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Ageing of DSSC studied by electroluminescence and transmission imaging

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ABSTRACT

Outdoor stability testing of ionic liquid based dye sensitised solar cells under short circuit (SC) and open circuit (OC) modes has been followed using electroluminescence (EL) and transmission imaging. The study showed a significant influence of the ageing conditions on the stability of the solar cell parameters in the exposure period from zero up to 31 kWh/m^2 (four summer days) of solar irradiation. Initial exposure is beneficial for all performance parameters regardless the operating mode under which the cells were aged. After 8 kWh/m^2 ageing of the cells in SC mode downgrades all parameters, mainly J_{sc} and consequently η, while continues ageing in OC mode slightly increases V_{oc} and consequently η. The EL imaging demonstrated that ageing, regardless the operating mode, is associated with the growth of the EL inactive areas that appear as black spots or defects, which we associate with the formation of iodine species in the electrolyte that have been captured under confocal microscope. The stability testing demonstrates that growth of the defects is more pronounced for cells operated in SC mode, which primarily reduces stability of J_{sc}.

1. Introduction

Dye-sensitised solar cells (DSSCs) are recognised as a potential alternative technology to conventional photovoltaic technologies, especially due to the low cost manufacturing based on printing technology. In the last decade the research in the field of DSSCs has bloomed in race of more efficient and more stable components [1]. In this respect a variety of new sensitisers, electrode materials, electrolytes as well as redox systems have been tested or/and developed [1]. The highest certified efficiency of the DSSC has reached 11% [2] and the fabrication of first fully up-scaled 60×100 cm^2 dye solar modules have been reported [3]. Although the long-term stability of the DSSC is the key for successful penetration of the DSSC technology to the photovoltaic market only a few papers present the stability studies of DSSC at different ageing tests [4–7].

The stability studies of DSSCs usually examine the variation of the solar cell performance parameters such as short circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and efficiency (η). In addition, electrochemical impedance spectroscopy (EIS) has proven to be a very powerful technique to distinguish resistive and capacitive cell components and interfaces, along with charge transfer and electron or/and ion diffusion processes [8,9]. Nevertheless these techniques provide solely integral information. To explain the variation of the performance in batch of the DSSCs during operation the spatial characterisation methods must be applied. For DSSCs these studies are very rare. A pioneering work was reported by Macht et al. [10] who studied the patterns of efficiency and degradation in DSSC using the basic light-beam-induced-current (LBIC) imaging technique.

In the recent publication [11] we have analysed and classified different defects in DSSCs with LBIC and electroluminescence (EL) imaging. The results have shown that EL imaging is efficient and powerful method for observation of spatial distribution of DSSCs' performance enabling to detect a variety of inhomogeneities present in DSSCs. Relatively short acquisition times enabling frequent inspection of large series of cells or modules make EL imaging advantageous over LBIC measurements. Apart from inspection tool in production, EL imaging is suitable for studying the structural changes associated with the ageing process, as recently reported also for organic and polymer solar cells in an inter-laboratory publication [12].

In this paper we present an analysis of the DSSCs exposed to outdoor testing under open circuit (OC) and short circuit (SC) mode that were tracked by periodic transmission and EL imaging along with I–V scans under standard test conditions (STC, 1000 W/m^2, AM 1.5, 25 °C). The SC mode is typically regarded to better reflect the ageing under real operating conditions of the solar cell, since the current flows, while the OC mode could simulate the ageing of the cells exposed to the sun under non-operating conditions.

To avoid the encapsulation challenge of highly volatile nitrile based electrolytes containing iodide/iodine redox couple in our

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study an ionic liquid electrolyte with negligible vapour pressure was used [13]. Tetra-cyanoborate ionic liquid (IL) based electrolyte showing a stable response of DSSCs at elevated temperature and light soaking, as reported by Kuang et al. [14], was chosen. However, we noticed instable response of DSSCs that reflects temporal and spatial changes. Our intention was to track these changes with EL and transmission imaging.

2. Experimental

2.1. The dye sensitised solar cell

All the chemicals for the TiO_2 paste preparation and other components of DSSC were used as received. Unique titanium oxide (TiO_2) sol–gel paste as developed by M. Hočevar et al. [15,16] was used. The paste was deposited on the conduction glass electrode (TCO) using the “doctor blading” technique. Layers were sintered at 450 °C for 1 h and later immersed in the ethanol solution of the ruthenium complex dye (N719, Solaronix) for 12 h. For the counter electrode, 5 nm thick layer of platinum was sputtered onto a TCO glass substrate. The photoanode and the counter electrode were sealed together with a 25 μm thick polymer foil (Surlyn, DuPont) and the ionic liquid electrolyte containing 0.2 M I_2 [14,15] was injected through the two holes predrilled into the counter electrode. The average active area of the cells presented in this paper is 0.5 cm^2.

