PERFORMANCE AND LIGHT STABILITY STUDY ON ICBA AND PCBM FULLERENE ACCEPTORS RELATED TO THE CHOICE ON ELECTRON TRANSPORT MATERIAL

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Abstract. *Indene-C60 bisadduct (ICBA) has been used as alternative acceptor to the [6,6]-phenyl-c61-butyric acid methyl ester (PCBM) inside the field of bulk heterojunction solar cells due to its ability to provide improved open circuit voltage as reported in the literature. The promise to produce higher efficient solar cells keeping poly(3-hexylthiophene) (P3HT) as donor which is a common and well know relatively stable donor has drawn broad attention of researchers in the area. However, when the acceptor is changed, not only the photoactive layer is affected but the whole system needs to be reviewed. In this work, we show a comparative study between ICBA and PCBM keeping P3HT (as donor), same concentration and solvent mixture. An analysis on performance and stability under light is brought with a focus also on the interlayer directly related to acceptor which is the electron transport material (ETL). We employed either zinc oxide (ZnO) or a polymer-based material as ETL for preparing the devices. We show that ZnO and ICBA show higher power conversion efficiency of 2.9%, however the most stable system is shown to be the combination of the organic ETL and PCBM with an extrapolated T-80 of 790 hours.*

Keywords: *PCBM, ICBA, Zinc Oxide*

1. INTRODUCTION

Organic solar cell (OSC), which is based on solution-processed organic semiconductors, is a technology that can be classified as photovoltaic (PV) devices of third generation. First and second generations refer, respectively, to crystalline silicon (c-Si) and thin film such as amorphous silicon (a-Si), cadmium telluride (CdTe) and copper indium gallium selenide (CIGS). Although silicon solar cell is responsible for the major part of the solar market, it still faces obstacles such as high production costs and scarcity of some elements required. Thin film photovoltaics came with the promise to reduce the price by using less material, however, have some limitations such as high-temperature processes required. As mentioned by Hermes *et al.* (2015), CIGS and CdTe still necessitate rigid glass for support and encapsulation similar to c-Si products, and their efficiencies of roughly 12-14% are lower than those of c-Si (15-20%).

Plastic solar cell (PSC) technology stands on conjugated polymers and small molecules and attracts scientific and economic interest due to its potential of being flexible, low weight, cheap and efficient solar cells. Conjugated polymers combine the electronic properties of traditional semiconductors and conductors with the facility of processing besides providing mechanical flexibility of plastics. Solution processing allows compatibility to roll-to-roll and large-scale production. Apart from application in PV, plastic solar cells are expected to create a new market in the field of cheap electronics, which can already be possible with OLED – organic light emitting diode.

Organic solar cells are generally comprised of two different components that differ in electron donating and accepting properties. As Myung-Su Kim (2009) properly describes, with the input energy of an absorbed photon, an exciton, a bounded electron and hole pair, is formed. Once the excitons are dissociated, an electron is transferred from the electron donor, a p-type semiconductor, to an electron acceptor, an n-type semiconductor. In summary, the illumination of donor through a transparent electrode leads to a photo excited state of the donor, in which an electron is promoted from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the donor, as can be seen in Fig. 1. In sequence, the excited electron is transferred to the LUMO of the acceptor resulting in an extra electron on the acceptor and leaving a hole at the donor. The photo-generated charges are then transported and collected at opposite electrodes. (Li *et. al.*, 2010), Donor and acceptor are usually mixed together in solution prior to deposition and this is the reason of being called bulk heterojunction cells. Therefore, the interface between both components is all over the bulk and it allows better interaction than bilayer devices or planar heterojunction cells. According to Swart *et. al.* (2015), bulk heterojunction significantly improved organic solar cells (OSC) power conversion efficiencies by increasing the excitons access to the donor/acceptor interfaces.

