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# Calibration procedure for solar cells exhibiting slow response and application to a dye-sensitized photovoltaic device



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#### ABSTRACT

Dye-sensitized Solar Cells are generally known to possess a slow response to changes in photocurrent generation by incident light. Electrical power measurements of photovoltaic (PV) devices can only be accurately made if sufficient time is allowed for complete photocurrent generation. The generation time increases from typically a few milliseconds in the case of c-Si devices, over tens to hundreds of milliseconds for technologies like backcontact and hetero-junction solar cells, to even longer times for dye-sensitized and some types of perovskite solar cells. In this work we propose a procedure for calibration of slow responding PV devices based on an accurate evaluation of their response time. Starting from a quantitative analysis of the photocurrent signal versus chopping frequency on the spectral responsivity set-up, the measurement of a dye-sensitized solar cell was performed at 1 Hz chopping frequency. Then current-voltage (I-V) measurements were performed at different sweep-times and directions, in order to determine the correct parameters for I-V characterization. Combining appropriate spectral responsivity (for determination and correction of spectral mismatch) and I-V measurements yielded a reliable calibration of the device including measurement uncertainty estimation. Based on this work criteria for a reliable calibration of slow responding PV devices are formulated, fulfilling all requirements specified in the standards (IEC 60904 series and IEC 60891).

#### 1. Introduction

The rapid improvement of dve-sensitized (DSSC) and perovskite (PSC) solar cell performances and the related growing interest for these emerging photovoltaic (PV) technologies [1,2,3] clearly indicate the need for methods and procedures to reliably measure and characterize PV devices known to possess a slow response for photocurrent generation by incident light. Electrical parameters measurements of these devices under standard test conditions (STC), as defined in the IEC 60904 series of standards, can be accurately made only if sufficient time is allowed to complete the photocurrent generation. This time is usually much longer for DSSC's and PSC's than for typical crystalline silicon devices [4,5]. Their long response time to the incident light affects both spectral responsivity (SR) and power measurements [6,7,8] resulting in unreliable results, if the measurement time does not take the slow response of the device into account. Moreover, different devices can show different response times, i.e. a procedure valid for standard dye-sensitized devices with a liquid electrolyte may be inappropriate for dye-sensitized devices with a solid holes transport material or some perovskite devices.

IEC 60904-1 [9] contains a generic note warning that I-V measurements may be influenced by the voltage sweep rate and sweep direction and requests an analysis without giving much detail apart from the requirement for optimal overlap of current-voltage sweeps in opposite directions. Performance characterization of DSSC's was described previously [10] focusing on the sweep speed and direction and presenting complete SR measurements at different chopping frequencies. However, no clear criterion was formulated how to determine the appropriate chopping frequency. In a review [6] the shape and distortion of the signal under monochromatic chopped light was presented, but again without a clear quantitative criterion on selection of appropriate chopping frequency apart from simple visual inspection. As in [10] full SRs measured at different chopping frequencies were presented as well as IV curves in opposite sweep directions. More recently [11] electrical characterization of PSC's was discussed. The main feature of these devices was found to be their inherent instability, so that the measurement depended significantly on stabilization and degradation, both depended on the illumination of the devices prior to and during measurement. In this work we propose a procedure for precise calibration of these devices: it consists of firstly an evaluation of

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the response time of the device under test (DUT) and, consequently, a reliable calculation of the parameters to be used when characterizing them. The determination of the chopping frequency to be used in SR measurements is the first step of the procedure and is described in the time response analysis (Section 3.3). As opposed to previous works [6,10] we analyze the signals of the chopped light quantitatively to give a more objective criterion for the determination of the chopping frequency. The quantitative analysis is performed under chopped broadband light, providing a stronger output signal from the device under test. This condition allowed to freely and continuously vary the chopping frequency and to determine the device response in short time (5 min).

Once determined, the SR measurements were performed with the apparatus available at the European Solar Test Installation (ESTI) after necessary modifications and validation of the setup at the low chopping frequency. Prior to electrical characterization, I-V measurements were performed at different sweep times and sweep directions to ensure that the device was measured at equilibrium conditions. The combination of SR measurements with I-V characterization vielded a reliable calibration and associated uncertainties of the device at STC following IEC 60904 series and IEC 60891. The proposed procedure was applied, as a test, to the calibration of a dye-sensitized solar cell with a liquid electrolyte. This was one example; however, the procedure presented here and the criteria formulated are generally valid and can be widely applied when the response time of the DUT is unknown. Based on this work criteria for a generalized procedure for the calibration of PV devices with slow response are proposed, which may be included in future standards.