2.2. I–V characterisation

The measurements were performed with Keithley 238 source measure unit under the Oriel Class A sun simulator [17]. The level of standard irradiance (1000 W/m^2) was determined with a calibrated c-Si reference solar cell.

2.3. Outdoor ageing

Outdoor ageing was performed on faculty's roof testing facilities (latitude: 46°2′39.39“N, longitude 14°29′18.28“E) between 23th of June and 4th of July 2011. A calibrated reference pyranometer CMP 6 (Kipp and Zonen) was used to determine the horizontal light intensity in plane of the samples [18]. During the measured period the highest global light intensities during the day exceeded 940 W/m^2.

Two sets of DSSCs, each consisting of 3 DSSCs have been exposed to outdoor ageing with the photoanode oriented towards the sun. The first set of cells (SC1, SC2 and SC3) was aged under short circuit while the second set of cells (OC1, OC2 and OC3) was in open circuit. The solar cells were left outdoor for different time periods as described in Table 1 and analysed by *I–V* characterisation under indoor sun simulator and by imaging techniques after the specified outdoor exposure.

Table 1
The details regarding the outdoor exposure of the solar cells in short circuit (SC cells) and open circuit (OC cells) mode.

	23rd June 2011 (9:00–13:00)	29th June 2011 (8:30–13:00)	1st–4th July 2011 (14:30–9:00)
Time (h)	4	4.5	66.5
Irradiance (kWh/m^2)	3.6	4.4	23.2
SC cells	**X**	**X**	**X**
OC cells		**X**	**X**

2.4. Transmittance imaging

Transmittance image of the front side of the DSSC was acquired by a 2-mega pixel digital microscope camera, while the cells were illuminated with diffused white light from behind. In this manner, the spatial distribution of transmittance was obtained.

2.5. Electroluminescence set-up

The basic component of an electroluminescent setup is an imaging device. In our setup the CCD camera (FLI MLx285) has been used. It utilises a low noise monochromatic 1.5 megapixel CCD sensor with improved spectral response in the NIR region and a cooling system to further minimise the background noise. A 12 mm colour corrected VIS–NIR lens with wide focus range has been used. During the measurements the camera, the lens and the DSSC have been closed in a custom-built dark enclosure. The photoanode of the DSSC was oriented towards the camera.

A laboratory power supply has been used to forward bias the DSSC with the short circuit current, which has been previously measured under STC. The camera has been cooled to 0 °C, the exposure time was set to 300 s. Due to optical and spatial constraints only 600 × 600 pixels were effectively used for image acquisition.

3. Results

Two sets of the DSSCs were exposed to outdoor ageing/irradiation under shot circuit (SC) and open circuit (OC) modes. Before, during, and after the outdoor ageing the cells' performance was evaluated under STC and the cells were characterised by transmission and EL imaging to explain the variation of the DSSC's performance during the ageing process.

3.1. Performance parameters after operation in different modes

The *I–V* curves determined under STC for individual cells exposed to outdoor ageing under SC and OC regime for different time periods (see Table 1) are presented in Figs. 1 and 2, respectively. The results of the variation of the solar cell's parameters (J_{sc}, V_{oc} and η) of the cells vs. accumulated irradiation during outdoor exposure are summarised in Fig. 3a–c. The arrows on Fig. 3c indicate at which accumulated irradiation the *I–V* characterisation and EL imaging of the cells were performed.

The J_{sc} values of the freshly made identical cells varied between 11.6 and 12.9 mA/cm^2 (Fig. 3a). After a few hours of exposure of the cells to the outdoor irradiation (around 4000 Wh/m^2) almost identical J_{sc} values were measured for all the cells exceeding 13 mA/cm^2; regardless of the ageing conditions applied to the cells. Further exposure to the outdoor ageing decreases J_{sc}. The decrease of J_{sc} is very small for the set of cells aged under OC and much more pronounced for the set of the cells aged under SC modes (Fig. 3a). An exception was the cell SC2 aged under SC mode that shows a strong decrease of the J_{sc} after first exposure period (3.6 kWh/m^2) to outdoor testing, but the J_{sc} has recovered after the *I–V* characterisation of the cell repeated for five times under STC (Fig. 1B). Further ageing of the SC2 cell harms the cell and at irradiation of 30 kWh/m^2 already almost halves the J_{sc} (Fig. 2B).

On the other hand, the outdoor ageing shows a positive influence on the V_{oc} values for the set of the cells aged under OC mode (Fig. 2b), while in the case of the set of the cells operated in SC mode first an increase in V_{oc} is noticed while prolonged irradiation leads to a decrease in V_{oc} (Fig. 2b). Upon irradiation, regardless the operating regime, the *FF* follows the trends observed for the V_{oc} (not shown here). The average value of the *FF* prior ageing was 0.63, which at the end of ageing increased for