



Characterization and modeling of organic (P3HT:PCBM) solar cells as a function of bias and illumination



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ABSTRACT

We investigated the response of roll coated organic solar cells at different bias voltages and illumination levels to implement a detailed impedance model. The technique used for the investigation is based on the combination of standard DC characterization with the impedance spectroscopy at different bias and illumination intensity conditions.

We analyzed both fresh and intentionally degraded cells. The impedance spectra show different peaks evolutions, depending on the degradation of the cells. Moreover, the same trend appears by measuring the cell at different illumination levels. To describe the cell impedance behaviors we suggest an electrical model based on distributed elements. By fitting the model to experimental data, we extrapolate the parameters related to electron transport, recombination and accumulation. The main differences between fresh and degraded samples are underlined.

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1. Introduction

Polymeric solar cells have attracted the attention of many research groups as a low-cost and eco-sustainable alternative to conventional solar cells [1–3]. To describe the physical phenomena behind photo-generation on solid organic semiconductors, several works suggested both DC and AC models [4–8].

The simplest models proposed in literature link the phenomena related to the physics of organic solar cells (e.g., generation, recombination and transport) to linear equivalent components (resistors and capacitance). However, those first-order models rarely fit to experimental data with an acceptable degree of precision. In addition, the majority of the works in literature describe the polymeric solar cell impedances only at one selected bias point or illumination level. This may be a severe limitation both for the correct interpretation of the impedance data and the accurate description of the role of semiconductor/semiconductor and semiconductor/contact interfaces.

To achieve a better fit of experimental data, more sophisticated models introduce one or more constant-phase-element (CPE),

which is an easy mathematical artifice for justifying the dispersion in frequency of many phenomena especially in presence of irregular and porous interfaces. Although this strongly improves the quality of the fit of experimental data, it could bring some confusion on the correct association between model element and the corresponding physical phenomena [9]. In particular, some confusion may come from the correct interpretation of the value of the exponent of the CPE.

To overcome many of these limits, we analyzed the dependence of the cell impedance on both bias and illumination level, and we performed a complete AC and DC characterization of P3HT:PCBM solar cell. We proposed a more comprehensive model based only on distributed-impedance contribution, avoiding the use of CPE. We validated the model in a wide range of illumination level and operating bias conditions.

2. Experimental and devices

In this work we considered organic solar cells with P3HT:PCBM active layer in a 1:1 ratio, ZnO blocking layer and PEDOT:PSS as organic conductor. The active layer thickness is $L=315$ nm and the active area is 1 cm^2 . The samples are produced in roll-to-roll

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compatible process by the solar energy group at the Technical University of Denmark. The active layer is sandwiched between the front electrode (Flextrode) and a back electrode. The Flextrode consists of an Ag grid, PEDOT:PSS layer (100 nm) and ZnO (100 nm) electron transport/hole blocking layer [10–13] while the back electrode is made of a PEDOT:PSS hole transport/electron blocking layer and Ag grid. At the end of the building process, we annealed the completed solar cells at 140 °C for 20 min and then we encapsulated the cells with glass-to-glass protective layers, with only the Ag grid electrodes extensions reachable from the outside. The interested reader can find further details on the printing process in Refs. [14,15].

We carried out the characterization of the samples by using a Solartron SI1260 Impedance Analyzer and an Agilent E5263A Parameter analyzer. We illuminated the cells by using a white LED because the measurement noise floor generated by white LED is much lower, compared to a xenon solar simulator. Besides, the white LED optical power is easily controllable, since it is almost linearly dependent to the bias current.

However, the spectra of the white LEDs differ from the one of the solar simulator, as well as Si cell absorption is different compared to an organic solar cell. We calibrated the LED output power by mean of a reference solar cell and by considering the different shape of the illumination spectrum. We verified that the short circuit current measured on an organic solar cell with both solar simulator and white LED are the same after calibration and correction. Furthermore, we performed DC measurements using an AM 1.5 xenon lamp solar simulator to extrapolate comparative figure of merit that allow the reader a comparison between the measurements under LED and solar simulator.

We developed a custom sample holder, to reduce parasitic effects, such as series resistance and inductance. We also kept the overall cable length smaller than 40 cm, because excessive cable length might induce an unacceptable signal delay, with a consequent error on the measured impedance phase. After short-circuit and open circuit calibration, we achieved a reliable impedance measurement up to 8 MHz.

