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# Solar Energy Materials & Solar Cells

journal homepage: [www.elsevier.com/locate/solmat](http://www.elsevier.com/locate/solmat)

## Outdoor ageing of the dye-sensitized solar cell under different operation regimes



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### ARTICLE INFO

#### Article history:

Received 13 May 2013

Received in revised form

19 September 2013

Accepted 19 September 2013

Available online 14 October 2013

#### Keywords:

Dye-sensitized

Stability

Defects

Ageing

Degradation

### ABSTRACT

Ionic liquid based dye-sensitized solar cells (DSSCs) were exposed to outdoor irradiation for seven months (April–October, 906 kWh/m<sup>2</sup>, latitude 46°2′39.39″N, longitude 14°29′18.28″E) under short-circuit, open-circuit, and quasi maximum-power-point regime. As a reference we kept a series of DSSCs in the dark at room temperature under open-circuit regime. The performance of the DSSCs was evaluated indoor under standard test conditions prior to ageing, twice during ageing and after ageing. Additionally, the electroluminescence and transmittance imaging were used to follow the evolution of local defects with ageing. Operating regime has a strong influence on the ageing of DSSCs but despite this the performance of DSSCs remained remarkably stable. The exceptions were cells aged under short-circuit regime, which led to a significant decrease in  $J_{SC}$ . This resulted from the degradation of the dye molecules and a decrease in the tri-iodide concentration in the electrolyte.

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### 1. Introduction

Dye-sensitized solar cells (DSSCs) have been extensively studied as a low-cost alternative to silicon solar cells [1,2]. Several different dyes and electrolytes have been developed with the aim of improving conversion efficiency and cell stability. To date, the highest certified efficiency for a small area acetonitrile electrolyte based DSSCs (0.23 cm<sup>2</sup>) is 11.4% [3–5] while a small ionic liquid (IL) electrolyte based DSSCs (0.158 cm<sup>2</sup>) has an efficiency exceeding 8% [6]. There has been less effort undertaken to investigate the stability of cells under actual operating conditions. The International Electrotechnical Commission has set IEC61646 and IEC61215 standards describing the testing procedure for evaluating the stability of thin film and crystalline silicon photovoltaic modules [7,8]. These include light soaking, UV preconditioning, thermal annealing, thermal cycling and damp heat tests. Most types of conventional and thin film solar cells have successfully passed all the required tests, but this is not yet the case for DSSCs technology [9]. Studies do show that DSSCs could pass the thermal annealing test at 85 °C in the dark and the light soaking test under full sunlight at 60 °C [10,11], but they would not pass the light soaking test at 85 °C [9].

In general, most stability studies were performed indoors and focus on either individual degradation process or the individual

components of DSSCs. Several reasons why DSSCs degrade have been identified: (i) dye desorption [12–18]; (ii) changes in the dye structure in the presence of iodine [13]; (iii) gradual disappearance of the ligand or exchange of the ligand (with I<sub>3</sub><sup>-</sup>, H<sub>2</sub>O or OH) [9,15,18,19]; (iv) a decrease in the I<sub>3</sub><sup>-</sup> concentration [6,20,21]; and either (v) the degradation of the electrolyte [22], (vi) working electrode [9,15,23] or (vii) counter electrode [9,24,25].

A number of reports investigating the ageing of DSSCs outdoor have been published [13,22,26–31]. Amongst them Hagfeldt et al. [32] stresses the importance of collecting outdoor measurements from different locations under application-relevant conditions. However it is difficult to compare the results of these studies because they use different materials including dyes and electrolytes, and the cells/modules have different active areas and/or a number of the cells. Also, while the longest reported outdoor ageing period was 2.5 years [29] other studies lasted only a few months [13,26] and do not take into account seasonal effects (light intensity  $G$ , cell temperature  $T_C$ ). Studies also tested cells under different operating regimes *i.e.* the resistivity of the external load, which can influence how cells degrade. In some cases the operating regime is not reported. According to our knowledge there is no published systematic study that evaluates the influence of the operating regime on the degradation of DSSCs. The only exception is a study by Mastroianni et al. [31] who aged cells under open-circuit conditions for 1000 h before setting aside a number of samples to age at near maximum-power-point regime for a further 2200 h. The authors observe that the cells degrade more rapidly in devices working at the MPP. This is a result of a progressive decrease in the tri-iodide concentration in the electrolyte and

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changes at the  $\text{TiO}_2/\text{electrolyte}$  interface including an increased recombination rate, changes of density of localized states, and a positive shift in the  $\text{TiO}_2$  conduction band level [31].

