Received 19 September 2019; revised 23 December 2019; accepted 10 January 2020. Date of publication 20 January 2020; date of current version 27 April 2020. The review of this article was arranged by Editor A. Escobosa.

Digital Object Identifier 10.1109/JEDS.2020.2968001

Inverted Polymer Solar Cells Using Inkjet Printed ZnO as Electron Transport Layer: Characterization and Degradation Study

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This work was supported in part by CONACyT under Project 237213 and SEP-CINVESTAV Mexico, under Project 32, in part by the Spanish Ministerio de Ciencia, Innovación y Universidades through MICINN/FEDER under Grant RTI2018-094040-B-100, in part by the Agency for Management of University and Research through AGAUR under Grant 2017-SGR-1527, in part by ICREA through the ICREA Academia Award, in part by the "Laboratorio Nacional SEDEAM CONACYT" under Project 299061, and in part by FORDECYT under Project 297497. The work of Angel Sacramento was supported by CONACyT for supporting through Ph.D. Scholarships under Grant 587630. The work of Magaly Ramírez-Como was supported by CONACyT for supporting through Ph.D. Scholarships under Grant 587630. The work of Victor S. Balderrama was supported by CONACyT through "Cátedras CONACyT para Jóvenes Investigadores" under Project 2. The work of Salvador I. Garduño was supported by CONACyT through "Cátedras CONACyT para Jóvenes Investigadores" under Project 1268.

ABSTRACT In this work, stability and degradation of inverted organic solar cells (iOSCs) partially manufactured under air environment are analyzed. The degradation of iOSCs fabricated with inkjet printed ZnO and with spin coated PFN as electron transport layer (ETL) is compared. The PTB7 and PC₇₀BM materials are used as donor and acceptor in the active layer, respectively, for all photovoltaic devices. During all the degradation study of the iOSCs, performance parameters such as open circuit voltage (V_{OC}), short circuit current density (J_{SC}), fill factor (FF) and Power conversion efficiency (PCE), are extracted from the current density – voltage measurements (*J*–*V*) under dark and light conditions. The PCE of the unencapsulated iOSCs with PFN as ETL, left under N₂, decreased to 80% after 58 h, while the same PCE reduction for iOSCs with inkjet printed ZnO as ETL, occurred after 189 h. Under air environment, the PCE of unencapsulated iOSCs fabricated with ZnO as ETL devices decreases to 80% after 160 h.

INDEX TERMS Air environment, degradation study, inkjet printed ZnO, iOSCs, performance parameters, stability.

I. INTRODUCTION

Inverted organic solar cells (iOSCs), using polymer:fullerene as the bulk heterojunction (BHJ) active layer, have attracted much interest due to their high performance parameters. Efficiencies, up to 12.3 %, have been reached in the last year [1]. These devices are quite promising as a low-cost energy source, that can be fabricated on both rigid and flexible large area substrates, since all the fabrication process is done at temperatures below 50 °C [2], [3].

To improve the efficiency of the OSCs, the selection of the anode and cathode buffer layer material is crucial [4]. In a conventional solar cell, Calcium (Ca) is used as electron transport layer (ETL), while Poly-(3,4-ethylene dioxythiophene):poly-(styrenesulfonate), (PEDOT:PSS) is frequently used as hole transport layer (HTL). However, due to the low stability and rapid degradation of Ca, these cells degrade quite rapidly when are exposed to air environment.

The inverted solar cells improve significantly this situation, although the selection of more efficient electron and hole transport layers is still a very important issue. Materials such as Titanium oxide (TiO_x) [5], poly[9,9bis (3-(N,N-dimethylamino) propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN) [6] and Zinc oxide (ZnO) [7] have been used as ETL, while vanadium oxide (V₂O₅) [8], nickel oxide (NiO) [9] and molybdenum oxide (MoO₃) [10] have been used as HTL.

In this study, either inkjet printed ZnO or spin coated PFN layers were used as ETL in the fabrication of the iOSCs. The degradation of the electrical parameters of the iOSCs exposed under different environments (N2 and air) were analyzed. The active layer of the cells was prepared using a mixture of the polymer thieno[3,4b] thiophene-altbenzodithiophene (PTB7) with the fullerene [6,6]-phenyl-C71-butyric acid methyl (PC70BM), respectively. Three groups of iOSCs were analyzed: First group of devices with the structure ITO/PFN/PTB7:PC70BM/V2O5/Ag are the reference cells in this study and tagged as A group, which they were exposed and degraded under N2 environment. Second and third group of devices tagged as B and C groups have the same structure being ITO/ZnO/PTB7:PC70BM/V2O5/Ag. The difference between of them is that B group and C group were exposed and degraded under air and N₂ environments, respectively.

