

## Controlling photoinduced degradation in plastic photovoltaic cells: A time-resolved energy dispersive x-ray reflectometry study

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The electrode-active layer interface of organic photovoltaic cells, a critical point in the development of organic devices, was studied by the energy dispersive x-ray reflectivity (EDXR) technique applied *in situ*. An EDXR-based protocol allowing discrimination between the possible mechanisms that produce the aging process at the interface was established. The study detects photoinduced oxidation of the electrode at the buried interface, to which fading of the device performances could be attributed. This conclusion was further confirmed by results obtained on a new cell, of selectively modified architecture, whose performances turned out to be stable in time. © 2006 American Institute of Physics. [DOI: 10.1063/1.2227772]

Improvements in the last five years have been remarkable in organic devices, and light-emitting diodes have now reached the commercialization stage, with lifetimes of tens of thousands of hours.<sup>1,2</sup> At present, the highest power conversion efficiencies for photovoltaic devices based on organic materials (donor-acceptor heterojunctions) approach 5%.<sup>3,4</sup>

In the present case poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1, 4-phenylenevinylene (MDMO-PPV), is used as a conjugated polymer.<sup>5,6</sup> Indeed, ultrafast electron transfer may be photoinduced from an electron donor material to fullerene.<sup>7,8</sup> A great deal of research is still necessary in order to improve the current state of the art, particularly with regard to lifetime, which is an important factor for the development of efficient polymer solar cells.<sup>9,10</sup> New characterization techniques are therefore of extreme importance in order to better understand the changes of the organic layers upon cell working and their effect on the device's lifetime.<sup>11,12</sup> In the present study time-resolved energy dispersive x-ray reflectometry (EDXR) was applied directly *in situ* to investigate photoinduced degradation processes by observing the morphological changes of the cell layers.<sup>12</sup> In order to reveal the nature of this morphological evolution, a systematic study on different PV cells, whose architecture has been "selectively" modified, was performed. The final goal was the establishment of a link between the morphological evolution<sup>13</sup> and the performance of the device and to use this information to modify the architecture of the device in order to inhibit the decrease of (device) efficiency.

The use of EDXR<sup>14</sup> *in situ* prevents the problem of possible systematic errors in the removal and repositioning of the sample and allows the time evolution of the film morphology to be followed with extreme accuracy.<sup>15,16</sup>

The bulk heterojunction solar cells studied were made from a blend of methanofullerene[6,6]-phenyl C<sub>61</sub> butyric acid methylester, denoted by PCBM, and MDMO-PPV. The

cells consisted of an indium tin oxide (ITO) substrate cleaned in an ultrasonic bath with acetone and isopropanol, rinsed in de-ionized water, dried in an oven, and finally treated with UV ozone. For two of the cells studied, the substrate was then spin coated with a 50 nm film of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) (Baytron PH<sup>®</sup>). The active layer of MDMO-PPV:PCBM was deposited by spin casting from an anhydrous chlorobenzene solution, and the devices were completed by deposition of the cathode through a shadow mask with 6 mm diameter openings. The top contact was either a LiF/Al (0.8 nm/100 nm) layer or an Al (100 nm) layer. All the cells have an active surface of 32 mm<sup>2</sup>.

The devices were created and electrically characterized under controlled atmospheric conditions. The combinations for the structure of the cells studied are the following: (cell A) glass/ITO/PEDOT/MDMO-PPV:PCBM/Al and (cell B) glass/ITO/MDMO-PPV:PCBM/LiF/Al.

The *J/V* characteristics under simulated AM1.5, 80 mW/cm<sup>2</sup> illumination for cell A is shown, as an example, in the insert of Fig. 1. The PV parameters are  $V_{oc}=0.63$  V,  $J_{sc}=3.54$  mA/cm<sup>2</sup>, FF=0.46, and  $\eta=1.27\%$ .

The cells were first characterized by *ex situ* EDXR after each stage of their fabrication. These prior measurements allowed the identification of the various contributions to the overall signal.

