Degradation Analysis of Encapsulated and Nonencapsulated TiO$_2$/PTB7:PC$_7_0$BM/V$_2$O$_5$ Solar Cells under Ambient Conditions via Impedance Spectroscopy

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Supporting Information

ABSTRACT: Inverted organic cells are promising devices for sustainable and low-cost future electric generation. In this work, we present the degradation mechanisms studied in ITO/TiO$_2$/PTB7:PC$_7_0$BM/V$_2$O$_5$/Ag inverted organic solar cells (iOSCs) by impedance spectroscopy (IS). Measurements were performed on encapsulated (controlled environment) and nonencapsulated (ambient condition) cells following their temporal evolution under AM1.5 illumination for several voltage biases. From the impedance spectra, analyzed in terms of resistive/capacitive equivalent circuits, we were able to identify that the most sensitive layers inside of the device are contact layers. According with presented, IS technique is useful for determining the materials that have more influence on the degradation of organic solar cells. We demonstrate that IS is a powerful technique to identify the limiting mechanisms and to establish the limiting materials inside of the iOSCs.

1. INTRODUCTION

Organic solar cells (OSCs) have become an attractive alternative to inorganic solar cells in recent years because of their potential to be flexible, solution-coatable, low cost and weight, semitransparent, and easily integrated into different applications.1,2 Among all types of OSCs, bulk heterojunction-based polymers have been the most popular because of their high efficiencies.3 In general, this technology has adopted a standard device structure in which the active layer is located between the transparent indium–tin–oxide (ITO) bottom and a PEDOT:PSS commonly used as a electron-blocking layer (EBL) and the top cathode using metals such as aluminum (Al) or calcium (Ca) for hole blocking. However, to prevent the corrosive interaction between ITO and the EBL, it is necessary to devise another structure architecture. An alternative approach is an inverted organic solar cell (iOSC) in which a transparent hole-blocking layer (HBL) on the ITO electrode is introduced, placing the EBL between the active layer and the top metal electrode. Thus, high efficiencies (close to 10%) using inverted structures of polymeric materials as the active layer, such as [6,6]-phenyl-C$_7_1$-butyric acid methyl ester (PC$_7_0$BM) and semiconducting polymer (PTB7), are obtained.

Given its complexity, iOSC technology presents an enormous variability in many aspects, particularly in terms of stability and degradation.4,5 It is known that the performance of iOSCs is highly sensitive to oxygen and moisture, which can cause interfacial instabilities and permanent physical or chemical changes to the active polymer and other layers, resulting in a reduced device lifetime.4−6 Irradiation of the iOSCs can lead to even more complex degradation mechanisms involving factors such as degradation of the PEDOT:PSS layer, photooxidation of metal electrodes and other deposited layers, photooxidation of the active polymer material and inorganic oxide nanocomposite films, and chemical degradation of metal electrodes and the ITO electrode.4−8 To improve the stability of iOSCs, these devices are encapsulated by using barrier materials with low permeability toward atmospheric oxygen and moisture. Although some degradation processes are known in the device, it is not yet distinguishable where the degradation process takes place inside of the device. Different optical and electrical
techniques are useful for monitoring the degradation and to gain insights about each layer in the structures. In particular, impedance spectroscopy (IS) measures the complex dielectric properties of a material for a frequency spectrum, and the results can be interpreted in terms of the equivalent circuits with resistive/capacitive (RC) elements associated with each layer.

Figure 1. \( J-V \) curves under AM1.5 at different degradation times of encapsulated (a) and nonencapsulated (b) iOSC structures using TiO\(_2\) and V\(_2\)O\(_5\) as blocking layers and PTB7:PC\(_{70}\)BM as the active layer. Both devices were exposed to the air environment following the protocol for organic photovoltaics.