The time analyzes of degradation for A, B and C groups were done for 856 h, 844 h and 812 h, respectively. All iOSC groups were unencapsulated.

II. EXPERIMENTAL DETAILS A. MATERIALS

The substrates used were 220 nm thick Indium tin oxide (ITO)-coated glass, with a nominal sheet resistance of 10 Ω /square. They were purchased from PsiOTec Ltd. PTB7 and PFN were obtained from One-material and PC₇₀BM from Solenne BV. For silver (Ag) deposition, 99.99% purity Ag wire from Testbourne Ltd. was used. ZnO ink and V₂O₅ were purchased from Sigma-Aldrich.

B. DEVICE FABRICATION

All groups of iOSCs were partially manufactured under air environment as indicated in [11]. The preparation of PFN material was done dissolving a small amount of acetic acid $(1.84\mu l m L^{-1})$ as an additive in methanol. Then, in order to obtain 10 nm thick layers, the PFN solution was deposited by spin-coating technique on top of the pre-cleaned glass/ITO substrate at 4200 rpm for 60 s. The active solution was prepared by dissolving the polymer PTB7 and fullerene PC₇₀BM with a weight ratio of 1:1.5 in chlorobenzene (CB) and 1,8-diiodooctane (DIO) (97:3 by volume) to obtain a solution concentration of 25 mg \cdot mL⁻¹. Afterwards, the active solution was stirred and heated at 40 °C during 18 h. Subsequently, the blended solution was left aging for 48 h. Then, the active solution was deposited on the PFN layer by using spin coating technique at 750 rpm for 30 s. The obtained thickness of the active layer was around 100 nm. The PFN and the active layer solutions were formulated and

deposited inside a glovebox under N₂ environment. Before depositing the V₂O₅ as HTL and Ag as a metallic contact by thermal evaporation, all groups of devices were exposed under air environment for 10 min. Finally, the anode layer, consisting of 5 nm of V₂O₅, and 100 nm of Ag were deposited on top of the active layer at 1.8×10^{-5} Torr with a rate of 0.1 ± 0.08 nm/s and 0.2 ± 0.1 nm/s, respectively. The thicknesses of each layer were measured by Spectroscopic ellipsometry technique.

Inkjet printing conditions of the ZnO: The ZnO ink, used throughout patterning of the ETL, consisted on crystalline zinc oxide nanoparticles (NPs), 12±4 nm size. These ZnO NPs are dispersed at 2.5 wt.% in isopropanol and propylene glycol, presenting a viscosity of 11±3 mPa·s. The ZnO NPs ink was ultrasonicated during 10 min and filtered through 0.2 µm PTFE filter. Before printing the ETL, patterned ITOcoated glass substrates were UV-ozone treatment for 60 min to produce a hydrophilic ITO surface for the appropriate wetting of the ink. Using the DIMATIX DMP-2800 piezoelectric inkjet printer, a ZnO square pattern of 11×11 mm² was printed on the pre-treated substrate. A single piezodispenser of 1 pL drop volume was heated at the same temperature of the printer platen (\sim 30 °C), throughout the drops jetting process to optimize the uniformity of the ZnO printed layer. By fixing the drop spacing at 15 µm, the maximum jetting frequency at 4 kHz and controlling the speed drop of $\sim 15 \text{ ms}^{-1}$ to obtain a resolution of 1695 dpi, a continuous and appropriate ZnO pattern as ETL was successfully inkjet printed. Subsequently, the samples were sintered into a conventional oven at 200°C \pm 1°C, for 10 min under N_2 environment.

C. MEASUREMENTS

The current density-voltage (*J-V*) measurements of all iOSCs groups under illumination and dark conditions were done at room temperature $(21 \pm 2 \,^{\circ}\text{C})$ and a relative humidity (*RH*) of $50 \pm 5\%$. These measurements were performed using a Keithley 2420 source measurement unit, in combination with a solar simulator (Oriel Corporation Sol1A class type ABB, Xenon arc lamp). Appropriate filters were used to reproduce the AM 1.5G spectrum. A light intensity of 100 mW/cm² (1 sun) was applied to test all the iOSCs under light. The calibration of the light intensity of the lamp was done with a monocrystalline silicon photodiode, certified by Solarex Corporation.