A first *in situ* experiment was then performed on an expressively constructed PV cell (cell A), both in the dark and under illumination. In this way any photoinduced modification of the morphology of the device can be monitored.

Finally, a new device, of selectively modified design with respect to the previous devices, was fabricated and measured (*in situ*) to retrieve information on the nature of the above effect and on possible strategies to limit or, possibly, inhibit photodegradation (cell B).

All the measurements were performed under controlled atmospheric conditions (N<sub>2</sub> gas flux).

*Ex situ* EDXR: study of the intermediate stages of cell construction. The reflection patterns of samples that corre-

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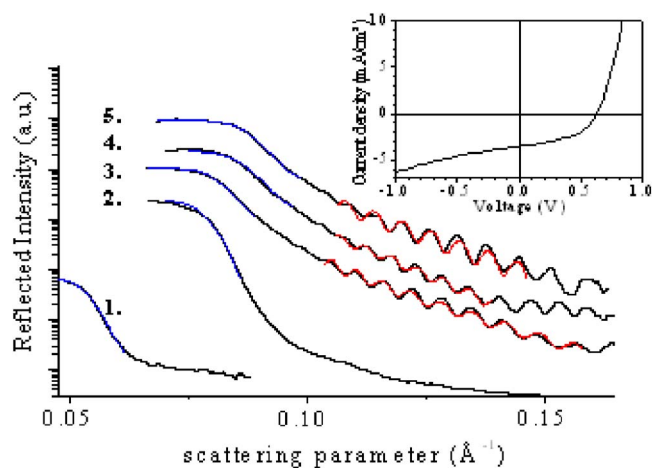


FIG. 1. (Color online) EDXR measurements of: (1) glass/ITO, (2) glass/ITO/LiF, (3) glass/ITO/PEDOT, (4) (cell A) glass/ITO/PEDOT/MDMO-PPV+PCBM/Al, and (5) glass/ITO/PEDOT/MDMO-PPV:PCBM/LiF/Al. The  $J/V$  characteristics are reported in the insert (cell A).

spond to the successive stages of the cell's construction were compared with the patterns of the complete cells (see Fig. 1). The Parratt formula<sup>17</sup> was utilized to fit the reflection patterns.

*In situ* EDXR measurements: Time-resolved investigation on the cells upon exposure to light. Two sequences of *in situ* time-resolved EDXR measurements on cells with different architectures, under the same experimental conditions, were performed.

The study had the following goals. *Dynamics of the photoinduced morphological changes.* The *in situ* experiment consisted of collecting a large number of x-ray reflection patterns, each acquired for 15 min. In each sequence the two initial patterns were collected, keeping the cell in the dark. The other patterns were collected over a period of several hours while the cell was illuminated with a white light lamp (10 mW/cm<sup>2</sup>). The results for cell A are reported in Fig. 2(a).

While the cell is being illuminated, a change in the EDXR profiles, consisting of a progressive compression of the oscillations in the 0.01 and 0.013 Å<sup>-1</sup>  $q$  range, is visible. It corresponds to an increase of the Al thickness as a consequence of the exposure to light, confirming the aging effects on the polymer PV cells morphology observed in preliminary x-ray reflectivity experiments carried out on a test cell.<sup>12</sup> The interpretation of the observed Al thickening process is not insubstantial.

The first hypothesis is that, since no increase in roughness is visible during the illumination of this device, this photoinduced process should not involve the Al surface but should be limited to the Al/organic layer interface, which is not thought to vary in roughness. The occurrence of an oxygen activated photochemical modification of the Al surface in contact with the organic film can be hypothesized. In this case, Al growth would be due to the formation of a layer of aluminum oxide at the interface with the organic film.