We characterized three groups of solar cells:

- 1) Fresh cells fabricated to reach the optimal performance.
- 2) PEDOT degraded cells, where PEDOT:PSS used as hole transport layer at the anode contact was exposed to a temperature of 80 °C with high moisture and in presence of air for 15 min before completing the cell manufacturing.
- 3) ZnO degraded cells, where the Flextrode [11] was exposed to UV radiation for 1 h during building process before the blend deposition and cells encapsulation.

In the following, we will show the curves of three representative cells taken from group 1, 2, and 3. Table 1 lists the three groups and the type of degradation.

We summarized the experimental procedure in Fig. 1. The bias voltages considered in this works are -1.5 V to 0.5 V, with 0.1 V

Table 1

Summary of some of the cells used though this work. First column is the cell number (in this work ref). Second column is the cell status (i.e., fresh or degraded). Third Column is the type of degradation the cell underwent during building process.

Group#	Status	Degradation performed
1	Fresh	None
2	Degraded	PEDOT has been exposed for 15 min to a temperature of 80 °C with high moisture and in presence of air
3	Degraded	"Flextrode" exposed to UV radiation for 1 h during building process

step and 10 mV ac signal amplitude, while the illumination levels are 0–2 Sun, with 0.2 Sun step.

In principle, because a complete characterization requires 8 h, in such long time the device degradation could be observable during the experiment. For this reason we did a quick characterization including one I-V and one IS in dark and under illumination before and immediately after the complete characterization, to assess any measurement-induced degradation. We verified that any changes induced by the entire measurement procedure (after 8 h) are smaller than 5% in the worst case, i.e., much smaller than the variation range of the extracted parameters. Hence, we can attribute the parameters variations mostly on the bias and illumination conditions, neglecting the measurement-induced effects.

3. Results

Fig. 2 represents the most important figures of merit of some of the characterized cells as a function of illumination levels. Fresh cells (group 1) and PEDOT:PSS degraded cells (group 2) feature a very similar behavior, showing small variation each-to-other (within the 10%). On the contrary, ZnO-degraded cells (group 3) exhibit a different behavior, indicating that UV exposure significantly changes the short circuit current, the open circuit voltage and the maximum output power. In particular, the short circuit current and the maximum power decreased to 50% and 25% of their initial value, respectively. Furthermore, in Fig. 2 we plotted the figure of merit calculated on the cells under the AM 1.5 solar simulator. Noticeably, there are no significant differences in performance parameters when the cell is illuminated with the solar simulator or with the white LED, confirming the correct calibration. Indeed, as observed in a previous work [16], different light sources may differently affect the cells in term of aging due to the presence of a strong UV component in the solar spectrum, but no significant differences appears during DC characterization.

Fig. 3 shows the I-V curves taken at different illumination levels and under the AM1.5 solar simulator on three representative cells of the groups listed in Table 1. The main differences between fresh and group 3 degraded cells are the S-shape appearing around V_{OC} (Fig. 3(b)) and the short circuit current reduction. We relate the S-shape appearing in the proximity of V_{OC} to a degradation of the photo-generated current due to UV exposure [17–19]. It is possible to associate the decrease in performances of cells group 3, with the increased resistance due to ZnO degradation by means of UV light exposure during cells building (which will be confirmed by IS-analysis and modeling presented in the following). On the contrary, the degradation induced by simply exposing PEDOT:PSS to high moisture and temperature during building process (group 2), only slightly reduces the short circuit current (see Figs. 2(c) and 3 (c)). For this reason, in the following we refer to fresh and degraded cells indicating group 1 and group 3 cells respectively.

4. Impedance model and discussion

Fig. 4 presents the proposed impedance model. Because the active layer might be intentionally or unintentionally doped, we divided the active layer in two parts: a carrier depleted region (SCR, Space Charge Region) and a quasi-neutral region (QNR).

In Fig. 4, the SCR is represented by the distributed impedance:

$$Z_{AL}(j\omega) = \sqrt{\frac{R_{RG}}{R_T} \frac{1}{(1+j\omega C_\mu R_{RG})}} R_T \coth \left(\sqrt{\frac{R_T (1+j\omega C_\mu R_{RG})}{R_{RG}}} \right)$$

where:

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