The degradation testing conditions were done in accordance with ISOS-D1 protocols [12].

III. RESULTS AND DISCUSSION

The power conversion efficiency (PCE) over time of the three groups of iOSCs is shown in Fig. 1 (a). The initial (0 h) PCE of iOSCs for A, B and C groups was 7.34%, 4.87% and 5.64%, respectively. As can be seen in Fig. 1 (a), the cells present the rapid decay in PCE at the first few hours, known as "burn-in loss" [13], [14] and reported as one of the degradation loss mechanism in iOSCs. This degradation



FIGURE 1. (a) Power conversion efficiency (PCE) over time for A, B and C groups. (b) Fit of the normalized PCE over time using Eq. (1) for A, B and C groups.

mechanism is related to the photochemical reaction between the different layers of the photovoltaic device [14]. Fig. 1 (b) shows the experimental (filled symbols) and fitted (solid line) degradation over time of the normalized PCE for the three groups (A, B and C). A fast initial decay, followed by a slower decay, is modeled by the superposition of two exponential functions with different time constants as was previously done in [15], [16].

$$\frac{PCE(t)}{PCE(0)} = A1e^{\frac{-t}{T_1}} + A2e^{\frac{-t}{T_2}},\tag{1}$$

where PCE (0) is the relative initial PCE (t=0 h). (T1, T2) and (A1, A2) are the time constant of degradation and the power degradation factors, respectively.

It well known and reported for different research groups that the degradation mechanisms represented by the first and second time constants T1 and T2 are due to water (H₂O) and oxygen (O₂) diffusion toward the active layer of the

TABLE 1. Time constants and power degradation factors.

_	Group	<i>A</i> 1	T1 (h)	A2	T2 (h)
-	А	0.50	130	0.50	680
	В	0.65	1000	0.35	450
_	С	0.50	1040	0.50	1000

photovoltaic device, respectively [15], [16]. If the values T1 and T2 are increasing, this mean that the solar cells are degraded slowly, and their performance parameters are decreasing slow too. In the case for C group, they were degraded under nitrogen atmosphere, so that, the degradation process is slower than that for the B group which they were degraded under air atmosphere. Therefore, the degradation that occur for C group can be attributed for the main degradation mechanism by chemical reaction between the polymeric and metallic materials and not by the effect of low content of H₂O and O₂ in the N₂ used inside of the glovebox. Table 1 shows a summary of the time constants of degradation and the degradation power factors for the three groups of iOSCs. The highest T1 and T2 are observed for C group of 1040 h and 1000 h, respectively. While that T1 and T2 for B group are 1000 h and 450 h, respectively. Finally, A group the values were 130 h and 680 h, respectively.

Fig. 2(a) shows the J-V characteristics for illuminated iOSCs of A group at an initial condition (0 h) and after 43, 280, 546 and 856 h under N₂ atmosphere. The total time of the degradation study of this group was 856 h. As can be seen from the same figure, the S-shape is presented in the J-V characteristics under illumination condition. After many cycles of J-V measurements this S-shape is eliminated, although it reappears with time, see Fig. 2 (a). This phenomenon is commonly associated to different aspects such as the presence of injection and extraction barriers at the contacts, creation of traps, and/or formation of space charge limited current (SCLC), as was reported in [16]-[20]. The J-V characteristics that present the S-shape cannot be reproduced with the standard one-diode model. For this reason, it is necessary to use the equivalent circuit model of three diodes to fit the experimental curves under illumination conditions [21], [22]. In Fig. 1 inset, it is shown the equivalent circuit model for the analyzed iOSCs.

In this circuit model, diode D1 represents the PTB7:PC₇₀BM bulk heterojunction of the active layer, R_S and R_{SH} are series and shunt resistances associated with diode D1. The diodes D2 and D3 represent the interfaces between buffer layers (ETL and HTL) and metallic contacts.

