite electrode in air represent

the ideal bulk value of polarization resistance of OPV cell in operations.

Results and Discussion

It is obvious from Table 1 that the calculated value of $R_{p_{air}}$ of the pure Graphite ($4.3 \times 10^{-9} \text{ Ohm}$) is thirteen order and twelve order less than that of the Graphite (30420.5 Ohm) of the OPV cell in the deionized water and the Graphite (3892.7 Ohm) in the OPV cell in the polluted water, respectively. This implies that the Graphite would have an ideal situation as far as the PCE of the OPV in air because of the high conductivity of the Graphite in air. In contrast, the Graphite of the OPV cell in the deionized water has shown better protection performance against corrosion than the Graphite of the OPV cell in the polluted water. The Graphite of the OPV cell in the polluted water was found to have a less protection performance against corrosion than the Graphite of the OPV cell in the deionized water. This was probably occurred due to the high conductivity of the polluted water in comparison to the one in the deionized water. Furthermore, the contrast between the values of R_{p_s} of the Graphite in the polluted water (3892.7 Ohm) & the one in the deionized water (30420.5 Ohm), in comparison to the calculated values of $R_{p_{air}}$ of the pure Graphite ($4.3 \times 10^{-9} \text{ Ohm}$) would reflect a considerable consequence on PCE of the OPV cells in those media.

Table 1: Calculated parameters of the OPV cell, free of any metallic electrode, in air and the measured values in deionized water and the polluted water

Materials/Solution	ac impedance $ Z =R_p$ Polarization resistance (Ohm)	Ratio of ($R_{p_s}/R_{p_{air}}$)
Cin Air (29)	4.3×10^{-9}	1
C in Deionized Water	30420.5	7.1×10^{12}
C in Polluted Water	3892.7	0.31×10^{12}

Also, the pure Graphite was found to have a better conductive behavior ($R_{p_{air}}=4.3 \times 10^{-9} \text{ Ohm}$) than the pure silver (Ag) ($R_{p_{air}}=6.8 \times 10^{-9} \text{ Ohm}$) and the silver oxide (Ag_2O) ($R_{p_{air}}=3.42 \times 10^{-6} \text{ Ohm}$) in air [16,17,29]. Furthermore, the Graphite of the OPV cell in the deionized water ($R_{p_s}=30420.5 \text{ Ohm}$) and in the polluted water ($R_{p_s}=3892.7 \text{ Ohm}$) was observed to have better corrosion resistance than the silver oxide (Ag_2O) of the OPV cell in the deionized water ($R_{p_s}=5.15 \times 10^2 \text{ Ohm}$) and in the polluted water ($R_{p_s}=1.65 \times 10^3 \text{ Ohm}$) [16,17].

Figures 3 and 4 illustrate the $\lim(R_{p_s}/R_{p_{air}})$ versus time of exposure of the OPV cell in the deionized water and the polluted water, respectively. Figures 3 and 4 were plotted at time of exposure=0, ($R_{p_s}/R_{p_{air}})=7.1 \times 10^{12}$, and 0.31×10^{12} for Graphite of the OPV cell in the deionized water, and the polluted water, respectively. Also, at time of exposure=1000 hrs, Figures 3 and 4 were plotted; ($R_{p_s}/R_{p_{air}})=1$ and 1 for the Graphite of OPV cell in the deionized water, and the polluted water, respectively. The operational period of the OPV cell was assumed to last for 1000 hrs.

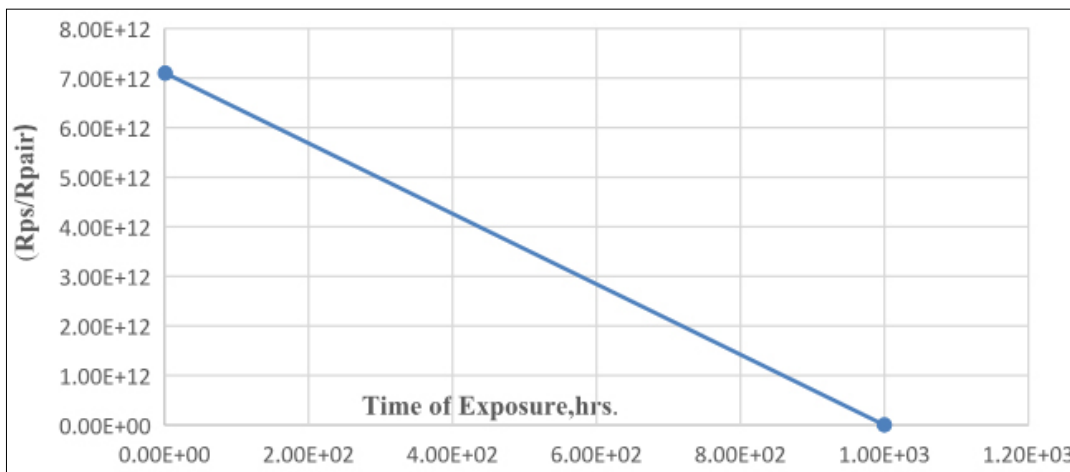


Figure 3: $\lim (R_{p_s} / R_{p_{air}})$ versus Time of exposure of the ZnO/PEDOT: PSS/Graphite cell in the deionized water

