

ANALYTICAL METHODOLOGY WITH EXPERIMENTAL VERIFICATION TO PREDICT OUTDOOR POWER CONVERSION EFFICIENCY

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ABSTRACT

The inverted organic solar cell (IOSC) devices with different concentration ratios of nanoparticles In_2S_3 have been studied under local solar spectrums (sunny and cloudy conditions) in Malaysia as compared to that of AM1.5G. The J-V curves of encapsulated IOSC devices were measured on-site using Ivium Potentialstat and local spectral irradiances were acquired concurrently using AVANTES spectrometer. Despite average photon energy (APE) of both local sunny (1.604 ± 0.010 eV) and AM1.5G conditions (1.603 eV) having almost the same values, the variation in their peak regions is significant in which local sunny condition shows spectral broadening effect with 450 - 640 nm as compared to AM1.5G condition with 447 - 588 nm. The spectral broadening under sunny condition and the bluish-enhancement under cloudy condition have matched well with the light absorption band of the IOSC device. Therefore, power conversion efficiency (PCE) of IOSC devices under local sunny condition relative to AM1.5G condition shows the substantial improvement with gain of 26.4 - 50.0%, while the devices operate at even higher PCE under cloudy condition with gain of 31.8 - 68.8%.

Keywords: inverted organic solar cell; local solar irradiance; average photon energy; power conversion efficiency; Standard AM 1.5 G spectrum; organic photovoltaic

1. INTRODUCTION

To ensure the standardization of the testing conditions for the commercial PV across the globe, standard AM 1.5G spectrum has been introduced by American Society for Testing and Materials (ASTM) to benchmark the performance of different PV technologies and products [1]. However, it is notable that local spectral irradiances usually vary according to geographical location, humidity, latitude, pollution level, solar zenith angle, cosine effect, etc. [2]. For better understanding on the device performance in outdoor condition, several research groups conducted on-site measurement to study the effects of the local solar spectrums towards the performances of different types PV modules including amorphous-silicon (a-Si), hydrogenated amorphous silicon/crystalline silicon (a-Si:H/c-Si), amorphous silicon/thin-film crystalline silicon (a-Si/ $\mu\text{c-Si}$), and polycrystalline-silicon (poly-Si) [3-5]. To date, the analyses on the impact of local spectrums were conducted based on two well-known parameters for quantifying the PV performance: (i) average photon energy (APE) and (ii) spectral factor (SF). APE is commonly used to characterize the average energetic distribution of spectral irradiance [6]. Higher APE value represents the presence of bluish-enhancement on the spectral irradiance under local cloudy condition in which transmission rate of photons with shorter wavelength is higher than that of longer wavelength after the sunlight passes through the cloud layers [7]. SF is practically used to investigate the deviation of PV performance when it is

subject to the illumination of local spectrum with respect to AM 1.5G. Investigations were conducted for various Si based PV modules revealed that the sensitivity of PV performance towards the spectral effect is noticeable. The results of these investigations are consistent with the calculation of SF by Nofuentes et al. in which the a-Si PV module with narrow light absorption band (from 300 to 700 nm) in visible region has the highest sensitivity towards the spectral effect [8]. All the aforementioned studies only relate APE (or SF) to output short-circuit current of PV module, which is not sufficiently accurate to quantify the performance of PV technologies because both the open-circuit voltage and fill factor are also crucial factors to influence the performance. To analyze the performance of PV module under local spectrum, power conversion efficiency (PCE) can reflect the real performance of PV module as compared to short-circuit current employed by previous studies. For this purpose, Chong et al. have proposed new analytical methodology to predict PCE of organic solar cell (OSC) under local spectral irradiance based on external quantum efficiency (EQE), J-V curves and local solar spectrum [9]. For this article, the verification of new analytical methodology will be presented.

2. SIMULATION METHODOLOGY

To evaluate performance of solar cell devices, the analytical methodology proposed by Chong et al. has been adopted to simulate the PCE under different spectral irradiance, and the simulated result is then compared with the measured PCE in the site. This analytical methodology required a series of computational process based upon the J-V curves at various intensities, the measured local solar spectrum, and EQE of the device.