In this study we aim to show how different operating regimes influence the stability of DSSCs. We have exposed ionic liquid based DSSCs to outdoor ageing on our faculty's roof here in Ljubljana (latitude  $46^\circ 2' 39.39''\text{N}$ , longitude  $14^\circ 29' 18.28''\text{E}$ ) for seven months under different operating regimes: short-circuit (SC), open-circuit (OC) and maximum-power-point regime (MPP) i.e. the regime where solar cells normally operate. However, it is difficult to follow the maximum-power-point of an individual solar cell due to constantly changing climatic conditions (cell temperature— $T_C$ , light intensity— $G$ ) and ageing. Normally, MPP trackers are employed which constantly adjust the load to follow the actual MPP, but this would require designing and building small size laboratory cell MPP trackers. In our study we tested two practical alternatives that mimic the MPP regime. This involved loading the solar cells with (i) a shunt resistor to assure maximal power point under specific conditions ( $T_C$ ,  $G$ ), and (ii) a diode (in our case two Schottky diodes) with a small shunt resistor connected in series. Reference cells were stored in the dark at room temperature under OC regime. In-situ outdoor monitoring of the relevant performance parameters was applied, while the current-voltage ( $I$ - $V$ ) characteristics at STC were measured indoor prior to, after two and four months and after ageing for a period of 7 months. In addition, electroluminescence (EL) and transmittance imaging (TI) were also performed to follow the evolution of spatial changes associated with ageing. Finally, to identify the causes of cell degradation we made a series of UV-vis spectroscopy (UV-vis) and external quantum efficiency measurements (EQE).

## 2. Experimental

### 2.1. Cell preparation

A fluorine-doped  $\text{SnO}_2$  coated glass (TCO) with a sheet resistance of  $8 \Omega/\square$  was used for the cell substrate. An optimized Pechini sol-gel  $\text{TiO}_2$  paste (based on P25, Degussa) [33,34] was then applied to the surface of the substrate using a “doctor blading” technique. The  $\text{TiO}_2$  layers were sintered at  $450^\circ\text{C}$  for one hour before being immersed for 12 hours in an ethanol solution of a Ruthenium complex based dye ( $\text{Ru}(2,2'\text{-bipyridyl-4,4'}\text{-dicarboxylate})_2$  (NCS) $_2$ , Solaronix). For the counter electrode, platinum (thickness  $\sim 5$  nm) was sputtered onto a TCO glass substrate. Both electrodes were then sealed using  $25 \mu\text{m}$  thick polymer foil (Surlyn, DuPont) which also acts as a spacer between the electrodes. Electrolyte was injected through two pre-drilled holes in the counter electrode. The electrolyte is a binary IIs mixture in a volume ratio 13:7 of 1-propyl-3-methyl-imidazolium iodide (Iolitec) mixed with 1-ethyl-3-methyl-imidazolium tetracyanoborate (Merck), 0.5 M methyl benzimidazol and 0.1 M guanidinium thiocyanate. The concentration of  $\text{I}_2$  was 0.2 M. Fifteen cells were assembled, each with an active area ranging from  $0.54$  to  $0.71 \text{ cm}^2$ , and stored in the dark for 24 h to allow the electrolyte to penetrate into the  $\text{TiO}_2$  pores.