Figure 2. Cole−Cole plots of the encapsulated (a−c) and nonencapsulated (d−f) iOSC. The IS measurements were taken at three different \( V_{bias} \): 0 V (a,d), 0.5 V (b,e), and 0.8 V (c,f). The experimental data were fitted using the 3RC circuit model (solid lines).
layer. This technique consists of overlapping a small voltage signal (in the frequency domain) on the direct current (dc) bias voltage so that the impedance can be determined under various conditions. The power of this technique results from its ability to separate events that occur at different time scales or rates and provides information about strong carrier accumulation at open circuits, rapid extraction at short circuits, transport in the photoactive layer, contacts, and bulk and surface capacitance. Several authors have used this technique in order to monitor the degradation under infrared illumination, AM1.5, and dark conditions in iOSCs. In this work, we show that impedance spectroscopy can be used to resolve the effect of degradation on each of the layers of hybrid polymer–inorganic solar cells. We study the degradation in encapsulated and nonencapsulated iOSCs under real operational condition (AM1.5 illumination and 45% relative humidity) by IS for different bias voltages. The precise structure, in which we base our study, is titanium oxide/PTB7:PC70BM/vanadium oxide/Ag deposited onto the glass/ITO substrate. IS measurements were taken up to 77 h, and the measured spectra were analyzed by fitting to an equivalent electrical model consisting of three resistor/capacitor elements in series. Each parameter was associated with a different layer, and its contributions at different frequency ranges were analyzed by superposition of the independent RC circuits. Finally, from the parameters extracted, the layer that presents the higher degradation evolution was identified.

2. RESULTS AND DISCUSSION

Figure 1 shows the $J-V$ characteristics under AM1.5 illumination for an encapsulated device (Figure 1a) and a nonencapsulated device (Figure 1b) for different storage times. It can be observed that the $J-V$ curve for the encapsulated device varies little with the time. On the other hand, Figure 1b
shows a severe degradation of the nonencapsulated solar cell. For the encapsulated device, the open-circuit voltage, the short-circuit current, and the fill factor do not change appreciably, whereas the short-circuit current for the nonencapsulated device is reduced by 40% after 77 h, resulting in a decrease in the efficiency by 11% with respect to its initial value (8.9%). More details from the \( J-V \) curve analysis are reported in Table S1. From the table, it can be seen that the degradation of the nonencapsulated device is caused not only by the reduction in the short-circuit current but also by the changes in the series resistance \( (R_s) \) and in the shunt resistance \( (R_{sh}) \), resulting in a drop in the efficiency by 77%. These results show quantitatively the amount of degradation of the encapsulated devices with respect to the nonencapsulated ones. In the following, this information will be used as a reference basis for the comparison of the IS results.

Although \( J-V \) curves show a different behavior in their shapes, they do not provide information on the effect of degradation on each layer within the devices. Figure 2 shows the Cole–Cole plots of the impedance spectra taken at the specified bias voltages for different times in the encapsulated (Figure 2a–c) and nonencapsulated (Figure 2d–f) iOSC devices under AM1.5 illumination. In addition, the solid lines show the best-fit curves for each measurement. All plots show the typical arc behavior, with some deviation from the perfect semicircle shape corresponding to an RC circuit, which indicates the presence of different RC components in the spectra. It can also be observed that the average radius of the arcs increases with increasing storage time at a faster rate for the nonencapsulated devices. This indicates that the impedances of the nonencapsulated devices reach much higher values than those of the encapsulated ones. It is important to note that for all cases the arc shape in the spectra is not