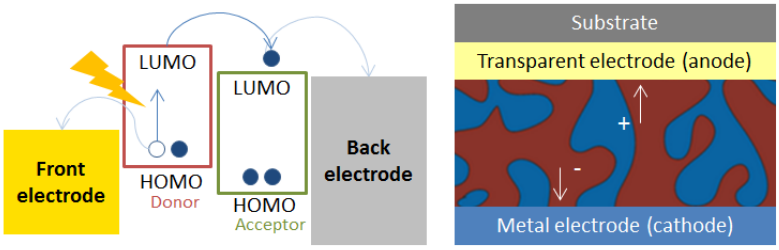

Figure 1- Energy diagram and layers view of a bulk-heterojunction concept.

There is a variety of combinations of donor and acceptor materials that have been used to build bulk heterojunction solar cells. One of the most promising and common combinations of materials is a blend of poly(3-hexylthiophene) (P3HT) as an electron donor and a fullerene, C_{60} derivative as acceptor, usually [6,6]-phenyl-C61-butyric acid methyl ester (PCBM). The power conversion efficiency (PCE) for the cells based on P3HT:PCBM achieved a PCE approaching 4%, as already reported by Ma and co-workers (2005). However, further improvement of PV performance of these cells is limited by the relatively large bandgap of P3HT (~2.0 eV - which narrows the harvest of light) and the relatively small energy difference between the LUMO of PCBM and the HOMO of P3HT which leads to low open circuit voltage (Voc) (~0,6 V for P3HT:PCBM based PSCs). The indene-C60 bisadduct (ICBA) offers an advantage in this aspect: it has higher LUMO energy, ~0.2 eV higher than that of PCBM. Hence, Voc for P3HT:ICBA based cells are expected to be around 0.8 V, enabling higher PCE, already reported 6.5%, by Zhao, He and Li (2010). According to Lin *et al.* (2012), compared to PCBM, ICBA also has more facile synthesis, higher solubility in common organic solvents, and stronger visible absorption for enhanced light harvesting in photovoltaic process. Chemical structures are shown in Fig. 2.

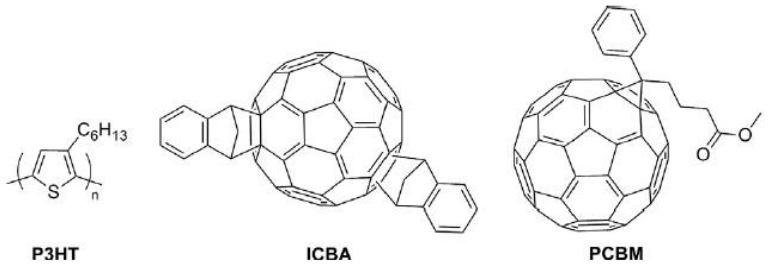

Figure 2 – Donor P3HT and acceptors ICBA and PCBM, commonly used in polymer-fullerene bulk-heterojunction solar cells.

In this work, PCBM and ICBA are the acceptors each one separately combined with P3HT-donor. The photoactive layer is sandwiched between two electrodes with different work functions: a transparent back electrode consisting of a layer of indium tin oxide/metal/indium tin oxide (IMI) coated by the electron collection material (ETL) and a top electrode of silver that covers the hole transport layer (HTL) of a conducting polymer polyethylenedioxythiophene:polystyrenesulfonate (PEDOT:PSS). For the electron transport material in this study, we use two different materials: a metal oxide (ZnO) and a polymeric material (simply referred here as ETL, from now on). The interfacial layers such as ETL and HTL are adopted for facilitating charge extraction at the cathode and the anode, respectively (Lai *et al*., 2013). In fact, in a bulk heterojunction solar cell architecture, once an acceptor is changed there is a modification on the HOMO and LUMO that must be adjusted by the electron extraction material energy levels while the donor matches the HTL energy levels.

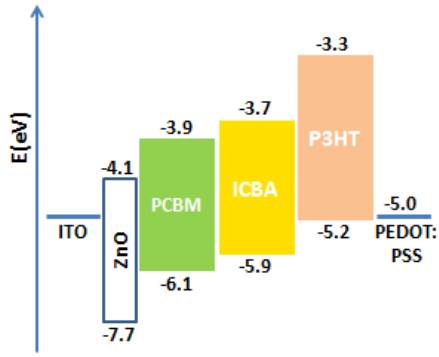

Figure 3 – Energy level diagram of PCBM/ICBA acceptors and P3HT donor system. Adapted from published work of Guerrero *et al.* (2012) and Chen *et al* (2014).