#### 2. Calibration procedure

In this work we will focus on two standards: the IEC 60904-1 [9] (measurements of the performance of PV devices), and the IEC 60904-8 [12] (measurements of PV devices spectral responsivity). The latter allows for the calculation of the spectral mismatch factor (MMF) as described in IEC 60904-7 [13]. Once this factor is known, it can be used to correct the electrical performance measured under a specific light source (whose spectrum is measured) to the reference solar spectrum (IEC 60904-3 [14]), taken as universal reference when characterizing terrestrial PV devices. The MMF is one of the required corrections to complete the calibration procedure applicable to every PV device. For standard c-Si PV devices the procedures to perform reliable measurements are well established among reference laboratories like ESTI [15]. However, in case of emerging PV technologies like DSSC and PSC, new procedures need to be specifically developed taking into account the device characteristics, e.g. the slow time response. In this work the procedure developed at ESTI for the calibration of emerging PV technologies having slow response is presented. An example of its application to the particular case of a single DSSC involving a liquid electrolyte is presented in Section 3. It consists of an initial quantitative time response analysis needed to determine the chopping frequency suitable for SR measurements and consequently of a set of multiple I-V measurements performed at increasing sweep times and changing of the sweep directions.

In the time response analysis we propose to illuminate the DUT with broadband light chopped at a specific frequency and measure the generated photocurrent. Varying the chopping frequency from low to higher values a threshold point can be found after which the peak-topeak amplitude variation of the current signal decreases. This is the maximum chopping frequency that can be used when measuring the SR to ensure that the DUT is measured under suitable conditions. Standard chopping frequency values for DSSC devices are, for instance, around 1 Hz. Additionally, SR measurements were performed at three chopping frequencies around the threshold frequency point with different wavelengths of monochromatic lights. This was done to check possible differences in DUT response depending on whether the chopped light is broadband or monochromatic. If the relative signals are independent of wavelengths, such an effect can be excluded. To ensure reliable I-V curves, not influenced by the sweep time, we propose to perform multiple I-V measurements at increasing sweep times and changing the sweep directions. Reproducible I-V curves are required in this case and quantitative agreement between measurements performed in opposite sweep directions must be found.

#### 3. Results

#### 3.1. Devices

Three devices were involved in the measurements presented. Two reference devices used to measure incident irradiance both in SR and I-V measurements (REF) and one DUT. The reference devices consisted of two calibrated c-Si cells with an active area of 400 mm<sup>2</sup> and with an internal temperature sensor (PX302C for SR measurements and PX305C for I-V measurements). The DUT was a dye-sensitized single cell in a glass-glass construction having an active area of 77.4 mm<sup>2</sup> (total device area 550 mm<sup>2</sup>) (ESTI code PL84). The latter was provided by an external laboratory under a sample transfer agreement. Electrical wires were glued with silver paste to the electrodes. A sample holder was built to attach a PT100 temperature sensor to the rear of the DUT. A picture of one REF and DUT taken during SR measurements is shown in Fig. 1.

#### 3.2. Spectral responsivity measurements setup

The SR of a PV device is one of the key characteristics and represents the device response (in term of generated photocurrent) to quasi-monochromatic light signals at various wavelengths. Practically, in the calibration of a PV device the SR is one of the inputs used to calculate the spectral mismatch factor and to correct the measured I-V curves to STC accommodating for any spectral mismatch between the reference spectrum and the spectrum of the light source used for measurement. Techniques for SR determination are well known [16,17] and the procedure to perform measurements on a PV device is described in the IEC 60904-8 [12]. At ESTI the AC method is implemented and a dedicated setup is available for SR measurements of PV devices (cells and mini-modules). The schematic of the setup has been described in more details [16,18] and is shown here in Fig. 2. The setup consists of a continuous monochromatic illumination generated by a Xenon light source coupled with band-pass filters (mounted on five filter wheels with 16 filters each), covering the wavelength range from 300 to 1750 nm with a band-width from 8 to 20 nm. The monochromatic light is chopped and additional continuous broadband bias irradiation is normally used. The DUT and REF are placed next to each other (Fig. 1), illuminated with the same light (bias and monochromatic) and measured simultaneously. Two lock-in amplifiers are



Fig. 1. Picture of two devices (DUT and REF) involved in the SR measurements...

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