Figure 4. Resistance of TiO\(_2\) (black star), V\(_2\)O\(_5\) (blue circle), and blend (red cross) over time. The values were extracted by modeling the IS measurements of the encapsulated (a–c) and nonencapsulated (d–f) iOSC. The IS measurements were taken at three different \( V_{bias} \): 0 V (a,d), 0.5 V (b,e), and 0.8 V (c,f).
completely closed (it does not reach zero impedance at very high frequencies). This is more evident for the encapsulated devices at bias voltages of 0.5 and 0.8 V, in which values at high frequencies are shown with decreasing real part of $Z'$ and constant imaginary part ($Z''$). Another feature that is common for the encapsulated and nonencapsulated devices is that for increasing applied bias voltage the radii of the arcs decrease. This is certainly related to the charge extraction (or injected charges, under illumination and high $V_{bias}$), which appears to be very efficient in these devices. The extracted capacitance values of the equivalent RC circuits are plotted as a function of the storage time in Figure 3 for the two kinds of cells and for the three considered applied bias voltages. The capacitance values can be separated in three ranges (delimited by horizontal lines in the graphs): the first one above 124 nF, the second one between 27 and 116 nF, and the third region below 11 nF. Furthermore, these ranges are the same for the encapsulated and nonencapsulated devices and for the different applied bias voltages. For each range, the average value is $C_1 = 169.1 \, \text{nF}$, $C_2 = 50 \, \text{nF}$, and $C_3 = 7.7 \, \text{nF}$. These capacitance ranges can be related to each of the layers in the structure. By considering the active area ($A$), the thickness of each dielectric layer ($d_{\text{blend}}$, $d_{\text{TiO}_2}$, and $d_{\text{V}_2\text{O}_5}$), and its relative dielectric permittivities ($\varepsilon_{\text{blend}}$, $\varepsilon_{\text{TiO}_2}$, and $\varepsilon_{\text{V}_2\text{O}_5}$) through the relation

$$C = \varepsilon_0 A \frac{d_{\text{layer}}}{d_{\text{layer}}}$$

where $\varepsilon_0$ is the vacuum dielectric permittivity, the capacitance of the layer can be obtained. The used values of thickness, relative dielectric permittivities (with the source reference in superscripts $^{[3,18,19]}$), and the corresponding capacitance are specified in Table S2. By comparing the obtained values with the results obtained from the experimental data analysis, the higher capacitance range can be related to the $\text{TiO}_2$ layer, the medium capacitance range can be related to the $\text{V}_2\text{O}_5$ layer, and the lower capacitance can be related to the active layer (blend).

The identification of the capacitance in each RC equivalent circuit permits also to identify the resistance for each layer. Figure 4 shows the resistances values as a function of the storage time, extracted from different conditions for the encapsulated (4a–c) and nonencapsulated (4d–f) devices. The results show that the resistance, for all layers in the encapsulated cells, varies only slightly with the degradation time. It is remarkable that only $R$ for $\text{V}_2\text{O}_5$ at null bias voltage reaches its highest value of around 50 $\Omega$, whereas the rest of the values for all biases are below 20 $\Omega$. On the other hand, the $R$ values are clearly correlated with the storage time for the nonencapsulated devices. In particular, the resistance of the $\text{TiO}_2$ layer increases from 119 $\Omega$ up to 662 $\Omega$ after 77 h at zero applied bias voltage, whereas the resistance of the other layers exhibited lower values that increase at smaller rates. The decrease in the performance of solar cells is mainly due to the degradation in the $\text{TiO}_2$ layer. Such degradation may arise because of the photochemical activation when it is in operation. Furthermore, the exposure to oxygen can also be a cause of the higher degradation with respect to the rest of the layers. The second highest capacitance and the second highest resistance increase with the storage time observed in the nonencapsulated layers correspond to the $\text{V}_2\text{O}_5$ layer. This indicates that the main source of degradation arises from the blocking layers, possibly due to the $\text{TiO}_2$ layer, which is photochemically activated, and oxygen exposure. In both the encapsulated and nonencapsulated cases, the values of resistances decrease when the applied bias voltage increases. This is related to the high charge extraction. From this analysis, it can be concluded that it presents greater resistance values because of the blocking layers, mainly $R_{\text{TiO}_2}$ resulting in a drop in the fill factor, such that for the nonencapsulated devices, $R_{\text{TiO}_2}$ is the main limiting factor in the performance. On the other hand, for the encapsulated devices, the limiting factor on the performance of the iOSC is $R_{\text{V}_2\text{O}_5}$ at low bias voltage but is $R_{\text{blend}}$ at high bias voltage.