2. MATERIALS AND METHODS

Device fabrication is described as follows. P3HT and PCBM were purchased from Merck, ICBA from Nano-C, PEDOT:PSS from Heraeus and zinc oxide from InfinityPV. IMI-coated PET was used as substrate as Fig. 4 shows. First, ZnO was blade coated at 45ºC and 5 mm/s and annealed in hotplate at temperature of 120ºC to give a final thickness of 30 nm. In the case of devices with polymeric ETL, thin layers of about 10 nm were deposited. In the next step, donor:acceptor P3HT:PCBM/ICBA blends 1:1 weight ratio (30 mg/mL) were prepared and blade coated with a thickness of approximately 250 nm. The photoactive layer were annealed in oven at 140ºC or 150ºC for five minutes for PCBM and ICBA acceptors, respectively. PEDOT:PSS was blade-coated and annealed at 140ºC for five minutes to form a 100nm-thick layer of HTL. Finally, 200-nm thick silver layer was thermally evaporated at rate of 1A/s.

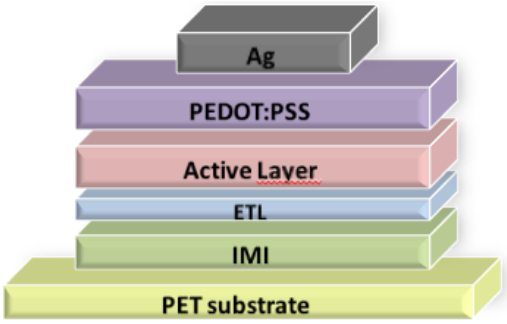

Figure 4 – Device architecture used in this work.

All devices were measured at room temperature in ambient air but under nitrogen-flow. A solar simulator model WXS-156S-10, AM 1.5G, with illumination of 100 mW/cm² was used to measure current density-voltage (J-V) curves. All samples were measure three times in different conditions: first, as cast, second, after post-annealing performed in hotplate in glove box filled with nitrogen for 15 minutes and then, third, for further 15, in a total of 30 minutes annealing after devices were finished. For stability investigation of samples previously encapsulated, a LED light soaker was used in order to simulate the sun-spectrum at 100 mW/cm² and calibration was done at 120k lux with additional LED UV spectrum. The encapsulation used a multilayer of PET barrier films with a water vapor transmission rate in the order of 10^{-3} g/cm^{2}day, glued together thanks to use of an UV-curable adhesive with barrier properties.

3. RESULTS AND DISCUSSION

3.1 Performance analysis

Highest average efficiency of about 2.9% and absolute value of 3.1% were achieved with the combination of zinc oxide and ICBA acceptor after post annealing for 30 minutes in inert air, as can be followed on Fig. 5. Tab. 1 brings all detailed numbers. Between devices that have not been undergone post-annealing process, PCBM-based samples gave best efficiency (around 2.1%), regardless of which electron transport material is chosen. PCBM-based active layer behave similarly for both ETL and ZnO and do not show such a significant change in performance between before and after post-annealing. On the other hand, ICBA-based devices experiment a large increase in performance of at least 65% mainly due to increase in short circuit current density (Jsc).

Table 1 – Photovoltaic parameters corresponding to P3HT:fullerene solar cells with different ETL. Best absolute efficiency value in brackets.

