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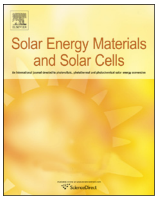

Probing individual subcells of fully printed and coated polymer tandem solar cells using multichromatic opto-electronic characterization methods

Thue T. Larsen-Olsen, Thomas R. Andersen, Henrik F. Dam, Mikkel Jørgensen, Frederik C. Krebs*

Department of Energy Conversion and Storage, Technical University of Denmark, Frederiksborgvej 399, 4000 Roskilde, Denmark

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ABSTRACT

In this study, a method to opto-electronically probe the individual junctions and carrier transport across interfaces in fully printed and coated tandem polymer solar cells is described, enabling the identification of efficiency limiting printing/coating defects. The methods used are light beam induced current (LBIC) mapping, External quantum efficiency (EQE) measurements, and monochromatic current–voltage (*I*–*V*) characterization. Using these methods, inherent limitations to the accuracy of EQE and LBIC measurements on non-ideal tandem solar cells are identified and described through the use of a small-signal electrical model. The model is able to predict the EQE spectrum of the non-ideal polymer tandem solar cell, using extracted values of shunt- and series resistance of the individual junction of the tandem cell. This finally enables LBIC mapping of the individual junctions of the tandem polymer solar cells, using a combination of light and voltage-biasing.

1. Introduction

As a renewable energy source, polymer solar cells (PSCs) have the celebrated potential of enabling energy deliverance on the TW scale, necessary for a fossil fuel-free future [1,2]. This potential is owed to the possibility of very fast and scalable fabrication using roll-to-roll methods and cheap readily available materials, coupled with the proven efficiency of the polymer-fullerene based photovoltaic conversion mechanism [3,4]. With laboratory efficiencies consistently pushing towards the 10% power conversion efficiency (PCE) limit predicted by the Scharber-model for a polymer-fullerene based single bulk heterojunction cell [5,6], the introduction of multiple junction PSCs have enabled to increase the record PCEs further [7–9]. However, the introduction of one, or indeed several, additional junctions infers both a considerable complication of the solar cell processing procedure and additional costs in terms of energy and materials. The latter has recently been investigated with the main finding that the additional embodied energy required in the processing of a two-junction tandem PSC would be balanced in terms of energy payback time, with only a 20% increase in performance as compared to the best performing single-junction cell [10]. The technical difficulties involved in the successful processing of multi-junction PSCs from solution is in most cases due to the fact that all active layers commonly have non-orthogonal solubility: they must be coated from similar and mutually dissolving solvents. This puts special demands on the sub-junction connection structure in serially connected tandem cells called the recombination layer (RL), which must both give a quasi-ohmic contact between the sub-junctions and act as a solvent barrier. This is a challenge, which so far has been solved almost exclusively for small area devices fabricated by spin coating on rigid substrates [7–9,11–15]. However, as previously shown, a process which yielded working tandem devices on glass substrates cannot by default be successfully transferred to a roll-to-roll (R2R) platform, as the change of substrate and processing conditions puts other strains on the RL [16,17]. The solution was to orthogonalize the process, by coating the second junction from water instead of a chlorinated solvent. This limits the available materials since there are few reports of donor polymers with such an alternative solubility. Another approach is to render the first processed junction insoluble using either thermo-cleavable materials or by cross-linking [18–20]. A more versatile solution would be to have a solvent resistant RL as this would give the freedom of choice in terms of active layer materials. Recently, Andersen et al. has reported one such RL, first demonstrated on a mini-roll coater system [21], and finally also shown to enable large scale, fully R2R manufactured tandem PSCs [22].

These large area tandem PSCs presents a very complex multilayer structure of up to 14 layers which are discreetly printed or coated on top of each other. Consequently, the task of locating processing defects

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* Corresponding author.
E-mail address: frkr@dtu.dk (F.C. Krebs).

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or weak points in the structure, in order to control the process and also optimize the efficiency of the devices, becomes an important challenge. In multilayer printing and coating in-line quality control is essential [23]. But a final verdict of the device performance is cast by the optoelectronic characteristics of the complete PSC, and as this study will show, special considerations must be made when assessing these for the case of large area tandem PSCs. Standard current–voltage (*I–V*) characterization yielding the overall PV-parameters have been demonstrated in a R2R setup for PSCs but gives limited information on the individual sub-junctions of the tandem cell [24]. Gilot et al. successfully extracted the individual sub-junction *I–V* characteristics when they combined external quantum efficiency (EQE) measurements and optical modeling [25,26]. Light-beam induced current (LBIC) mapping have recently been demonstrated as a very versatile and potentially fast method of R2R characterization of PSCs [27]. LBIC is a well-established technique within the field of photovoltaics [28–30], where it has found main usage as simple 2D photo response mapping for locating processing defects in single junction solar cells [28–30] and modules [31–34], while more advanced setups have enabled more detailed analysis [27,35–38]. In a few instances it has also been demonstrated on inorganic multi-junction solar cells [39,40]. Most LBIC systems rely on relatively slow lock-in techniques which are not applicable to fast in-line characterization. In the present work, a much faster LBIC method is presented, which uses different probe lasers combined with a voltage and light bias system, in order to enable characterization of non-ideal tandem PSCs.