Another possible explanation could be indium diffusion from the ITO through the organic layer. This phenomenon, which has been observed in organic light-emitting diode (OLED) devices of similar structures,<sup>2,3</sup> would imply the formation of an interfacial layer between the organic film and the metallic electrode, having a density very close to that of

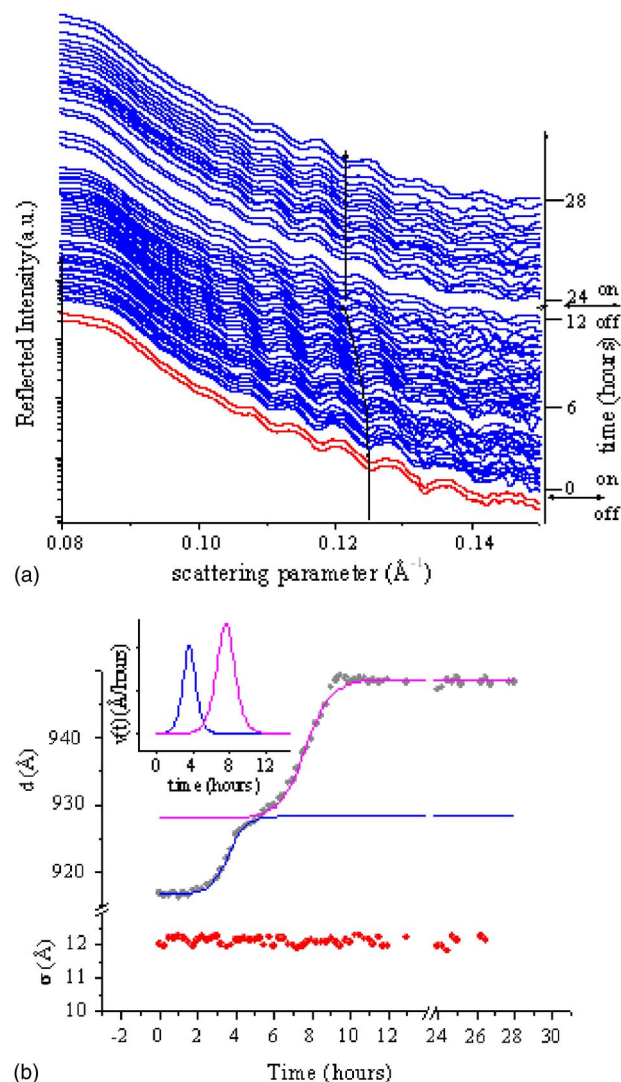


FIG. 2. (Color online) Results of the EDXR measurements for cell A.

Al. From the point of view of EDXR, such an increase of the polymer density in the proximity of the Al surface would be indistinguishable from the "thickening" of the Al film itself, since this technique is sensitive to the electronic density only. In the latter case, the diffusion process would involve the whole cell and would produce severe damage to the device.

*In situ* EDXR measurements were used to discriminate between these two hypotheses.

The  $d$  vs  $t$  data points are plotted in Fig. 2(b). The thickening is quite complex and cannot be described by a simple Boltzmann sigmoidal curve. Indeed, the  $d(t)$  plot shows that two sequential photoinduced phenomena, with different characteristic times, occurred at the buried interface. The data fit is obtained using two correlated Boltzmann curves. The delay between the two processes is evident in the inset of Fig. 2, in which the curve fit derivatives are reported. It can be noticed that the first process is almost concluded when the second is activated. This peculiar behavior supports the hypothesis of electrode oxidation. Indeed, the fact that the interface morphology between the Al electrode and organic material evolves in two steps is consistent with aluminum oxidation kinetics, in which the formation of a passivating layer of alumina is expected to be preceded by the formation of suboxides.<sup>18</sup> The thickening process approached its asymptotic value after 9 h, after a total increase in thickness

