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A building-block approach to the development of an equivalent circuit model for organic photovoltaic cells

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ABSTRACT

A novel approach to equivalent circuit modelling of organic photovoltaic (OPV) cells capable of simulating both optimal and degraded devices has been developed. Freshly made OPVs (composed of an active layer with a blended poly (3-hexylthiophene) (P3HT) and indene-C60 bisadduct (ICBA) film), that exhibit a characteristic 'J' shaped current-voltage (I-V) curve both in the dark and under illumination, are typically fitted to a one-diode equivalent circuit model. However, as device performance deteriorates, the I-V curve undergoes a series of changes resulting in the evolution of an 'S' shaped I-V curve, for which there is no widely accepted equivalent circuit model. Here we present a building-block approach to develop a simple equivalent circuit model which provides an excellent fit to experimental I-V data spanning the continuum from the ideal 'J' to degraded 'S' shaped curves. Applying this new model to P3HT:ICBA devices provides insights into the physical processes that occur during degradation.

1. Introduction

Organic photovoltaic (OPV) cells are an established solar energy conversion technology that are light-weight, flexible and can be easily fabricated at low cost [1–6]. Understanding the underlying physics of the OPV power conversion process is essential to determine the limiting factors that hinder their efficiency. One approach is to understand the electrical behaviour of OPVs when modelled with an equivalent electrical circuit. The most common equivalent electrical circuit used to model OPVs is the one diode model (ODM) [7–10]. This model has been adapted from inorganic photovoltaic cells (IPVCs), where it is derived by considering their electrical behaviour as a p-n junction [11]. The application of the ODM to OPVs seems reasonable given that bulk heterojunction OPVs consist of a p-type organic material (acting as an electron donor) blended with an n-type organic material (acting as an electron acceptor) to form an intermixed array of p-n junctions [12,13].

Although the ODM has been widely applied to OPVs, it is unable to account for all of the features of the OPV current-voltage (I-V) characteristics. In particular, a common feature of these I-V characteristics is the presence of a kink, which produces an 'S' shaped I-V curve. In these circumstances, the ODM is simply incapable of fitting the I-V characteristic. The kink reduces the fill factor (FF) which in turn lowers the power conversion efficiency (PCE) of the OPVs [14]. The cause of this behaviour has been variously attributed to cathode evaporation resulting in a low quality interface [15], cathode oxidation [16], oxygen diffusion into the device through an aluminium cathode [16], charge accumulation [17], imbalance in mobility of the charge carriers [18], restricted charge transport at interfaces [19,20], photodesorption and oxygen redistribution [21], and hole-transport limitations in the donor (hole transport) layer [22]. Other reports have suggested the S-shaped curve is caused by interfacial dipoles, defects, and traps [23]. Dynamic Monte Carlo modelling further shows that efficient organic photovoltaic systems are more susceptible to exhibiting 'S' shaped I-V curves due to interface effects [24].

Over the past decade or so, several authors have proposed modifications to the ODM to better describe the S-shaped electrical behaviour of OPVs, with an excellent review reported recently [25]. In 2006, Mazhari proposed a 3-diode model to describe a voltage-dependent photocurrent in OPV devices [26]. The first attempt to model 'S'-shaped I-V curves in OPVs directly was described in 2008 using a 2-diode model by de Castro et al. [27]. In 2010, del Pozo et al. [28] used de Castro's model to extract the electrical parameters of 'S' shaped I-V curves in polymer/fullerene OPVs. But none of these models are capable of fitting the full voltage range of the OPV's I-V curve, especially the quadrant beyond V_{oc}, which is related to the series resistance of the cells. In 2013, García-Sánchez et al. proposed a solution to fitting the I-

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V curve far beyond V_{oc} through the addition of a third diode [29]. In 2016, a further modification of this 3-diode model was proposed by de Castro et al. who included an additional shunt resistance and removed the associated series resistance [30].

Previous work in this laboratory has focussed on developing a new building block approach to modelling OPV devices [31]. This model has already been implemented by others, for example, Furchi et al. have used it to explain the behaviour of MoS_2: WSe_2 cells and other cells where the photocurrent generation relies on high exciton binding energies [32]. In addition, Pozza et al. have used this model to characterise the response of R2R printed P3HT:PCBM devices tested under ISOS conditions [33]. However, a complete description of the model, including the origin of the building block approach, has yet to be reported.

In light of the interest in this new model, in this paper we detail fully our building-block approach to the development of an equivalent circuit model for OPV devices. In particular, we show how we start by identifying the key features of the I-V curve and then discuss how discrete circuit elements can be used to fit these features. Using this approach, we demonstrate that it is now possible to fit the full OPV I-V curve using the minimum number of circuit elements. Finally, we apply the new model to the degradation of OPV devices and show that the model provides physical insights into the degradation process.