Using the equivalent circuit model, the current flowing through the series-connected subcircuits is given by either one of the following two equations:

$$I = I_{01} \left[e^{\frac{(V_1)}{n_1 * V_{th}}} - 1 \right] + \frac{(V_1)}{R_{SH}} - I_L$$
(2)

$$I = -I_{02} \left[e^{\frac{-V_2}{n_{2*}V_{th}}} - 1 \right] + I_{03} \left[e^{\frac{V_2}{n_{3*}V_{th}}} - 1 \right]$$
(3)



FIGURE 2. (a) Experimental (open symbols) and modeled (solid lines) of current density-voltage (*J-V*) characteristics under illumination of A group. (b) Normalized performance parameters for A group regarding to their initial values as a function of time. *J_{sc}* is the short current density, *V_{oc}* is open circuit voltage and *FF* is fill factor. All measurements were done under AM 1.5G spectrum condition (100mW/cm²) in nitrogen environment. (c) Dark *J-V* curves for A group of devices under nitrogen environment and its degradation process over time for 856 h. (d) Variation of series (R_{S0}) and shunt resistance (R_{SH0}) per unit area over time.

where I_{01} , I_{02} and I_{03} are the reverse saturation current of the diodes; $V_{th} = k_B T/q$ is the thermal voltage; n_1 , n_2 and n_3 are the ideality factor of the diodes; I_L is the photogenerated current; k_B is the Boltzmann constant; T is the temperature and q is electron charge.

 I_L was determined by the following expression [23]:

$$I_L = I_{sc} \left(1 + \frac{R_S}{R_{SH}} \right) + \left(I_{sc} - \frac{V_{oc}}{R_{SH}} \right) e^{\left(\frac{-V_{oc}}{n \cdot V_{th}} \right)} \cdot \left[e^{\left(\frac{I_{sc} - R_s}{n \cdot V_{th}} \right)} - 1 \right]$$
(4)

All performance parameters variations over time, such as short circuit current density (J_{sc}) , open circuit voltage (V_{oc}) , fill factor (FF), and power conversion efficiency (PCE), were obtained from the experimental *J*-*V* measurements. The performance parameters were normalized with respect to their initial values. For cells fabricated with PFN as ETL (A group), the *FF* parameter shows the most important degradation, falling 77% after 856 h. The J_{sc} and V_{oc} decay to 26% and 33%, respectively, see Fig. 2 (b). The decrease of *FF* can be attributed to the increase over time of the series resistance, probably caused by the reduction of the mobile charge density and mobility associated to the creation of deep and shallow traps by the interaction of oxygen and water with the polymer [15], [24]. Another possible cause is the creation of an insulation layer between the blend active layer and the metallic contact, hindering the collection of charge carriers [15]. Fig. 2 (c) shows dark *J-V* curves at initial time (0 h) and degraded after 71, 280, 570 and 856 h for A group devices under N₂ environment. Fig. 2 (d) shows the behavior of R_{S0} and R_{SH0} for the same group of samples. R_{S0} shows a moderate increase from 2.97 Ω -cm² to 9.27 Ω -cm² after to 856 h under N₂ environment. R_{SH0} decreases from 171 Ω -cm² to 63 Ω -cm² in the same interval of time.

Fig. 3 (a) shows the illuminated J-V (experimental and modeled) curves for B group of iOSCs for an initial condition (0 h), and after 97, 360, 507 and 844 h under air environment.



FIGURE 3. (a) Experimental (open symbols) and modeled (solid lines) of current density-voltage (*J-V*) characteristics under illumination of B group. (b) Normalized performance parameters for B group regarding to their initial values as a function of time. All measurements were done under AM 1.5G spectrum condition (100mW/cm²) in air environment. (c) Dark *J-V* curves for B group of devices under air environment and its degradation process over time for 844 h. (d) Variation of series (R_{S0}) and shunt resistance (R_{SH0}) per unit area over time.

The total time of the degradation study for this group was 844 h. As can be seen in Fig. 3 (a), the S-shape is present in the illuminated J-V curves, but it is less pronounced than it is for A group cells. Fig. 3 (b) shows the normalized behavior of J_{sc} , V_{oc} , and FF over time for B group cells. For the cells manufactured with ZnO as ETL, exposed under air environment (B Group), the main degradation of the PCE was due to the degradation of the J_{sc} , which fell 55 % after 844 h. This behavior can be attributed to oxygen and water molecules, diffusing into the device active layer and producing the reduction of the short circuit current [7], [20]. During this time, parameters Voc, and FF, decreased only 4% and 18%, respectively. The FF parameter decay was smaller than that for PFN cells (A group), even when these cells were kept under ambient conditions without encapsulation. Fig. 3 (c) shows dark J-V curves of initial (0 h) and degraded (during 97, 360, 507 and 844 h) B group devices under air

environment. Fig. 3 (d) shows the behavior of R_{S0} and R_{SH0} for the same group of samples. R_{S0} shows an increase from 13.05 Ω -cm² to 27.9 Ω -cm² after 844 h. R_{SH0} decreases from 162 Ω -cm² to 137 Ω -cm² in the same time interval.

