Application of Equivalent Circuit Models to Monitor the Degradation of Organic Photovoltaic Cells

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Abstract

Organic photovoltaic (OPV) devices have lower efficiency, shorter lifetimes, faster degradation, and poorer stability than inorganic photovoltaics (IPV) in ambient conditions. In this paper, the equivalent electrical circuit of a two-diode model effectively extracts the model-fit electrical photovoltaic (PV) parameters from degraded OPV devices, especially the series (R_s) and shunt (R_sh) resistances. The result shows a better correlation between the resistances of the devices and performance of the devices over the degradation process where the devices are deliberately exposed to ambient conditions under constant illumination. The degradation of the devices is mostly caused by the degradation of the aluminum (Al) electrode from water and oxygen, which correlates to the R_s. However, it is possible that the degradation of the bulk active layer can also occur due to the constant illumination on the device, which causes a reduction of photocurrent.

Keywords: degradation, electrical circuit model, organic photovoltaics, resistances

Introduction

One of the drawbacks of OPV cells is their shorter lifetime or poorer stability compared to IPV cells. In the previous studies, the complex sources of this faster degradation are: (1) Light [1-5], (2) oxygen (O_2) [2,4], [6-9], (3) water (H_2O) [1,7,8,10], (4) metal electrode [11], (5) active layer–metal interface [12,13], (6) Poly(3,4-ethylenedioxy-thiophene):Poly(styrenesulfonate) (PEDOT:PSS) [5,14], (7) thermal stress [3], and (8) lamination [15]. Jorgensen et al. [16] classified all of these causes into two classes: (1) Chemical degradation (light, oxygen, water, metal electrode, active layer–metal electrode interface, PEDOT:PSS) and (2) Physical and mechanical degradation (thermal stress/treatment, lamination).

In the absence of being able to remove the source of OPV degradation, this problem has been tackled in various ways: (1) through the encapsulation process [17-19], (2) by inverting the structure of OPVs [20-22], and (3) by using barrier materials [18,22-24].

The first purpose of this paper is to compare the degradation of devices under ambient conditions using our approach to and devices with and without an interfacial layer of calcium (Ca). Our approach was to deposit a thin layer of Al on top of the active layer, annealed at 140 C, and then to deposit a thicker Al on top. The second purpose is to apply the equivalent electrical circuit of the two-diode model [25] to extract the model-fit to data parameters, especially the R_s and R_sh, to determine how their behavior varies over the degradation time.

Abstrak

Aplikasi Model Rangkaian Setara untuk Memantau Degradasi Sel Fotovoltaik Organik. Divais fotovoltaik organik (OPV) memiliki efisiensi yang lebih rendah, masa hidup lebih pendek, degradasi lebih cepat, dan stabilitas lebih rendah dari photovoltaics anorganik (IPV) pada kondisi udara terbuka. Pada tulisan ini, rangkaian setara dari model dua-dioda secara efektif mengekstrak parameter-parameter listrik fotovoltaik (PV) dari divais OPV yang terdegradasi, khususnya resistansi seri (R_s) dan resistansi paralel (R_sh). Hasilnya menunjukkan suatu korelasi yang lebih baik antara resistansi divais dan kinerja divais selama proses degradasi dimana divais diberi pengurangan konstan pada kondisi udara terbuka. Degradasi divais ini sebagian besar disebabkan oleh degradasi elektroda aluminium (Al) yakni oleh air dan oksigen, yang berkerelasi dengan R_s. Namun, ada kemungkinan bahwa degradasi lapisan aktif juga dapat terjadi karena pengurangan konstan pada divais, yang menyebabkan pengurangan photocurrent.

Keywords: degradation, electrical circuit model, organic photovoltaics, resistances
Materials and Methods

This section covers the details of the process used to prepare and build the devices. All current-voltage (I-V) characteristics presented are taken from the unmasked devices that were tested under the calibrated halogen light in the ambient air.

Device structure. The bulk heterojunction architecture for OPV devices in this study is shown in Figure 1. The substrates were 17.5 mm x 12.5 mm x 0.7 mm glass slides with a patterned coating of indium-tin-oxide (ITO) on one side. On top of this anode, a thin coating (≈50 nm) of PEDOT:PSS is deposited. The active layer of Poly(3-hexylthiophene) (P3HT) and Phenyl-C61-butyric acid methyl ester (PCBM) blend is laid down on top of the PEDOT:PSS. Finally, the top cathode is evaporated, completing the device.