2. Experimental details

2.1. Device fabrication

Patterned indium tin oxide (ITO) substrates were cleaned in an ultrasonic bath using detergent, acetone and iso-propanol. After drying the slides, a 75 µl filtered poly (3,4-ethylenedioxythiophene)/(poly (styrenesulfonate) (PEDOT:PSS, Baytron P) solution was spin-coated onto each ITO slide at 4000 rpm for 90 s. The slides were then dried in an oven at 140 °C for 30 min. The active layer solution for the BHJ devices was prepared by blending the poly (3-hexylthiophene) (P3HT) with a novel indene-C60 bisadduct (ICBA, Lumtec Corp.) in a 1:0.8 ratio. The blend was dissolved in a chloroform solution at a concentration of 18 mg/ml and sonicated for 60 min. The P3HT: ICBA BHJ blend was spin coated onto the ITO/PEDOT: PSS substrates, which were then dried on a hot plate at 50 °C for 4 min in a nitrogen glove box. These active layers were then transferred into a vacuum chamber for electrode evaporation. A calcium/aluminium cathode (Ca = 20 nm, Al = 90 nm) was then evaporated on top of the active layer. Eight individually addressable devices were fabricated on each substrate, with the active area of each device (determined by the overlap between the ITO and the metal) being approximately 14 mm^2.

2.2. Device characterization

The devices were firstly annealed on a hot plate at 140 °C for 4 min. Then four devices (Fig. 1, devices 3, 4, 5 and 6) were encapsulated using PVC tape as a protection layer from humidity and oxygen ingress, and the remaining four devices (Fig. 1, devices 1, 2, 7 and 8) left unencapsulated. Continuous photocurrent-voltage (I-V) measurements were conducted every hour under ambient conditions using a 12 V halogen lamp to illuminate all eight devices. The light intensity was measured to be 100 mW/cm^2 by a silicon reference solar cell (FHG-ISE). The I-V data of each device were automatically recorded for several days.

3. Development of the equivalent circuit model

The ideal (or 'J'-shaped) photovoltaic I-V curve has been described traditionally using the ODM (Fig. 2).

Using this equivalent circuit model, the total current is given by:

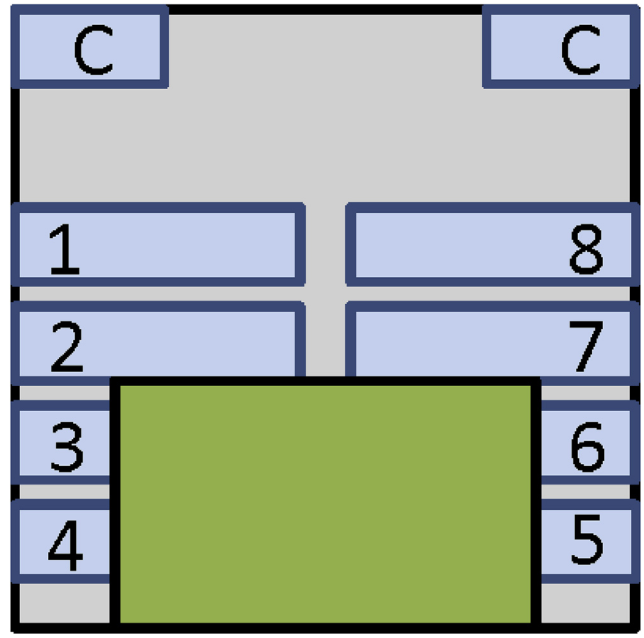

Fig. 1. Schematic drawing of the OPV device geometry and degradation study. Each substrate has 8 individual devices (electrodes 1–8) and a common contact (electrode C). Devices 3, 4, 5 and 6 were encapsulated as shown by the green area and devices 1, 2, 7 and 8 were left unencapsulated. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

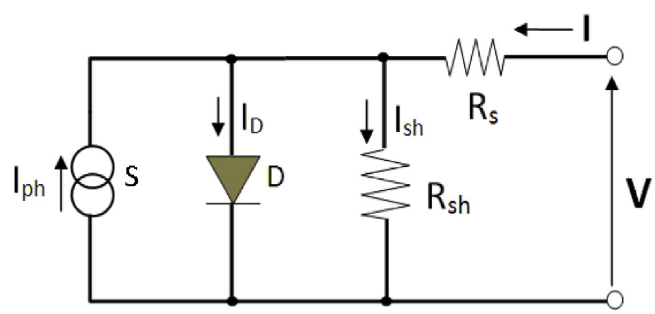

Fig. 2. The ODM equivalent circuit, incorporating a current source, S, diode, D, shunt resistance, R_{sh} and series resistance, R_s.

$$I = -I_{ph} + I_D + I_{sh} \tag{1}$$

where I_{ph}, I_D, and I_{sh} are the photocurrent, diode current and shunt current respectively. Thus, by substituting expressions for the diode equation and the shunt current this expression can be expanded to give the well-known ODM:

$$I = -I_{ph} + I_0\left[\exp\left(\frac{q(V - IR_s)}{nkT}\right)\right] + \frac{V - IR_s}{R_{sh}} \tag{2}$$

where k, T, q are the Boltzmann constant, temperature, and the elementary charge, respectively. The main parameters I_o, I_{ph}, n, R_s, and R_{sh} are the saturation current of the diode D, the photocurrent, the ideality factor of the diode, the series resistance, and the shunt resistance, respectively. For optimised OPV devices, Equation (2) provides a good fit to the ideal 'J'-shaped diode characteristics.

However, the need for a new approach to the development of an equivalent circuit model for OPVs is perhaps best illustrated in Fig. 3, which shows the I-V characteristic for an as-fabricated OPV device (Fig. 3 (a)) and an OPV device fabricated under the same conditions following exposure to ambient air (Fig. 3 (b)). These two plots highlight the fact that the OPV I-V characteristic transitions from the ideal 'J'-