The first step of the methodology is to obtain J-V curves of the IOSC devices under different intensities of local solar spectrums, which can be carried out either in the laboratory or in outdoor environment. From the J-V curves, we can obtain the photovoltaic relationships, including the open-circuit voltage (V_{oc}) versus short-circuit current density (J_{sc}) and fill factor (FF) versus short-circuit current density (J_{sc}). The formula to relate between V_{oc} and J_{sc} can be derived from the original Shockley equation as the following:

$$J = \frac{R_p}{R_s + R_p} \left\{ J_s \left[\exp\left(\frac{q(V - JR_s)}{nkT}\right) - 1 \right] + \frac{V}{R_p} \right\} - J_{ph}(V) \quad (1)$$

where the R_p is the device parallel resistance, R_s is the device series resistance, q is the electron charge, n is the device ideality factor, k is the Boltzmann constant, T is temperature in Kelvin and J_{ph} is the voltage-dependent device photo-generated current density.

Based on the Shockley equation, V_{oc} can be derived as the following formula provided that $J = 0$, $V = V_{oc}$ and $J_{sc} = J_{ph}(0) \gg J_s$:

$$V_{oc} = \frac{nkT}{q} \ln(J_{sc}) + \left[V_{oc1} - \frac{nkT}{q} \ln(J_{sc1}) \right] \quad (2)$$

where a set of values (J_{sc1} , V_{oc1}) is obtained from the plotted V_{oc} versus J_{sc} graph.

The values of FF and PCE can be determined based on the Eq. (3) and Eq. (4), respectively.

$$FF = \frac{J_{max} V_{max}}{J_{sc} V_{oc}} \quad (3)$$

$$PCE = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}/A} \quad (4)$$

where J_{max} and V_{max} are denoted as maximum current density and maximum voltage respectively at the maximum power output point of the J-V curve. I_{in} is the incident light intensity with unit W/m^2 in which P_{in} is input power of incident light in unit W and A is the corresponding area (m^2). The acquired spectral irradiances from the AVANTES spectrometer can be used to compute incident illumination intensity through Eq. (5).

$$I_{in} = P_{in}/A = \int_{\lambda_1}^{\lambda_2} S_L(\lambda) d\lambda \quad (5)$$

where the $S_L(\lambda)$ is the acquired local spectral irradiance from the spectrometer, λ_1 and λ_2 are 300 nm (lower limit) and 1700 nm (upper limit) respectively. J_{sc} can be computed via the integration of the local spectral irradiances and the spectral responsivity, $R(\lambda)$ as follow:

$$J_{sc} = \int_{\lambda_1}^{\lambda_2} S_L(\lambda) \cdot R(\lambda) d\lambda \quad (6)$$

Spectral responsivity, $R(\lambda)$ is defined as following:

$$R(\lambda) = \frac{q\lambda}{hc} \cdot \eta_{EQE}(\lambda) \quad (7)$$

where h is the Planck constant, c is the speed of light, η_{EQE} is the EQE of solar cell device.

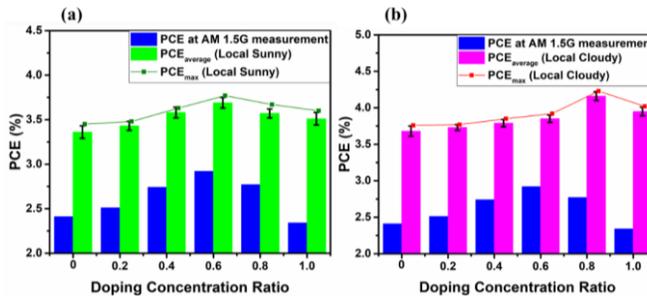


Fig. 1: Measured power conversion efficiency (PCE) for IOSC devices with different doping concentration ratios of In_2S_3 under outdoor and AM 1.5G illuminations: (a) On-site measurement results under local sunny condition, and (b) On-site measurement results under local cloudy condition. For a comparison, the blue block of bar chart indicate measured PCE of the IOSC devices under AM 1.5G illumination.