### 2.2. Characterization

Cells were routinely characterized as described in Table 1. After an initial characterization ( $I$ - $V$ , EL and TI) three reference cells were stored in the dark at room temperature under OC regime for a period of seven months, while twelve cells were exposed outdoor under different operating regimes (see Section 2.2.2). After 244 and 606  $\text{kWh/m}^2$  irradiation (approximately two and four months of aging, respectively) the aged cells were characterized indoors ( $I$ - $V$ ,

**Table 1**

The sequence of methods used to characterize the reference and aged DSSCs ( $I$ - $V$  current-voltage characteristics, EL electroluminescence, TI transmittance imaging, UV-vis spectroscopy, and EQE external quantum efficiency measurements).

Date	Outdoor aged DSSCs	Reference DSSCs
13/03-01/04	indoor: $I$ - $V$ , EL, TI	indoor: $I$ - $V$ , EL, TI
02/04-31/05	outdoor: <b>244 kWh/m<sup>2</sup></b>	
01/06-06/06	indoor: $I$ - $V$ , EL, TI	
07/06-06/08	outdoor: <b>362 kWh/m<sup>2</sup></b>	
07/08	indoor: $I$ - $V$ , EL, TI	
08/08-22/10	outdoor: <b>300 kWh/m<sup>2</sup></b>	
23/10-25/10	indoor: $I$ - $V$ , EL, TI, UV-vis, EQE	indoor: $I$ - $V$ , EL, TI, UV-vis, EQE

EL, TI). Then after a further  $906 \text{ kWh/m}^2$  irradiation (7 months in total) both the aged and reference cells were characterized indoors ( $I$ - $V$ , EL, TI, UV-vis, and EQE).

#### 2.2.1. Indoor characterization

**2.2.1.1.  $I$ - $V$ .**  $I$ - $V$  characterization was performed using an Oriol Class ABA solar simulator equipped with a 1.5 G air mass filter, the spectrum of which closely matches the required AM1.5 spectrum. In accordance with the IEC 60904-3 standard the short-circuit current mismatch parameter was calculated and in conjunction with a calibrated c-Si reference solar cell, covered with a KG5 glass filter, the level of standard illumination (1 sun,  $1 \text{ kW/m}^2$ ) was determined. The cells were also masked to leave only the active area of the cell exposed, which is stated as the most rigorous condition regarding the cell's efficiency.  $I$ - $V$  characteristics of the cells were then measured using a Keithley 238 source meter by applying a voltage and measuring the current. The cells were scanned stepwise (10 mV) from 0 V (SC regime) to 0.9 V (beyond  $V_{OC}$ ).

**2.2.1.2. TI.** The transmittance image (TI) of the semi-transparent DSSCs was acquired using a 2-mega pixel digital microscope camera. The cell was backlit using a diffused white light emitting diode.

**2.2.1.3. EL.** The basic component for electroluminescent measurements (EL) is an imaging device. In our setup a CCD camera (FLI MLx285) was used. It utilizes a low noise monochromatic 1.5 megapixel CCD sensor with improved EQE in the NIR region and a cooling system to minimize background noise. The camera was also equipped with a 12 mm color corrected Vis-NIR lens with a wide focus range. During measurements the camera, the lens and the cell were housed in a custom-built dark enclosure. The working electrode was oriented towards the camera. A laboratory power supply was then used to forward bias the cell with the short-circuit current, which had been previously measured under STC. The CCD array was kept at  $0^\circ\text{C}$  and exposure time was 300 s. Optical and spatial constraints meant that only  $600 \times 600$  pixels were effectively used for image acquisition.

**2.2.1.4. UV-vis.** The UV-vis optical measurements (total transmittance  $T_{TOT}$  and reflectance  $R_{TOT}$ ) were made using a Lambda 950 Perkin Elmer spectrophotometer. The cells were scanned from 800 nm to 300 nm in decrements of 5 nm, while light was collected using a 150 mm Ulbricht integration sphere coated with Spectralon. Absorption was calculated afterwards as  $A = 1 - R_{TOT} - T_{TOT}$ .

**2.2.1.5. EQE.** External quantum efficiencies (EQEs) were measured without bias light using a Xe lamp and a monochromator (70525

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