	Voc (V)	Jsc (mA/cm²)	Fill factor (%)	Efficiency (%)
ZnO/ICBA	0.756 ± 0.007	4.20 ± 0.13	51.9 ± 1.3	1.65 ± 0.07 [1.79]
ZnO/ICBA annealed for 15min	0.748 ± 0.015	6.57 ± 0.22	54.8 ± 4.7	2.59 ± 0.32 [2.91]
ZnO/ICBA annealed for 30min	0.749 ± 0.004	6.92 ± 0.22	55.1 ± 1.2	2.86 ± 0.10 [3.07]
ZnO/PCBM	0.531 ± 0.010	7.67 ± 0.34	51.8 ± 3.4	2.11 ± 0.21 [2.32]
ZnO/PCBM annealed for 15min	0.541 ± 0.009	8.26 ± 0.25	46.8 ± 2.0	2.09 ± 0.13 [2.21]
ZnO/PCBM annealed for 30min	0.543 ± 0.004	8.17 ± 0.21	46.3 ± 0.8	2.05 ± 0.03 [2.10]
Organic ETL/ICBA	0.646 ± 0.016	3.88 ± 0.14	42.0 ± 0.9	1.06 ± 0.07 [1.16]
Organic ETL/ICBA annealed for 15min	0.640 ± 0.016	6.46 ± 0.18	44.4 ± 1.0	1.83 ± 0.08 [1.99]
Organic ETL/ICBA annealed for 30min	0.609 ± 0.020	6.66 ± 0.18	43.2 ± 1.2	1.75 ± 0.10 [1.93]
Organic ETL/PCBM	0.542 ± 0.003	7.54 ± 0.28	52.0 ± 1.0	2.13 ± 0.10 [2.30]
Organic ETL/PCBM annealed for 15min	0.558 ± 0.003	7.72 ± 0.24	48.5 ± 1.2	2.09 ± 0.10 [2.25]
Organic ETL/PCBM annealed for 30min	0.558 ± 0.003	7.67 ± 0.26	49.7 ± 1.3	2.12 ± 0.11 [2.30]

As expected, open circuit voltage (Voc) is higher for ICBA samples than for PCBM ones which stands around 0.55 V for the latter. However, Voc is highly sensitive to the electron transport material that is combined with P3HT:ICBA active layer. Prior to post-annealing, Voc is around 0.76 V when zinc oxide is used and only 0.65 V when organic ETL is chosen instead, and can get even lower to around 0.61 V after submitted to post-annealing. Short circuit current density starts much lower for ICBA samples (close to 4 mA/cm²) than for PCBM (7.5 mA/cm²). However, it is observed a large increase for ICBA-samples after post-annealing and values reaches almost 7 mA/cm². This phenomenon suggests that this close-to-75% increment in current is due to a rearrangement on active layer morphology made possible by the heating transfer during the post-annealing process.

Fill factor (FF) values are high around 52 to 55% for combination of ZnO and ICBA and low as 42 to 45% for polymeric ETL and ICBA, which suggests that ICBA may hold low compatibility to this type of organic ETL that is probably due to a misalignment of HOMO and LUMO energy levels between them. For PCBM samples, FF holds numbers close to 52% that slightly decrease with heating provided by post-annealing. All mentioned above may suggest that PCBM-based active layer is already on the state of best morphology when devices have been just finished to receive silver top electrode. On the other hand, ICBA-based samples seem to be strongly dependent to temperature in order to achieve its best morphology and to be able to efficiently transfer electrons.