ITO slide preparation, PEDOT:PSS deposition, active layer deposition and cathode evaporation:

ITO slide preparation. ITO glass for this study was purchased pre-patterned from Kintec. It had a sheet resistance of 15 Ω/square and an optical transmission of greater than 80%. The ITO-coated slides were cleaned using the following procedure: The slides were placed in a glass beaker of acetone and sonicated at room temperature for 5 minutes. After sonication, the slides were rinsed three times with acetone. The slides were then submerged in isopropanol and sonicated at room temperature for 5 minutes. After sonication the slides were rinsed three times with isopropanol. Another rinse using reverse-osmosis water was performed three times. Each slide was then dried under a flow of nitrogen gas (N₂). When dry, all ITO-coated slides were then placed in an ozone treatment box for a minimum of 15 minutes. After ozone treatment, the ITO-coated slides were used as soon as possible.

PEDOT:PSS deposition. The PEDOT:PSS solution used in the fabrication of these films was purchased from Heraeus. There are now many variants of PEDOT:PSS on the market; however, in this study, standard “Clevios P” was used, which is an aqueous dispersion of PEDOT:PSS (1.2% by weight). This dispersion has a viscosity of 60-100 mP, and the resulting solid film has a conductivity of 1 S/cm. Before use, the PEDOT:PSS solution was filtered through a 0.45 μm PECD syringe filter to remove large aggregates. Once filtered, the PEDOT:PSS was deposited on the substrate using the Laurell spin coater. Each PEDOT:PSS film was spun at 4000 rpm for 90 seconds, with an acceleration of 1680 rpm per second to give a film ~50 nm thick. A 70 μL of PEDOT:PSS solution was deposited and spread to cover the whole substrate before spinning. After spinning, the finger and common contacts ITO pad of each slide were gently cleaned using a cotton bud. Coated substrates were then placed on a hotplate and baked at 140 °C for 30 minutes.

Active layer deposition. P3HT was purchased from Rieke Metals, Inc., and PCBM was purchased from Solenne BV. P3HT and PCBM were dissolved in a 1:0.8 by weight ratio in chloroform with a total concentration of 18 mg/mL for the formation of the active layers in this study. The solutions were sonicated for 60 minutes to aid dissolution. Once dissolved the solution was transferred to an inert atmosphere (N₂) glove box, along with the PEDOT:PSS-coated cells for active layer deposition. The P3HT:PCBM solution was deposited by spin coating. Then, 65 μL of solution was pipetted onto each PEDOT:PSS-covered substrate. This deposited solution was then spread evenly across the surface using the pipette tip. The substrate was then spun at 2000 rpm for one minute (1680 rpm/s acceleration) to create a thin film of 60–90 nm. Once the film was deposited, the finger and common contacts to the ITO pad were cleaned again using a cotton bud wet with chloroform. Film-coated substrates were transferred to a hotplate in the glove box and heated at 50 °C for 10 minutes to aid the removal of chloroform before evaporating the top layer of Al cathode.

Cathode deposition. An Ångstrom Engineering evaporator was used to deposit the top electrode. All evaporative depositions of metal took place at a pressure lower than 2 x 10⁻⁶ torr. Three evaporative depositions were separately run in this process: Al only (our approach), Ca + Al, and Al only. Ca was deposited at 0.4 Å/s to a thickness of 20 nm. An Al layer was then evaporated over the top with a thickness of 60 nm in each deposition process. The devices were built using the following cathode layer compositions: Device A: 20 nm Al (annealed)/60 nm Al (our approach), Device B: 20 nm Ca/60 nm Al, Device C: 60 nm Al.

Figure 1. Illustration of Device Architecture in Cross-section
Device characterization. Figure 2 shows the I-V measurements system used in this study. The halogen lamp of the overhead projector was used as a light source (Figure 2a). Its intensity at the bottom of the sample holder was measured to be between 0.9 and 1 Sun (90–100 mW/cm²) using a calibrated solar-meter from Solartech, Inc. The communication between the measurement circuit and the computer was achieved using a National Instruments USB data acquisition card, as shown in Figure 2b. The measurement was programmed to continuously run and to hourly record the I-V data using a LabVIEW program. Because the measurement system can only run two fresh samples for each measurement, the experiments in this study were conducted over two separate times of measurement. The first measurement was run for devices A and B. The second one was run for devices A and C. The measurements were continuously run for 66 hours, except in the first experiment, which was run until the efficiency of device B reached 50% of its initial value.

Results and Discussion

To start the discussion, let us again consider the device structures in this study, namely: Device A: (ITO/PEDOT:PSS/P3HT:PCBM/20 nm Al (annealed)/60 nm Al), Device B: (ITO/PEDOT:PSS/P3HT:PCBM/20 nm Ca/60 nm Al), and Device C: (ITO/PEDOT:PSS/P3HT:PCBM/60 nm Al).