Fig. 4 (a) shows the illuminated *J*-*V* curves (experimental and modeled) for C group (cells fabricated with ZnO as ETL), at initial condition (0 h), and after 142, 310, 501 and 812 h under N₂ environment. The total time of the degradation study for this group was 812 h. The S-shape is also present in the illuminated *J*-*V* characteristics, but it is less pronounced than it was in A and B groups, see Fig. 4 (a). Fig. 4 (b) shows the normalized behavior of J_{sc} , V_{oc} , and *FF* over time for the same group of devices. After a first abrupt decay, *FF* remains stable up to 800 h. J_{sc} practically remains without reduction in the same time interval. V_{oc} is not affected during the first 500 h, after which it reduces abruptly in around 30%. Afterwards, it remains



FIGURE 4. (a) Experimental (open symbols) and modeled (solid lines) of illuminated current density-voltage (*J-V*) characteristics under nitrogen of C group. (b) Normalized performance parameters for C group regarding to their initial values as a function of time. All measurements were done under AM 1.5G spectrum condition (100mW/cm²) in nitrogen environment. (c) Dark *J-V* curves for C group of devices under nitrogen environment and its degradation process over time for 812 h. (d) Variation of series (R_{S0}) and shunt resistance (R_{SH0}) per unit area over time.

without further change up to the tested 812 h, see Fig. 4 (b). This group of cells presented the lowest variation in their performance parameters during the degradation study. The variation of PCE over time was mainly due to the variation of *FF* and V_{oc} . Fig. 4 (c) shows dark *J*-*V* curves at initial (0 h) and degraded (during 142, 310, 525 and 812 h) C group devices under nitrogen environment. Fig. 4 (d) shows the trend of R_{S0} and R_{SH0} for C group. R_{S0} shows an increase from 11.25 Ω -cm² to 19.8 Ω -cm² after 812 h. R_{SH0} decreases from 252 Ω -cm² to 63 Ω -cm² in the same interval of time.

The PCE degradation of cells using ZnO as ETL is less than those using PFN. This behavior is observed even in cells left under ambient conditions and without encapsulation. ZnO has attracted interest due to its excellent electronic properties, high transparency, high air-stability, high electron mobility, among others. Moreover, ZnO can be easily solution processed on ITO substrates at room temperature by several methods (i.e., spin-coating, spray-coating and dip coating). Also, ZnO with a range of different morphologies such as nanoparticles and nanorods have been used as buffer layers [7], [25]. We consider that the improvement in the stability of the iOSCs can be attributed to presence of the ZnO layer, which can block UV light and protect the organic materials from photo degradation under UV light irradiation more efficiently than the PFN layer. Moreover, ZnO seems to act as a barrier preventing the diffusion of oxygen and water to the active layer, reason why cells fabricated with ZnO showed similar stability under air and N₂ environments.

There are some studies regarding the mechanism of degradation of OSCs though different pathways. Norman *et al.* developed a technique for isotopic labeling used in conjunction with imaging mass spectrometry that was later applied for studying the degradation of organic solar cells using

Group	<i>Time</i> (h)	PCE ^a (%)	V _{OC} ^b (mV)	J _{sc} ^c (mA⋅cm⁻²)	J ^{_d} (mA·cm⁻²)	n1 ^e	J ₀₁ ^f (mA·cm ⁻²)	n2 ^e	J ₀₂ ^f (mA⋅cm⁻²)	n ₃ e	J ₀₃ ^f (mA cm ²)
	1	7.34	756	18	18.33	1.880	2.433E-6				
	43	6.11	756	17.78	18.76	1.885	2.778E-6	0.550	0.314	0.580	0.149
А	280	3.2	623	17.22	18.97	1.900	5.000E-5	1.200	0.259	2.500	0.049
	546	1.94	544	15.67	17.31	1.905	1.667E-4	1.650	0.226	2.840	0.012
	856	1.24	508	15.56	17.28	1.960	2.000E-4	1.850	0.114	2.950	0.011
	1	4.87	741	15.33	16.62	1.760	1.322E-7				
	97	4.11	750	14.67	16.71	1.830	1.400E-7	0.740	0.049	1.960	0.482
В	360	3.92	751	13.06	14.89	1.840	1.422E-7	0.770	0.048	1.960	0.482
	507	3.06	734	10.78	12.44	1.843	1.428E-7	0.830	0.043	2.420	0.471
	844	1.71	713	7.369	8.88	1.846	1.433E-7	0.995	0.0376	2.920	0.127
	1	5 64	755	16	16 78	1.810	1 544F-6				
С	142	4 54	747	15.94	17.40	1.815	1.544E 0 1.600E-6	0.750	1.033	1 000	1.027
	310	4 2 5	737	15.94	17.52	1.820	2.156E-6	0.850	0 944	1.050	1.004
	501	3.13	571	15.89	18.73	1.825	7.711E-5	0.450	0.833	1.150	0.882
	812	2.45	500	15.56	20.50	1.830	3.267E-4	0.300	0.722	0.800	0.838