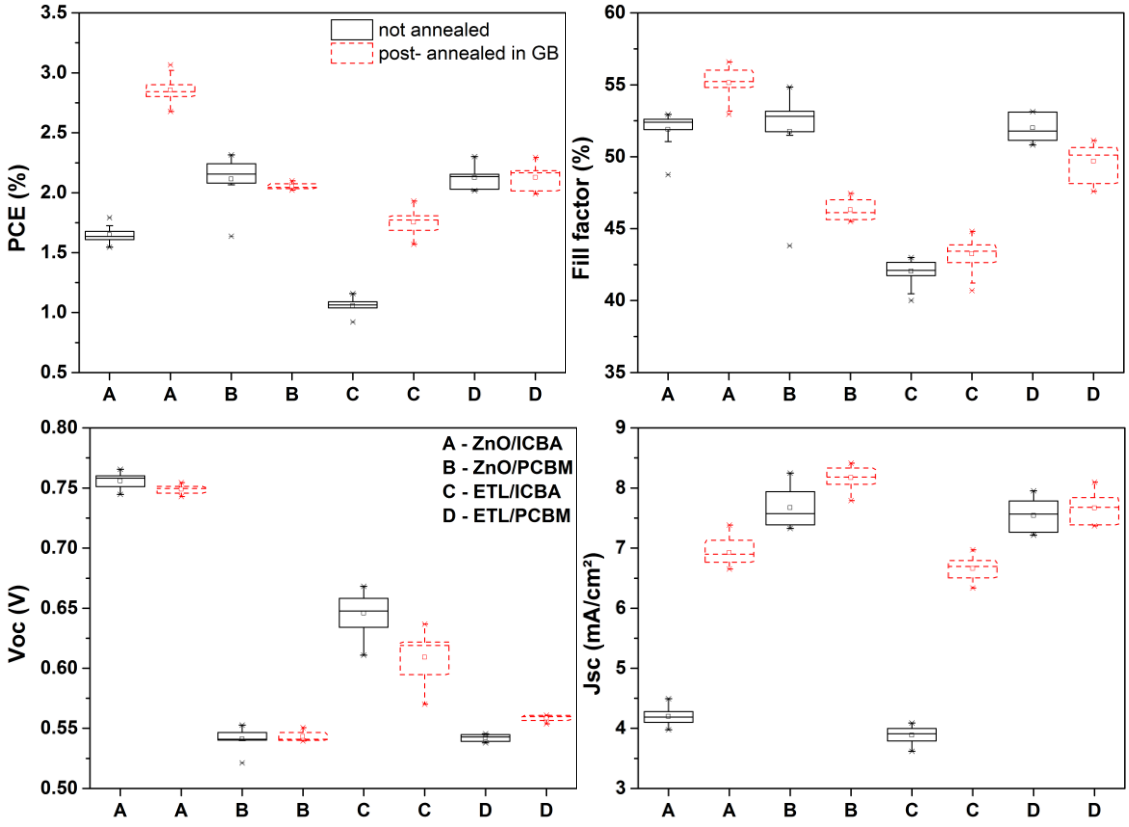

Figure 5 – Photovoltaic parameters for devices before and after post-annealing, where A represents the combination: ZnO and ICBA, B: ZnO and PCBM, C: Organic ETL and ICBA, D: Organic ETL and PCBM. Post-annealing is performed in glovebox for 30 minutes on a hotplate at 140˚C.

The temperature-dependence for ICBA acceptor can once more be verified by Fig. 6. We carried out a two-step post-annealing process: samples were measured after 15 minutes exposed to the temperature and then again after further 15 minutes in a total of 30 minutes under heating. 15-minuttes post-annealing more than double the PCE for ICBA-samples while for PCBM-based ones efficiency values seem to be stabilized and are not significantly affected by additional heating. Such improvement on performance of ICBA-based samples are expected and well known in the scientific field. When the blend film is annealed, the surface of the blend film shows a more uniform distribution of P3HT and ICBA, and the interpenetrating network of P3HT:ICBA is improved as consequence, which is beneficial to the exciton charge separation and charge transportation. (Zhao *et al.*, 2010) Further 15 minutes thermal annealing gives extra benefit for ZnO-samples that have PCE increased in 5% and appears to be close to achieve a *plateau*, however, for same ICBA-acceptor and ETL, efficiency values face a slight decrease of 4% that may be due to degradation in the ETL organic-based material.