After running two separate measurements, we found that both devices A perform similarly closely to each other over the degradation process (see panels a and b in Figure 3). This result shows that the conditions of measurement do not vary much, even though the measurements were conducted at two different times. Therefore, it allows us to compare the performance of all devices in these measurements with confidence.

The results clearly show that device B (the device using an interfacial layer of Ca) has better long-term performance than devices A and C, which parallels previous studies [12]. Over 66 hours of continuous illuminated measurement, all the PV parameters of device B stayed above 60%. Interestingly, device A has a very stable open circuit voltage ($V_{oc}$) and degrades more slowly than device C. There is also a large difference in the amount of time it takes for devices A and C to reach the half-value of their PV parameters compared to device B (see Table 1). Table 1 shows that device A has a better performance through our degradation compared to device C, despite both of them being built without using an interfacial layer Ca. However, after achieving the half-value time, device C shows an exponential degradation for each parameter that is slower than device B, which degrades with a straight line trend.

Figure 4 shows the direct comparison of the degradation of each of the raw PV parameters for devices A, B, and C. The efficiency plot for these devices shows that there is a big drop in the efficiency between the first and second hour for each device. This phenomenon is related to the quick oxidation process of Al forming its native oxide layer in direct contact with oxygen and moisture during the first and second measurements [26], [27]. The graph also shows that the efficiency of device B degrades slowly with a straighter line trend, whereas devices A and C initially degrade faster with an exponential trend. Even though both device A and device C degrade exponentially, they show different exponential trends. Device A has a lower negative exponential power than device C, which means device A degrades slower than device C.
Table 1. The Half-value Time of Device PV Parameters

<table>
<thead>
<tr>
<th>PV parameters</th>
<th>Device A</th>
<th>Device B</th>
<th>Device C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>First meas.</td>
<td>Second meas.</td>
<td></td>
</tr>
<tr>
<td>$V_{oc}$</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>$I_{sc}$</td>
<td>66</td>
<td>63</td>
<td>&gt; 130</td>
</tr>
<tr>
<td>FF</td>
<td>45</td>
<td>54</td>
<td>&gt; 130</td>
</tr>
<tr>
<td>$\eta$</td>
<td>21</td>
<td>18</td>
<td>130</td>
</tr>
</tbody>
</table>

Note: meas. = measurement  n/a = has not achieved yet in this measurement

Figure 3. The Normalized Value of the Efficiency (Circles), $V_{oc}$ (Triangles), $I_{sc}$ (Diamonds), and FF (Squares) for all Devices. Panel (a) and (b) Correspond to the Devices A in the First Measurement and the Second Measurement, Respectively; Panel (c) to Device B; and Panel (d) to Device C

Figure 4. The Comparison of the Raw Values of the Efficiency (a), $V_{oc}$ (b), $I_{sc}$ (c), and FF (d). The Curve with: Circles Correspond to the Device A; Triangles to Device B, and Diamonds to Device C
Panel b shows that the devices have a mostly stable $V_{oc}$ over the degradation time. However, device A performs with a better stability and shows dominance over devices B and C. The stability of the $V_{oc}$ is not followed by the short-circuit current ($I_{sc}$), shown in panel c. Both device A and device B have a linear degradation. However, device A has a higher gradient coefficient, which means it degrades faster than device B (at ~3 times the rate). While the $I_{sc}$ of devices A and B degrades linearly, the $I_{sc}$ of device C tends to degrade exponentially over time, approaching a linear degradation with a slope similar to device A after 40-50 hours.

Panel d again shows linear degradation of fill factor (FF) for device B. By comparison, devices A and C degrade faster with an exponential trend. Overall, only device B shows linear degradation for each PV parameter, while devices A and C show mixed trends.

Instead of comparing the PV parameters of the devices, Figure 5 shows the first and last of the I-V characteristics taken from the degradation study for devices A, B, and C. These plots clearly show that after 66 hours, measurement device B maintains a normal “j-shaped” I-V curve whereas devices A and C show “s-shaped” I-V curves.

The equivalent electrical circuit used to extract the $R_s$ and $R_{sh}$ is the two-diode model [25] as shown in Figure 6. In these equivalent circuit models, the direct current source $I_{ph}$ represents current production in the active layer under illumination. Then, resistors and diodes represent current loss and the dark characteristic of the PV cells, respectively. $R_s$ strongly corresponds to the internal $R_s$ of PV cells, which in turn correlates to the contact quality of each PV layer and the ease of charge transfer between layers. $R_{sh}$ is related to the loss of current through any type of charge recombination and trapping inside PV cells.

