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Charge extraction with linearly increasing voltage: A numerical model for parameter extraction

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Abstract

An accurate determination of the charge carrier mobilities is essential to model and improve organic solar cells. A frequently used method to determine charge carrier mobilities is the charge extraction by linearly increasing voltage technique (CELIV). In this technique a voltage ramp is applied to the device in order to extract free charge carriers inside the bulk. The free charge carriers can be created by injection or by a short light flash (photo-CELIV). With a simple analytical formula the mobility is commonly estimated on the basis of the temporal position of the current peak.

We simulate the photo-CELIV experiment with a fully-coupled electro-optical model to analyse the accuracy and limitations of the analytical formulas that are used to calculate the mobilities. We show that for thin film solar cells RC-effects are problematic and can lead to inaccurate results. If RC-effects are negligible only the order of magnitude of the fast carrier mobility can be determined using the analytical formula. We measure CELIV currents for several voltage slopes and transient photo-currents of an organic bulk heterojunction solar cell. By fitting our numerical model to the multiple curves we show that important material parameters like the electron mobility, hole mobility, charge generation and recombination efficiency can be determined using numerical parameter extraction.

Keywords: CELIV; Charge carrier mobility; Numerical simulation; Parameter extraction; Drift-diffusion

1. Introduction

Record solar power conversion efficiencies up to 8.1 % (Solamer, 2010) for organic solar cells are encouraging but still too low for large scale energy production. To further improve the efficiency and also the lifetime of organic solar cells it is essential to understand the device physics and to both identify and quantify the limiting factors. Measuring current–voltage-characteristics is restricted to the determination of performance parameters like the power conversion efficiency and the fill factor and thus gives only a limited insight into the underlying physical processes. More fundamental physical parameters including charge carrier mobilities and recombination efficiency become accessible by transient measurement techniques. One of these dynamic measurement techniques is charge extraction with linearly increasing voltage (CELIV) and is frequently used to determine mobilities of organic and inorganic solar cells.

In order to measure charge carrier mobilities, the CELIV technique has some significant advantages compared with other known techniques. For time-of-flight (TOF) (Mark and Lampert, 1970; Mort and Pai, 1976) measurements a special sample preparation is needed. TOF is only possible with thick layers (above 2 μm) which is not feasible for spin-coated organic materials. CELIV can be done with regular solar cells. An other well-known technique is the steady-state, trap-free, space-charge limited current method (TF-SCLC) and the dark injection

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space-charge limited transient current method (DI-SCLC) (Mark and Lampert, 1970). Both techniques can only be used for unipolar devices whereas CELIV can extract the faster charge carrier mobility in bipolar devices.

In the CELIV experiment free charge carriers that are inside the device are extracted with a linearly increasing voltage. The free charge carriers are either equilibrium carriers (due to doping or impurities), the charge carriers are injected by the electrodes or they are generated by a light pulse typically performed with a short laser flash.

Due to the linearly changing voltage a constant displacement current occurs due to the capacitance of the cell. The charge carriers that are extracted lead to an additional current that peaks at a characteristic time t_{max}. With the peak-time t_{max}, the thickness of the sample d and the voltage slope A the mobility of the faster carrier μ can be calculated according to Juska et al. (2000, 2001).

$$\mu = \frac{2 \cdot d^2}{3 \cdot A \cdot t_{max}^2} \cdot \frac{1}{\left(1 + 0.36 \cdot \frac{\Delta j}{j(0)}\right)} \quad (1)$$

The factor $1 + 0.36 \cdot \Delta j/j(0)$ is an empirical correction for the redistribution of the electric field where $j(0)$ is the displacement current offset and Δj is the current overshoot (Juska et al., 2001). The model used to derive the basic equation $\left(2 \cdot d^2/(3 \cdot A \cdot t_{max}^2)\right)$ is a simple unipolar drift-only model that assumes perfect extraction and an initially constant charge distribution.

Bange and co-workers recently presented a new correction function for the analytical CELIV expression. In their study a numerical model is used to solve the drift-diffusion equations to derive an empirical correction function depending on Δj and $j(0)$.

Lorrmann et al. (2010) generalised the CELIV theory and presented a parametric equation as a solution for the differential equation that has been derived by Juska et al. (2000). The CELIV formula $2 \cdot d^2/(3 \cdot A \cdot t_{max}^2)$ is the analytical solution of this differential equation and is derived with the assumption of low conducting materials. In contrast the parametric equation is valid for all conductivities but needs to be evaluated computationally.

All the mentioned techniques to analyse transient CELIV currents follow the same basic assumptions like a spatially constant charge carrier distribution at the beginning. For a more comprehensive description of the physical processes we introduced a fully-coupled, electro-optical, numerical simulation (Neukom et al., 2010). We solved the drift-diffusion equations spatially resolved, calculated the initial distribution of electrons and holes and considered the creation and recombination of charge carriers, the energetic barriers (thermionic injection) and the series resistance in the electric circuit of the measurement.

In this paper we present a method for numerical parameter extraction on the basis of CELIV currents and compare numerical simulation with the analytical approach. The comparison of all different techniques to analyse transient CELIV currents is beyond the scope of this study. Because all the mentioned analytical approaches are based on the same basic simplifications, its deviation to our comprehensive numerical approach is similar. For the comparison of analytical calculation and numerical simulation we use the most frequently used formula (Eq. (1)).

2. Experimental

The device investigated in this study consists of a layer structure as listed in Table 1. The active layer of the solar cell consists of novel small bandgap p-type polymer PT5DPP (Fig. 1) provided by BASF blended with PCBMC70. The samples are fabricated by spin-coating of PEDOT and the active polymer blend on a glass substrate with pre-structured ITO-electrodes. The top electrode is deposited by thermal evaporation in vacuum. For more details about the fabrication see (Offermans et al., 2010). The active area of the solar cell is 0.04 cm^2.

The voltage ramp used in the CELIV experiment is applied by an arbitrary waveform-generator (Picotest G5100A). The cell is illuminated by a pulsed LED (Kingbright L-7113PBC-Z) with a peak wavelength of 468 nm and driven by a second arbitrary waveform-generator of the same type. The transient current is measured by a 12 Ω resistor in combination with a voltage amplifier (Femto HVA-10M-60-B). The transient voltages were measured by a digital storage oscilloscope (Acute DS-1302).

3. Model

In this study we use a fully-coupled opto-electrical model to analyse the experimental photo-current transients. The model described in this chapter is implemented

Table 1
Layer structure of the organic solar cell.

Layer	Thickness	Material
0	Semi-∞	air
1	2 mm	Glass
2	75 nm	ITO
3	60 nm	PEDOT:PSS
4	90 nm	PP5DPP:PCBMC70 (1:2)
5	1 nm	LiF (neglected)
6	100 nm	Aluminium

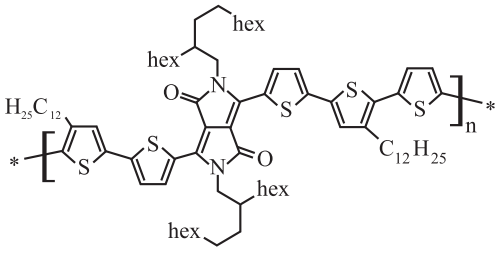

Fig. 1. Chemical structure of PT5DPP (BASF).