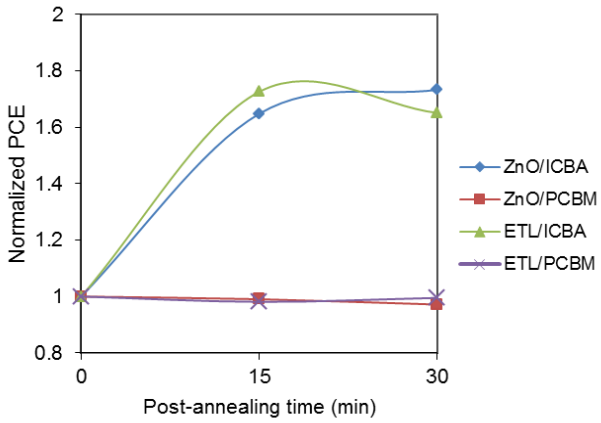

Figure 6 – Normalized PCE over post-annealing time

3.2 Stability study

Samples were placed under a LED light soaker system composed of white and UV LEDs. The irradiance provided by the system was set to be one Sun (1000 W/m^2). Stability tests were carried out for 450 hours; solar cells were kept under light all the time and were measured every 7 minutes up to the end of the test. In each measurement, all photovoltaic parameters were recorded, which allowed us to follow all these parameters along the time. As the objective of this study is to compare different ETL materials and different fullerene acceptors, the analysis of these data was carried out taking into account the type of ETL and acceptor utilized.

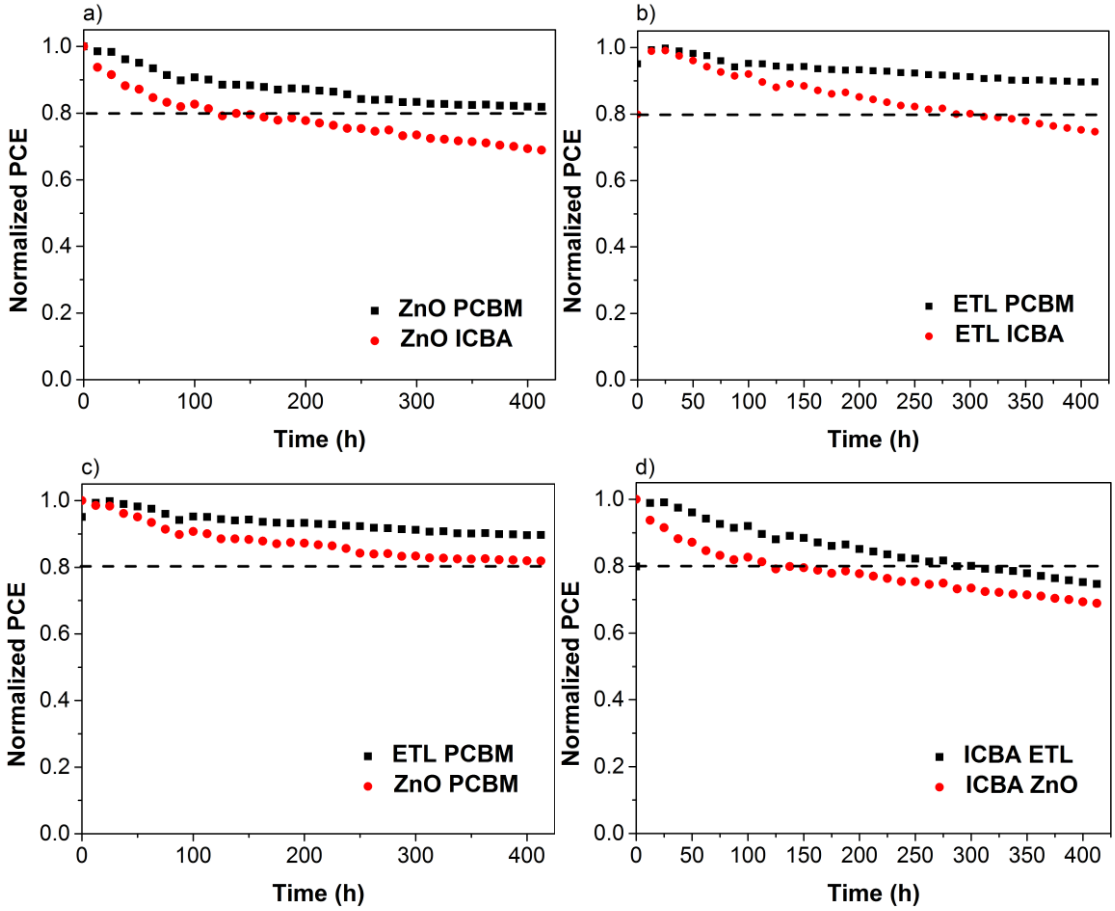

Figure 7 – Normalized PCE over time for different combinations of acceptors and electron transport materials. a) ZnO with PCBM or ICBA; b) ETL with PCBM or ICBA; c) PCBM with ETL or ZnO and d) ICBA with ETL or ZnO.