To synthesize electron transporting layer (ETL) on FTO substrates (Sigma Aldrich, $R = 7 \Omega/\text{sq}$), specifically zinc oxide nanorods (ZNRs) was carried out through a sol-gel assisted hydrothermal method. Then, 20 mg of P3HT (Rieke Metals 4002-E) and 20 mg PCBM (Sigma Aldrich $\geq 99.0\%$) were dissolved in 500 μl chlorobenzene respectively. Both solutions were stirred separately at 600 rpm and 60°C for 2 hours. After that, both solutions were blended together (40 mg/ml), and a 20 μl of 1,8-octanedithiol (ODT; Sigma Aldrich $\geq 97.0\%$) was dropped into the blended solution, and the solution was continued to stir at 800 rpm and 60°C for another 20 hours. 0.25 mM of In_2S_3 aqueous solution was prepared by dissolving anhydrous indium (III) sulfate (Sigma Aldrich, $\geq 98.0\%$) and sodium sulfide (Sigma Aldrich) in the distilled (DI) water, and stirred at 500 rpm at the room temperature for 30 minutes. The In_2S_3 solution was added to the P3HT:PCBM blend at different concentration ratios, i.e. 0.2, 0.4, 0.6, 0.8, 1.0. For the convenience, the abbreviation of 0.2-, 0.4-, 0.6-, 0.8-, 1.0-IOSCs will be used to denote the volume ratios between In_2S_3 and P3HT:PCBM blend at 0.2, 0.4, 0.6, 0.8, 1.0 respectively. 0-IOSC signifies the pristine IOSC. Subsequently, the samples of P3HT:PCBM with different concentration ratios of In_2S_3 at the volume of 55 μl was spin-coated onto the as-growth ZNR substrates at 1150 rpm for 1 minute, and followed by baking at 120°C for 10 minutes. Finally, silver (Ag) as anode contact was deposited at the pressure less than 5×10^{-5} mbar inside the vacuum chamber for 1 minute, and the device stack was subsequently encapsulated by laminating with laboratory glass slide. The structure of the device is

FTO/ZNR/ P3HT:PCBM (with varying In_2S_3 ratios)/Ag, and the device active area is 0.07 cm^2 .

3. RESULTS AND DISCUSSION

The J-V curves of encapsulated inverted organic solar cell (IOSC) devices with different concentration ratios of In_2S_3 have been acquired under local solar spectrums during sunny and cloudy conditions. The corresponding on-site measured results are illustrated in **Error! Reference source not found.1(a)-(b)**. From **Error! Reference source not found.1(a)**, the trend of relationship between the measured PCE and different concentrations ratios of In_2S_3 is similar for both local sunny and AM 1.5G conditions in which 0.6-IOSC device shows the best PCE result. However, as shown in **Error! Reference source not found.1(b)**, the performance trend of IOSC device under local cloudy condition shows slight deviation from that of local sunny condition in which the best performing device in cloudy condition is 0.8-IOSC. Discrepancy in devices performance trend for sunny and cloudy conditions requires detailed investigation on the effect of local spectral irradiance towards the photovoltaic performance of IOSCs.

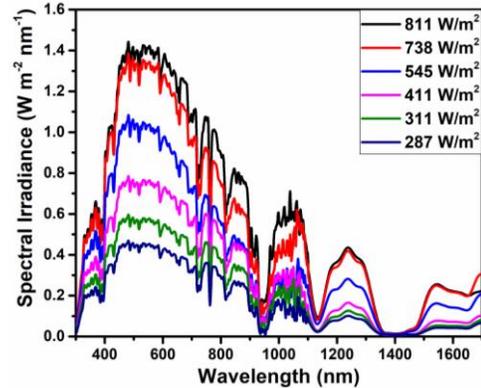


Fig. 2. Local spectral irradiances measured in UKM ($2^\circ 55' 38.106'' \text{ N}$, $101^\circ 46' 57.333'' \text{ E}$) from 4th to 19th December 2017 at the local time of 11:00 AM to 1:00 PM (GMT+8).

A comprehensive analytical methodology was proposed by Chong et al. to predict the PCE of IOSC device in an outdoor condition under different local spectral irradiances [9]. Typically, the different local spectral irradiances (from 277 W/m^2 to 811 W/m^2) were measured using an AVANTES spectrometer. The experiment was carried out in the campus of UKM ($2^\circ 55' 38.106'' \text{ N}$, $101^\circ 46' 57.333'' \text{ E}$) from 4th to 19th December 2017 at the local time from 11:00 AM to 1:00

PM. The spectral irradiances were depicted in Fig. 2. The local spectral irradiance measurement was inevitably used in J_{sc} calculation. From Fig. 2, the intensity of spectra irradiance is linearly increase with the power irradiance measured from solar meter. There is no significant shift in the peak position and emergent of new peaks. The increase of FWHM in dominant peak (550 nm) can be attributed to the local weather condition. For example, the low intense irradiance spectra measured at the irradiance of 287 W/m² (cloudy) showed broader peaks at visible region, which can be related to the high density of cloud coverage in the sky that increases the light scattering. In contrast, an intense irradiance spectra can be detected under a sunny condition owing to the direct sunlight penetrate through the Earth's atmosphere.