By combining three methods of opto-electrical characterization and a small-signal equivalent circuit model, this study aims at characterizing the individual sub-junctions in the tandem PSC to identify defects and efficiency limiting areas. The methods can be tailored as either in-line fast assessment tools or for more in-depth analyses. On the basis of the small-signal model, current–voltage (*I–V*) characterization using monochromatic light sources allows for assessing the *I–V* characteristics of the individual junctions, while EQE and light-beam induced current (LBIC) mapping allows 2D mapping of the spectral response of the individual junctions. Furthermore, the robustness of the small-signal model is shown through the simulation of tandem EQE spectra, which also allows for identification and explanation of inherent challenges concerning the extraction of correct individual sub-junction *I–V* characteristics and EQE spectra for non-ideal tandem PSCs.

1.1. The tandem solar cell basics

For the two-terminal serially connected tandem PSCs used in this study the challenge is that an electrical characterization will give a combined response from the two junctions in accordance with Kirchhoff's laws for serial connections. These current–voltage characteristics are shortly reviewed in the following:

For a serially connected two-terminal tandem cell with ohmically connected subcells (1 and 2), one has:

$$V_T = V_1 + V_2 \tag{1}$$

$$I_T = I_1 = I_2 \tag{2}$$

At open circuit this leads to the following prediction of the tandem V_{OC}:

$$V_{OC,T} = V_{OC,1} + V_{OC,2} \tag{3}$$

At short circuit, one has:

$$V_T = 0 \Rightarrow V_1 = -V_2 \tag{4}$$

$$\Rightarrow I_{SC,T}(0) = I_1(V_1) = I_2(-V_1), \tag{5}$$

where $I_{SC,T}$ is the tandem short circuit current, and the operation voltage is given in the parenthesis. As suggested by Eq. (5), the tandem short-circuit current will depend on the *I–V* characteristics of the individual subcells, so without assumptions on the shape of these, one has only a general estimating constraint:

$$\min(I_{sc,1}, I_{sc,2}) \le I_{sc,T} \le \max(I_{sc,1}, I_{sc,2}) \tag{6}$$

It is more instructive to look at the subcell-tandem *I–V* relations graphically as in Fig. 1 showing how the tandem *I–V* curve is constructed according to Eqs. (1) and (2) from the subcell *I–V* characteristics. As can be seen, the *I–V* curves in Fig. 1 represent a realistic case for PSCs, with relatively low shunt resistance and high series resistance reflected in sloped characteristics around short circuit and open circuit respectively.

As mentioned, the two-terminal tandem cell only allows measuring the tandem *I–V* curve while the actual subcell *I–V* characteristics are unknowns. They can most simply be estimated by fabrication of single junction reference cells which mimic the subcell structure in combination with corrections for spectral mismatch [41]. Another already mentioned method combines EQE-measurements with optical simulation. However, as we will show in this study, non-ideal *I–V* characteristics (as exemplified in Fig. 1) as well as defects induced by processing, makes these methods of prediction imprecise for some tandem PSCs.

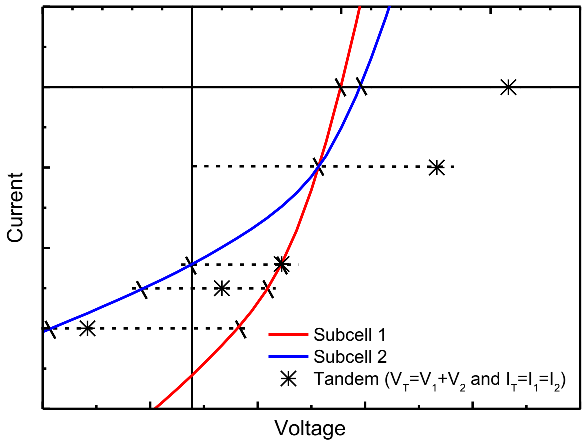

Fig. 1. Principle relationship between the *I–V* characteristics of the two-terminal serially connected tandem and its two subcells. The subcell voltages add up at equal current, as indicated by the dashed lines.

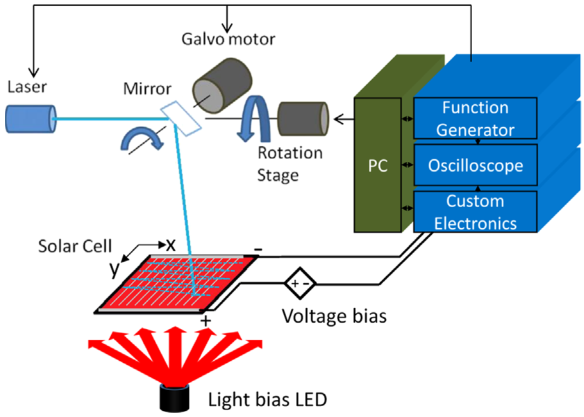

Fig. 2. The LBIC setup as described earlier [27]. With the addition of light biasing using LEDs with wavelengths of either 445 nm or 660 nm.