In Fig. 7 the time evolution of the power conversion efficiency (PCE) is shown for solar cells with the same ETL, but different acceptors. In Fig. 7-a it is possible to observe the data for the combinations ZnO with PCBM or ICBA. According to this combination ZnO/PCBM is more stable than the ZnO/ICBA, the former appears to approach T_{80} after 450 h, while the latter reached T_{80} after about 125 h. Fig. 76-b shows similar data, but for the combination ETL with

PCBM or ICBA. Once again the combination using PCBM is more stable than the one using ICBA. The data for ETL/PCBM reveals that, the sample assembled with this combination, have not reached T_{80} after 450 h, and the extrapolation of these data suggests that T_{80} will be reached after about 790 h. In the case of the combination ETL/ICBA T_{80} was reached around 280 h. As PCBM leads to more stable devices, independently of the ETL used, we may conclude that PCBM is more suitable than the ICBA, for the fabrication of stable devices. In Fig. 7-c and d similar analysis was done, but at that time keeping the acceptor and changing the ETL. In Fig. 7-c it is possible to observe that the combination ETL/PCBM is more stable than ZnO/PCBM. Fig. 7-d shows a comparison between the combinations ICBA/ETL or ZnO. In summary, the combination ETL/PCBM is the more stable and the combination ZnO/ICBA is the less stable. At that point it is important to notice that at the end of the test, the cells based on ELT/PCBM have lost less than 11 % of its maximum efficiency, while the sample for the combination ZnO/ICBA has lost more than 31 %, in comparison with its maximum efficiency. It is also true that the initial performance, for the combination ZnO/ICBA, was more than 34 % higher, so after 450 h of test the samples with the combination ZnO/ICBA have still presented a PCE slightly higher than the samples based on ELT/PCBM.

Time evolutions of the photovoltaic parameters, for the different conditions analyzed in this study, are depicted in Fig. 8. These parameters for the ZnO as ETL are shown in Fig. 8-a, in combination with ICBA, and in Fig. 8-b in combination with PCBM. According to the graphs losses in performance for these devices occur in different ways. For the system based on ZnO/ICBA it is clear that only V_{OC} remains constant, while all other parameters undergoes some type of degradation, being the losses on PCE a combination of losses in all other parameters. For the system based in ZnO/ICBA, short circuit current decreases around 10%, FF more than 18%, R_{SH} more than 40% and R_S nearly doubled. The combination of these effects leads to a decrease of around 30% on the PCE. The time evolution of the photovoltaic parameters for the sample based on ZnO/PCBM reveals that, for this sample, V_{OC} and FF remains almost constant, while the value from the R_S fluctuate close to its maximum value. In that system the losses in PCE are mainly due to losses in J_{SC}. After 450 h of testing, losses for both, J_{SC} and PCE approach 20%. The samples based on ZnO/PCBM seem to be more stable and an important fact that can lead to it is that its degradation mechanism is due to mainly a decrease in J_{SC}, while the degradation for samples based on ZnO/ICBA seem to be more complex, being affected by all other photovoltaic parameters. Similar conclusions may be taken from the analysis of samples that used ETL; again when the ELT is combined with ICBA all the parameters are causing the degradation of the solar cell, but when the ETL is used in combination with PCBM only the degradation of J_{SC} really matter for the degradation of the solar cell. Comparing performance of the samples with PCBM/ZnO or ETL, one can note that the samples assembled with ETL can retain more current along the tests. In Fig. 8-b one can see that the solar cell based on ZnO/PCBM loses 20% of its initial J_{SC}, which impact in losses of same magnitude on the PCE. On the other hand, for the solar cell based on ETL/PCBM, losses in J_{SC} and PCE were on the order of 10%.