 TABLE 2. Modeling parameters obtained from circuital model.

^a Power conversion efficiency. ^b Open circuit voltage. ^c Short circuit current density. ^d Photogenerated current density. ^c Ideality factor of diode 1, diode 2 and diode 3. ^f Saturation current density for diodes 1, 2 and 3. All parameters were extracted from the circuit model shown in Fig. 1 (inset).

 $^{18}O_2$ and $H_2^{18}O$. These experiments made it possible to map the oxygen/water diffusion process into OPV devices by detecting the reaction products. This was carried out by exposing OPV devices to isotopically labeled oxygen $({}^{18}O_2)$ or isotopically labeled water $(H_2^{18}O)$ during either storing in darkness or illumination with a subsequent mass spectrometry analysis employing time-of-flight secondary ion mass spectrometry (TOF-SIMS). It was found that oxygen and water diffuse through the outer electrode (counter electrode to ITO) [26]-[28]. Using TOF-SIMS methodologies, Krebs and Norrman have demonstrated that the oxygen was diffused into the Al electrode through Al grains and microscopic holes on the Al film [28]. Once inside the devices, oxygen was continually diffused in the lateral and vertical plane until reaching the counter electrode. Another prominent degradation pathway was found to be the diffusion of electrode materials into the devices. The degradation is also due to the change of the interface of the devices [28].

When the iOSCs are left in ambient conditions, the extrinsic degradation occurs in both the dark and in the illumination conditions. This is due to oxygen and water molecules, diffusing into the device active layer and producing the reduction of the short circuit current, as is shown in Fig. 3 (b) [29]–[31]. We consider that this mechanism is the main cause of the degradation observed in our cells. It is worth to remark that, in the case of ZnO cells, overall stability is significantly better than that observed for PFN ones, even when the cells are degraded under air environment.

Finally, Table 2 shows the extracted parameters from the modeled *J-V* curves for A, B and C groups. The ideality factor of diode 1 (n_1) represents the dominant transport mechanism in the active layer of the cell. The ideality factor for diodes 2 and 3 correspond the dominant transport

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mechanism between the buffer layers and metallic contacts. When the predominant transport mechanism is diffusion n = 1, if n = 2 indicates that the predominant transport mechanism is recombination and if n is between 2-3 indicates that the predominant transport mechanism is a combination of diffusion, recombination and hopping [11].

IV. CONCLUSION

Stability and degradation analysis of inverted organic solar cells (iOSCs) manufactured with inject printed ZnO as ETL showed better stability than iOSCs with PFN as ETL, when these cells were exposed under N_2 or even under air environment. Although the cells using PFN started with the highest efficiency (A group), after 856 h, these cells showed the lowest PCE of all studied groups, that is, their degradation was the fastest.

After 58 h under nitrogen, PCE of the PFN cells (A group) reduced to 80 %. Conversely, ZnO cells (C group) reached to 80 % in PCE after 189 h. When the cells were left in air, the ZnO cells (B group) reduced to 80 % after 160 h.

The ZnO printing process is carried out at room temperature and under air conditions. This work demonstrated that it is possible to perform the iOSCs fabrication partially in air environment, with an increase in stability, by using inkjet printing deposition technique. The process is compatible with R2R processes, with the possibility of patterning without any chemical processes and it can be used for the fabrication of iOSCs on a large scale.

Using the three-diode circuit model, the behavior of the J-V experimental curves of iOSCs can be fitted. The extracted values from this model help to determine the predominant transport mechanism in the iOSCs. Using this model, it was possible to reproduce the S-shape effect presented on the J-V characteristics.

ACKNOWLEDGMENT

The authors acknowledge Ing. L. Abad and I. A. Hernandez for the technical assistance during this work.

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