Table 1. Summary of calculated device parameters based on the proposed numerical analysis

Power	Pristine			0.6-INPs		
	J_{sc}	V_{oc}	FF	J_{sc}	V_{oc}	FF
292	1.34	0.29	0.50	2.03	0.22	0.41
364	1.67	0.32	0.51	2.25	0.23	0.41
422	1.94	0.33	0.51	2.81	0.26	0.42
502	2.36	0.36	0.52	3.82	0.30	0.43
728	3.26	0.40	0.53	5.07	0.33	0.44
840	3.57	0.41	0.53	5.18	0.34	0.45

Table 2
Percentage difference between measured and calculated PCE of the pristine ZNR and 0.6 vt% INPs based IOSC

Power	PCE(%)			
	Pristine		IZNR	
	Measured	Calculated	Measured	Calculated
292	0.80	0.67	0.28	0.61
364	0.91	0.73	0.31	0.65
422	0.85	0.78	0.38	0.75
502	1.03	0.87	0.45	0.91
728	1.01	0.94	0.94	1.00
840	1.10	0.92	1.34	0.97

Table 3
Device parameter for x vt% INPs-IOSC under indoor and outdoor measurements with two climates change of sunny and cloudy conditions.

x vt% INPs-IOSC	Climate Change													
	AM 1.5G				Sunny				Cloudy					
	J_{sc}	V_{oc}	FF	PCE	J_{sc}	V_{oc}	FF	PCE	Gain	J_{sc}	V_{oc}	FF	PCE	Gain
Pristine	7.43	0.62	0.52	2.4	7.31	0.61	0.50	3.16	31	4.88	0.55	0.45	3.41	42
0.2	8.39	0.57	0.52	2.5	8.79	0.56	0.47	3.25	30	4.33	0.49	0.52	3.65	46
0.4	8.24	0.61	0.54	2.7	9.27	0.54	0.47	3.34	22	4.30	0.48	0.54	3.71	35
0.6	8.31	0.63	0.56	2.9	9.12	0.57	0.50	3.62	24	4.81	0.53	0.48	3.84	32
0.8	8.72	0.61	0.52	2.8	10.20	0.55	0.48	3.50	26	5.26	0.51	0.53	4.19	51
1.0	7.41	0.60	0.53	2.3	9.88	0.48	0.47	3.12	33	6.63	0.50	0.45	3.84	64

**The unit for J_{sc} is mA/cm²; V_{oc} is V; PCE and Gain is %.

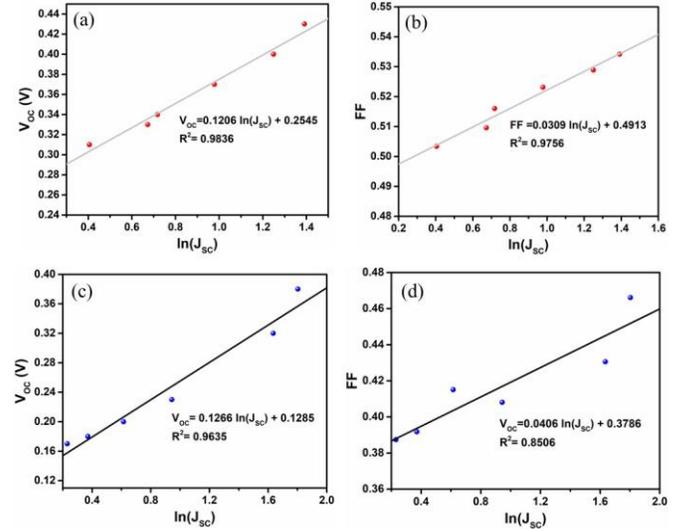


Fig. 3: The plots of V_{oc} - J_{sc} and FF - J_{sc} for (a),(b) pristine ZNR and (c),(d) 0.6 vt% INPs based IOSC, respectively