Figure 5. The Current-voltage (I-V) for the First (Left) and the Last (Right) Measurement (After 66 Hours); I-V Curves: Panel (a) Corresponds to the Device A; Panel (b) to Device B, and Panel (c) to Device C.
Figure 6. The Equivalent Electrical Circuits of Two-diode Model for OPV. $I_{ph}$, $D_1$, $D_2$, $R_s$, $R_{sh}$, and $I_a$ are the Photocurrent, Diode, Current Flow through the Diode, Series Resistance, Shunt Resistance, and Current Flow Through the $R_{sh}$, Respectively.

Figures 7 and 8 show the $R_s$ and $R_{sh}$, respectively which extracted from the I-V curves. Figure 6 shows that the $R_s$ calculated as an inversion of the I-V curve slope at the last data point has a similar trend and value to the $R_s$ obtained from the model-fit to I-V data. However, the $R_s$ calculated as the inversion of the slope at the $V_{oc}$ has a much larger value in the order of kΩ and tends towards a more random trend, especially for device C. Overall, the $R_s$ obtained from model-fit to data has lower value, showing a better trend.

Generally, the series resistance of all devices using Al only as a top electrode increases over time. According to the degradation process in the OPV device [16], this effectively occurs as a result of the continuous oxidation of the Al electrode forming Al oxide ($\text{Al}_2\text{O}_3$). In our approach, the annealing process of a thin layer of Al before a thicker layer of Al prevents a broader oxidation. We know that the $\text{Al}_2\text{O}_3$ exhibits excellent electrical insulation [28], [29]; therefore, the resulting increase of $R_s$ during the measurement makes the device degrade by lowering the charge extraction, therefore performing a lower efficiency. Interestingly, the $R_s$ values of device B are constant over the time of this degradation experiment. This result shows that the Ca interface in this device protects Al from degradation (water and oxygen) and maintains a better transport of the charges at the interface. If this is happening, what causes the degradation of $I_{sc}$ of this device as shown in Figure 4 panel c? One possible answer is that degradation occurs in the active layer as a result of the continuous light illumination on the device, as mentioned in the introduction section as one of the degradation sources [1-5]. If this is true, then the degradation in devices A and C is caused not only by the degradation of the Al cathode but also by the degradation of the active layer due to the light illumination.

On the other hand, Figure 7 shows the degradation of the $R_{sh}$ for devices A, B, and C. The $R_{sh}$ presented in this figure is calculated by two approaches: the $R_{sh}$ as a value of the inversion of the I-V curve slope at the $I_{sc}$ and the $R_{sh}$ as extracted using the equivalent electrical circuit.
Figure 8. The Shunt Resistance $R_{sh}$ Extracted from the I-V Curve every Three Hour. Panel (a) Corresponds to the Device A; Panel (b) to Device B, and Panel (c) to Device C. Resistance Curve: Diamonds Corresponds to the $R_{sh}$ from Model-fit to I-V Data and Circles to $R_{sh}$ Calculated from the Inversion of the Slope at the $I_{sc}$ model. Both of these approaches give a relatively similar result with the same trend, except for device B. The $R_{sh}$ value of devices A and C shows relatively constant compared to device B with a linear trend. Even though device B does not show a better trend for $R_{sh}$ and indeed shows a large error across the data set, the value of this resistance is relatively higher than devices A and C, suggesting a lower recombination in the device.

**Conclusions**

It has been shown that the equivalent electrical circuit model effectively extracts the model-fit electrical PV parameters, especially the $R_s$ and $R_{sh}$. A better correlation has been achieved between the resistances of the devices and performance of the devices over the degradation process in this study where the devices are deliberately expose to ambient conditions under constant illumination. The degradation of the device is mostly caused by the degradation of the Al electrode from water and oxygen. This degradation is correlated to the $R_s$. However, it is possible that the degradation of the bulk active layer can also occur due to the constant illumination on the device, which causes a reduction of photocurrent.

Even though the devices using our approach are dominated by the devices using interfacial layer Ca, our approach still shows potential as it exhibits a stable $V_{oc}$ and a higher efficiency for at least 5 hours under ambient conditions when it reaches the efficiency of the device using interfacial layer Ca. If this measurement is taken for encapsulated devices, the device using our approach should exhibit a better performance, or at least a performance similar to the device using an interfacial layer of Ca. Furthermore, the device with an added interfacial Al$_2$O$_3$ layer shows much better performance and slower degradation than the devices with Al-only electrode.

This prospect is very promising for a reel-to-reel large-scale printing of OPV devices. Instead of using two different materials, i.e., Ca and Al, for a cathode electrode, our approach just uses Al. Building devices using this approach is a considerably easier process and could result in a lower production cost than the conventional design.

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**References**


Application of Equivalent Circuit Models to Monitor

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Materials/Thermal_Spray/ProductInformation/Ceramics_Aluminum_Oxide/DSMTS_0005_1_AlO.pdf.