We analyze the contribution of each RC equivalent circuit element in lower, medium, and high frequencies, which dominates the performance in both iOSC, nonencapsulated (Figure S2) and encapsulated (Figure S3) devices. We found the contribution of each layer in three frequency regions (low, medium, and high) in a Cole–Cole feature. The main contribution comes from the active layer at high frequencies (above 100 kHz), whereas at low and medium frequencies, the contributions depend on the blocking layers. For the encapsulated devices, $\text{TiO}_2$ and $\text{V}_2\text{O}_5$ layers contribute at low and medium frequencies, whereas in the nonencapsulated devices, the $\text{TiO}_2$ layer contributes at low frequencies (below 400 Hz) and the $\text{V}_2\text{O}_5$ layer contributes at medium frequencies (between 400 Hz and 1000 kHz). The contribution is also affected by degradation.

We obtained the resistivity of each layer by the relation

$$\rho = \frac{R_{\text{layer}} A}{d_{\text{layer}}}$$

where $R_{\text{layer}}$ is the fitting value of the resistance, $A$ is the area of the structure, and $d_{\text{layer}}$ is the thickness of each layer. Table 1 shows the range of the resistivity associated with each layer. The range of the resistivity in the blocking layers ratifies the hypothesis that charges cannot be efficiently extracted through the contacts. These values are in the range of those reported by other groups for $\text{TiO}_2$ and blend and are 2 orders of magnitude with respect to $\text{V}_2\text{O}_5$ obtained by electron beam evaporation.

### 3. CONCLUSIONS

We presented the electrical degradation study in terms of $J$–$V$ curves and IS of ITO/$\text{TiO}_2$/PTB7:PC$_{70}$BM/$\text{V}_2\text{O}_5$/Ag iOSC with two possible configurations: encapsulated cells used as a reference and nonencapsulated cells for accelerated degradation. The $J$–$V$ curves show that the efficiency of the nonencapsulated devices drops by 77% with respect to that of the encapsulated devices because of the interaction of ambient. On the other hand, IS analysis allowed to separately study the influence of each layer on the degradation inside of the cells. The analysis of the impedance spectra performed by fitting a model with RC equivalent circuits in series allowed to identify the obtained RC parameters in three intervals, each one...
related to the three active layers inside of the structure: TiO$_2$, V$_2$O$_5$, and blend layers. Besides, this led to the important conclusion that degradation does not affect the capacitance but the resistance of each layer. Moreover, using this technique, it was possible to identify the main source of the degradation in the cells: the TiO$_2$ layer. Overall, it was demonstrated that IS is a powerful technique to establish the limiting materials and to identify the limiting mechanisms inside of the iOSCs.

4. EXPERIMENTAL METHODS

4.1. Preparation of Devices. All fabrication process was performed under inert atmosphere. The inverted organic devices were fabricated on prepatterned ITO-coated glass (cathode) substrates with a sheet resistance of $\sim$10 $\Omega/\square$. Titanium oxide (TiO$_2$), used as HBL, was synthesized by a sol–gel method.$^{24}$ The precursor solution was diluted in anhydrous methanol with a volume ratio of 1:6 and was spincast in air on the top of the ITO substrates at 6000 rpm in order to obtain a TiO$_2$ layer with about 20 nm of thickness. Samples were left in ambient conditions for 1 h followed by thermal annealing at 400 $^\circ$C for 20 min. The active layer, PTB7:PC$_{70}$BM, was obtained by depositing a blend solution by spin coating, yielding a thickness of 100 nm. Blend solution with a concentration of 25 mg L$^{-1}$ was prepared by dissolving PTB7 and PC$_{70}$BM (1:1.5 weight ratio) in chlorobenzene and 1,8-dioctooctane (97:3 by volume). A thermally evaporated TiO$_2$ layer, equivalent circuit model consisting of three parallel resistor/capacitor elements: $R_C$, $C_s$, 1, 2, and 3) in series$^{9}$ (Figure S1b). Each RC element is associated with the resistance and the capacitance of each layer in the device. The fitting was carried out by minimizing the relative error between the data and the model using conventional algorithms such as simulated annealing.$^{25}$ The error in all cases was below 2%.

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