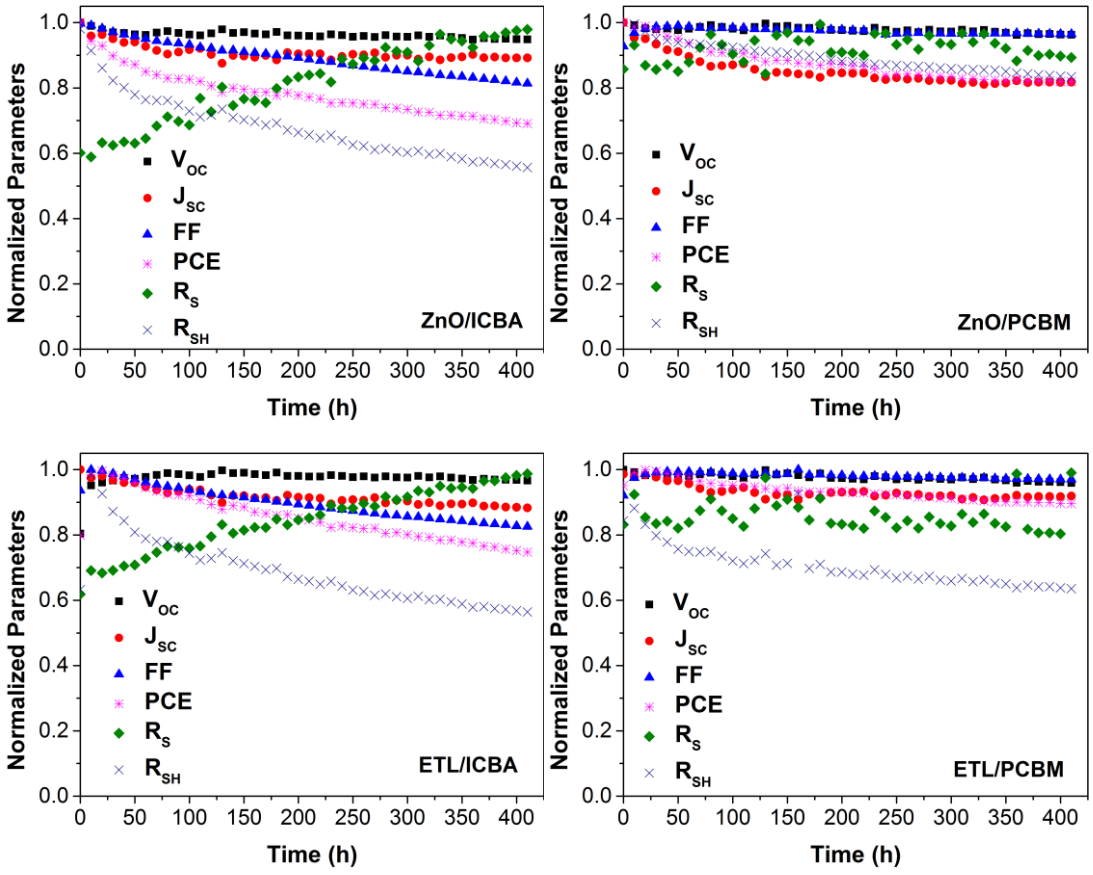

Figure 8 – OPV parameters over time for different combinations of acceptors and electron transport materials.

In terms of stability under light, ETL/PCBM is the most stable system followed by ZnO/PCBM in the second place, ETL/ICBA comes in third and ZnO/ICBA holds the fourth and last place. In summary, these results strongly indicate that PCBM acceptor is more stable than ICBA and ETL is a more stable electron transport material than ZnO.

4. CONCLUSION

In conclusion, ICBA and ZnO combined together reached best performance 2.86% in average and 3.07% as maximum although ETL and PCBM achieved best results of stability under light, despite of its comparatively lower PCE, 2.11% in average and 2.30% as maximum. ETL and PCBM showed an extrapolated T80 of 790 hours in contrast to 125 hours of the combination of ZnO and ICBA. These results suggest that not only the performance can be affected by the ETL chosen, but also the stability of the cells. In addition, an increase of over 65% in performance after post-annealing indicates that ICBA must be strongly temperature dependent for achieving its best morphology. Furthermore, P3HT donor shows to be very temperature stable what can enhance morphology of the active layer by post-annealing process and improve efficiency values, in consequence.

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