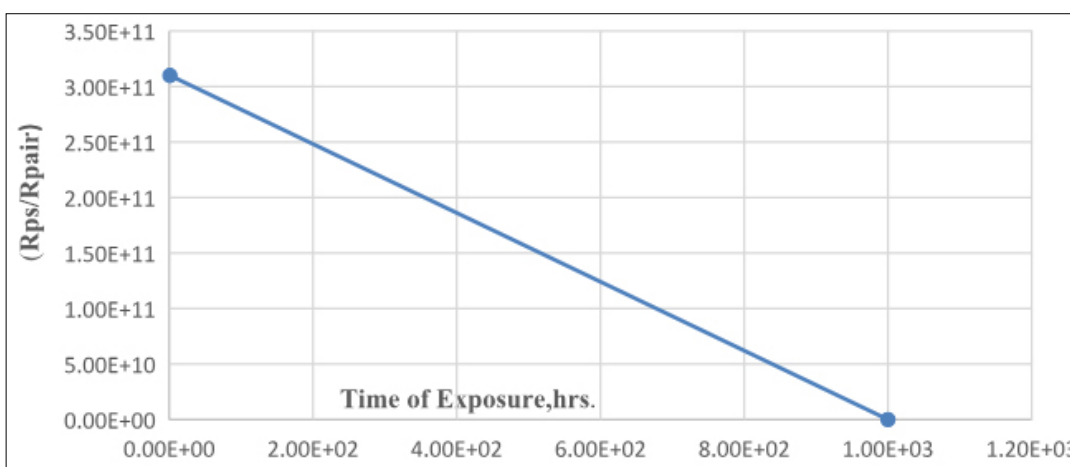


Figure 4: $\lim (R_{p_{air}} / R_{p_s})$ versus Time of exposure of the ZnO/PEDOT: PSS/Graphite cell in the polluted water

Figures 3 and 4 show two regions. One region is above the line in the Figures, in which the OPV cell is not susceptible to degradation with respect to the implemented criterion of Eq. (2). The other region is below the line in the Figures in which the OPV cell is required a mitigation of the problem of the degradation, with respect to the implemented criterion of Eq. (2). In this case, a maintenance (cleaning) of the material is essential for better PCE of the OPV cell. The ideal situation of the Graphite electrode of the OPV cell when the electrode was only in contact with the air. In contrast, the worse scenario case of the Graphite of the OPV cell when the electrode in the polluted water ($R_{p_s} / R_{p_{air}} = 0.31 \times 10^{12}$) (Figure 4) in a comparison to the Graphite of the OPV cell in the deionized water ($(R_{p_s} / R_{p_{air}} = 7.1 \times 10^{12})$) (Figure 3).

In general, the ratio of ($R_{p_s} / R_{p_{air}}$) as a function of 1000 hrs of operational time of the Graphite of the ZnO/PEDOT: PSS/Graphite cell was found higher than the Ag_2O electrode of the ZnO/PEDOT: PSS/Silver cell in both the deionized water and the polluted water [16,17]. Consequently, the ZnO/PEDOT: PSS/Graphite cell, free of metallic electrode, would perform better than the ZnO/PEDOT: PSS/Silver cell against degradation/oxidation of the OPV in the operational surroundings.

The PCE of the OPV cell can be assessed by monitoring the

behavior of the $\lim (R_{p_s} / R_{p_{air}})$ on a frequent basis during a predetermined operational time of the OPV cell. Then, the obtained value of $\lim (R_{p_s} / R_{p_{air}})$ can be compared with a standard plot of $\lim (R_{p_s} / R_{p_{air}})$ like those in Figures 3 and 4 with a specific time of operation. So, Figures 3 and 4 can be standard plots of mitigating any problems of the OPV cell for different kinds of electrode materials. Therefore, experimental data on the ratio of ($R_{p_s} / R_{p_{air}}$) as a function of 360, 648, and 960 hrs of exposure time of the Graphite (C) of the ZnO/PEDOT: PSS/Graphite cell were obtained in deionized water and polluted water. The data are given in Table 2.

Table 2: Experimental data on the ratio of ($R_{p_s} / R_{p_{air}}$) as a function of exposure time of the Graphite of the ZnO/PEDOT: PSS/Graphite cell in deionized & the polluted water

Time of the exposure (hrs.)	Ratio of ($R_{p_s} / R_{p_{air}}$) C in Deionized Water	Ratio of ($R_{p_s} / R_{p_{air}}$) C in Polluted Water
360	4.2×10^{12}	1.5×10^{13}
648	4.6×10^{12}	1.34×10^{13}
960	4.4×10^{12}	1.5×10^{13}

From the experimental data of Table 2, the points of ($R_{p_s} / R_{p_{air}}$) versus 360, 648, and 960 hrs of exposure time of the Graphite (C), of the ZnO/PEDOT: PSS/Graphite cell, were found to be on or

above the lines in the standard plots of Figures 3 & 4 in deionized water and polluted water, respectively. This indicates that the ZnO/PEDOT: PSS/Graphite cell, free of metallic electrode, has good degradation resistance during the 1000 hrs exposure to deionized water and polluted water.

Conclusions

An implemented criterion of the degradation/oxidation of the ZnO/PEDOT: PSS/Graphite cell was used to identify the degradation of the OPV cell in the deionized water and the polluted water. The ratio of ($R_{p_s}/R_{p_{air}}$) as a function of operational time was observed to vary for the Graphite electrode of the OPV cell from one medium to another. The ratio of ($R_{p_s}/R_{p_{air}}$) of the OPV cell was found the highest (7.1×10^{12}) for the Graphite in the deionized water and the lower for the Graphite in polluted water (0.31×10^{12}). Also, the ZnO/PEDOT: PSS/Graphite cell, free of metallic electrode, was found to perform better than the ZnO/PEDOT: PSS/Silver cell against degradation/oxidation of the OPV in similar operational surroundings. In the meantime, the ZnO/PEDOT: PSS/Graphite cell was found to have good degradation resistance during the 1000 hrs exposure to deionized water and polluted water with respect to the standard plots of $\lim(R_{p_s}/R_{p_{air}})$ versus time of exposure, Figures 3 and 4.

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