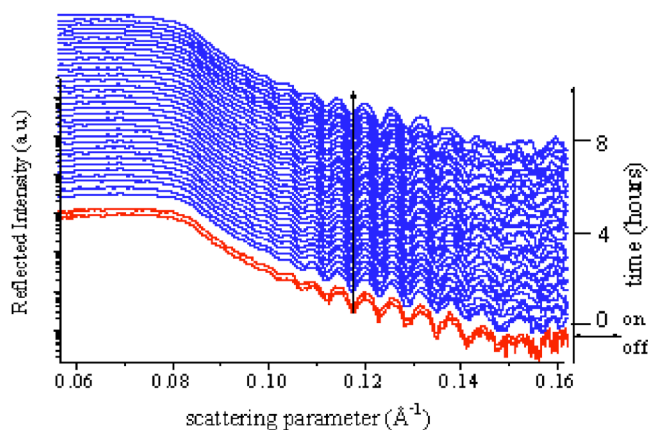


FIG. 3. (Color online) *In situ* EDXR measurements of cell B.

of approximately 32 Å. When this plateau was reached, the light was switched off for 12 h and then turned on again for five more hours to confirm that this photoinduced effect is irreversible and totally completed.

*Elucidating the nature of the photoinduced process.* *In situ* experiment was performed on another device (cell B). It differs from cell A only in that it has an oxygen-free layer (LiF) under the Al electrode, capable of preventing metal oxidation. On the other hand, this thin LiF layer would have no effect on a possible indium diffusion process.

In Fig. 3 the sequence of EDXR patterns collected *in situ* on cell B upon irradiation is compared with those collected before commencing the illumination (two lower curves).

All the patterns overlap perfectly, with no change in the oscillation period being visible. This therefore indicates that the morphology at the Al/LiF interface does not undergo any modification upon working conditions of the device. Hence, it is possible to conclude that this thin buffer layer inhibited the degradation of the Al electrode and, as a consequence, that the effect observed in the case of cell A is due to the Al oxidation. The hypothesis that an indium diffusion process has taken place is therefore ruled out (in contrast to what was observed in the case of OLEDs). Furthermore the morphological stability of cell B confirms that the oxidation of the electrode, observed in the others cells, is limited to the buried interface, as already predicted.

*Quantifying the effect on performances of the device of the photoinduced electrode degradation process.* The efficiency versus time curves are reported in Fig. 4. The curve relative to cell A is characterized by a first (first 15 h) fast

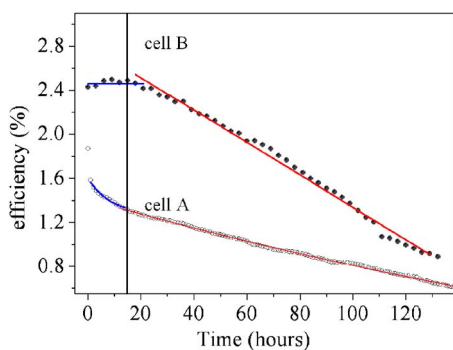


FIG. 4. (Color online) Efficiency curves for cell A and cell B.

exponential decay and a second part that is almost linear, indicating that also in the case of the aging curve, as two subsequent processes take place. It is interesting to compare the efficiency curve of cell B in Fig. 4 with the data of the EDXR experiments [Fig. 2(b)] on the same cell: The Al oxidation that we observed by EDXR is connected to the first aging process described by the exponential decay in Fig. 4. Conversely, the curve in Fig. 4 relative to cell B does not exhibit the same two-step process. In the first 15 h there is no loss of efficiency, as expected observing the EDXR data, which demonstrated that in this case the morphology at the Al/LiF interface is stable and that no oxidation process was present. The interposition of a LiF layer therefore prevents the faster photoinduced degradation occurring in the first 15 h of work.

In conclusion, the results obtained in this systematic study allowed the association of the observed morphological variation with an oxidation process of the Al electrode at the interface with the active layer. The morphological data were compared with the efficiency versus time curves measured for the same devices, showing that this process is responsible for a fast reduction of the efficiency of the device. This negative effect was completely inhibited by interposing a buffer layer of LiF between the electrode and the active organic layer in a new sample. It is worth stressing that the above conclusions were retrieved on the base of real-time *in situ* EDXR measurements only, with no need for any other complementary technique for morphological or structural investigations. It can therefore be predicted that a systematic application of EDXR will be extremely helpful in the development of new organic electronic devices.

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