To obtain the correlation between the device parameter, the I-V characteristic of pristine ZNR and 0.6 vt% INPs based IOSC was measured under an outdoor condition. The linear correlation coefficient between the V_{oc} - J_{sc} and FF- J_{sc} are plotted in Fig. 3. For the numerical analysis, the J_{sc} of the devices was calculated from Eq. (9) and the values of V_{oc} and FF can be obtained from the respective linear empirical expressions as stated in Fig. 3. The calculated devices parameters were summarized in Table 1. The measured and calculated PCEs of both devices were also determined and tabulated in Table 2.

From **Table 2**, a similar data trend was noticed in PCEs in both measured and calculated values. It is important to emphasize that the fabrication of this batch of devices are different as before. For sunny condition with I_{in} in the range of 850 - 1100 W/m², Δ PCE is reasonable low in the range of 4.88 - 10.29 %. For cloudy condition with I_{in} in the range of 340 - 500 W/m², Δ PCE is obviously higher with the range of 22.81 - 32.15 %. The Δ PCE is consistent with the ΔJ_{sc} as all the parameters that involved in PCE calculation is dependent on the simulated J_{sc} . The obvious differences of Δ PCE and ΔJ_{sc} between sunny and cloudy conditions can be explained by the APE of cloudy condition of 1.704 eV that is higher than that of APE of sunny condition at 1.614 eV. For cloudy condition, a higher APE can increase the generation rate of energetic exciton and hence to increase the charge collection rate in the IOSC device so that the measured J_{sc} is higher than the expected value. Conclusively, the prediction of measured PCE during sunny condition is reasonably accurate by the analytical methodology but the prediction becomes less accurate

during cloudy condition. To study the dependency between the I_{in} and PCE of the x wt% INPs-IOSC, the gain (percentage difference) of the device under a sunny and cloudy condition with respect to AM 1.5G was herein calculated. It is found that the gain of IOSC measured under cloudy condition showed a higher different which is in the range of 32% to 64% as compared to IOSC measured under the sunny condition that fell in the range of 22% to 33%. This claim can be due to the different of I_{in} from the sunlight under the climate change. It is signified that the percentage difference in corresponded I_{in} is linearly dependent on the gain of the device. For example, the percentage difference of I_{in} under a sunny condition with respect to AM1.5G is only calculated to be 27.8% as compared to the cloudy condition of 66.7%. Thus, the gain of the device under the cloudy condition is higher than the sunny condition as shown in **Table 3**.

4. Conclusion

In this work, the J-V curves of encapsulated IOSCs with different volume ratios of In_2S_3 have been measured outdoor during sunny and cloudy conditions. From the spectral analysis, the APE values of local cloudy condition (1.704 ± 0.023 eV) is higher than that of local sunny condition (1.614 ± 0.018 eV) by 5.58% in which the cloudy condition has attributed to the bluish-enhancement of the local solar spectrum. Despite average photon energy (APE) of both local sunny (1.614 eV) and AM1.5G conditions (1.355 eV) having almost the same values, the variation in their peak regions (more than 90 % of normalized intensity) is significant in which local sunny condition shows spectral broadening effect with 450 - 640 nm as compared to AM1.5G condition with 447 - 588 nm. The spectral broadening under sunny condition and the bluish-enhancement under cloudy condition have matched well with the light absorption band of P3HT:PCBM in the IOSC device, which contributes to additional photocurrent generation and hence to enhance photovoltaic performance. More than 50 % of the normalized responsivity of the IOSC device are fallen in the narrow spectral range of 384 - 634 nm, which are closely matched with peak regions of both local sunny spectrum (450 - 640 nm) and local cloudy spectrum (448 - 608 nm). Therefore, power conversion efficiencies (PCE) of IOSC devices under local sunny condition relative to AM1.5G condition shows the substantial improvement with gain of 22 - 33 %, while the devices operate at even higher PCE under cloudy condition with gain of 32 - 64 %. Last but not the least,

we have successfully verified the analytical methodology to predict device performance by comparing between the simulated and measured PCE values for different irradiance intensities whereby the prediction of PCE is better under sunny condition (deviation of 4.88 – 10.29 %) as compared to cloudy condition (deviation of 22.81 – 32.15 %).

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