# MEASUREMENT SCAN RATE DEPENDENCE OF PHOTO-ELECTROCHEMICAL SOLAR CELL PERFORMANCE

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# ABSTRACT

Although numerous reports on the research and development of photo-electrochemical (PEC) solar cells have been published, there are still some unresolved issues in the field. For instance, the voltammetric hysteresis behavior seen in PEC solar cell measurements is one of the issues not resolved completely. Most of such issues are possibly caused by the existence of unidentified parameters and/or charge transport and transfer hysteresis that governs the cell efficiency. In the present work we investigated the dependence of solar cell parameters on the scan rate of the potential used for the current density-voltage (J-V) measurements. For this purpose, quasi-solid-state DSSCs were prepared using a TiO<sub>2</sub> photo-electrode sensitized by N719 dye, a gel polymer electrolyte based on polyacrylonitrile (PAN) (Mw. 150,000) and a Pt counter electrode. J-V measurement were conducted by varying the scan rate and the direction (from forward bias to reverse bias and reverse bias to forward bias) for the cells, with a 1000 Wm<sup>-2</sup> irradiation. In this study the scan rate of the potential was varied from 0.01 to 0.1 V s<sup>-1</sup> using a potentiostat. The short-circuit current density  $J_{sc}$  of the cell increased from 20.2 to21.3 mA cm<sup>-2</sup> whereas the energy conversion efficiency increased from 5.21 to 5.63% respectively with the increase of the scan rate. The cell efficiency thus increased by 5.4% merely due to the increase of scan rate from 0.01 to 0.1 V s<sup>-1</sup>. However, two different trends of efficiency variation were observed when the scanning direction was altered. The scan rate dependence of cell performance can be understood by studying the capacitive effects at the two interfaces, namely, the electrolyte /photo-electrode and the electrolyte/ counter-electrode interface. This work underlines the importance of mentioning the scan rate together with solar cell performance parameter. Since the cell efficiency increases with the scanning rate of the potential during the measurements the cell efficiency can be artificially boosted by increasing the scan rate. Therefore, whenever DSSC results are reported the potential scan rate and the scan direction are important parameter to be mentioned.

Keywords: Dye solar cell, Scan rate, Current voltage, Electrolyte, Efficiency.

## **1. INTRODUCTION**

Solar energy is one of the most reliable renewable energy resources that reaches the doorstep free of charge. Hence, solar cells are capable of supplying a huge amount of useful energy for mankind. They are zero emission devices and thus toxic or greenhouse gas effluents are not released during their operation. O'Regan and Grätzel (1991) introduced the concept of dye sensitized solar cells (DSSC) or commonly known as Grätzel cells, by using metal-organic dyes as light absorber on a nano-crystalline titanium dioxide (TiO<sub>2</sub>), mesoporous structure[1]. The reported energy conversion efficiency in 1991 by Brian O'Regan and Michael Grätzel is ~ 7.1%. The report [1] quickly received wide attention, due to the high energy conversion efficiency and the possibility of using low-cost starting materials and also simple fabrication technology in comparison to conventional thin film solar cells preparation methods [2,3,4]. The dye-sensitized

solar cell (DSSC) has been studied intensively during the last two decades since they have been recognized as a low cost and environmental friendly alternative to fulfill future energy needs [5].

Generally, in DSSCs, the working electrode is a thin layer of a mesoporous wide-bandgap semiconductor sensitized by adsorbing dye molecules which have the ability to capture a wide range of photons from the solar spectrum. Metal oxide semiconductors such as  $TiO_2$ , ZnO, SnO<sub>2</sub> and ZrO<sub>2</sub> with a variety of morphologies, nano-structures and arrays, as well as with different dopants, have been studied as photo-anode material [6,7]. Since the report by O'Regan and Grätzel (1991), mesoporous  $TiO_2$  has shown its potential as a material suitable to prepare photo-electrodes with diversity of nanostructures with remarkable efficiencies [8,9,10]. Therefore,  $TiO_2$  is the state of the art wide band-gap semiconductor material for the preparation of the photo-electrodes in dye sensitized solar cells.

However, mesoporous and nano-structured  $\text{TiO}_2$  thin films with the desired thickness are needed for the high performing DSSCs [7,10,11]. Various film preparation methods have been tried out to prepare efficient and effective photo-anodes for DSSCs. The doctor blade method, atomic layer deposition (ALD), spray pyrolysis, sol–gel and dip coating, spin coating etc. are some examples [9,12]. However, some of these techniques, for example the ALD method, are costly and time consuming. However, the spin coating method is a very simple and low cost preparation method for thin films which offers remarkable reproducibility of the film thickness and surface morphology. Spin coating can be used to fabricate thinner, more homogeneous and compact films than the doctor blade and screen printing methods [13]. Spin coated TiO<sub>2</sub> films have been used in DSSCs, however spin coating is mostly used to produce the compact layer in the photo-anode [10,14]]. In this study the spin coating method is selected to prepare all the layers of the nano-structured TiO<sub>2</sub> film in the photo-anode considering the reproducibility and facile preparation.

ADSSC composed of electrolyte and counter electrode in addition to the crucial photo electrode that contains thin layers of a mesoporous semiconductor sensitized by a suitable dye. Dye sensitizers absorb photons in the visible light and inject the exited electrons in dye into the conduction band (CB) of the semiconductor. After electron injection, the ground state of the dye is subsequently restored by electron donation from the reducer (in general  $\Gamma$ ) in the electrolyte. The reducer is regenerated at the counter-electrode where the oxidizer ( $I_3$ ) in the electrolyte is obtaining electrons from the counter electrode. Many processes are involved in the solar cell mechanism and some give positive influences on cell performance (marked using solid line arrows) and some processes devastate the cell performances (marked using dotted line arrows) as illustrated in Fig 1 [6,15].Some of the processes involved are very fast and some are very slow, roughly estimated time scales are also marked in Fig.1.



Fig. 1 Charge transport and transfer mechanism of a DSSC [6,15].

Solar cells are conventionally characterized by voltage (V) and current (I) measurements made using potentiostats when the cell is under light illumination. In general, the I-V curve is used to calculate DSSC performance parameters such as short circuit current density ( $J_{sc}$ ), open circuit voltage ( $V_{oc}$ ), fill factor (ff), and energy conversion efficiency ( $\eta$ %). Or, in practice, the current density-voltage (J-V) characteristic is presented which is normalized by the photo-active cell area of the device. With the present work we demonstrate the dependence of solar cell parameters on the scan rate of the potential used for the current-voltage (I-V) measurements [16,17]. The scan rate dependence of the cell performance can be understand by studying the capacitive effects at two interfaces, namely, the electrolyte/photo-electrode and electrolyte/counter-electrode interface. With this work we underline the importance of mentioning the scan rate together with the solar cell performance parameter.

### 2. EXPERIMENTAL

## 2.1 Preparation of electrodes

Nano-crystalline TiO<sub>2</sub> layers were deposited on fluorine doped tin oxide (FTO) coated conducting glass substrates using the following procedure. FTO glasses (sheet resistance, 7  $\Omega$ ) were purchased from Solaronix SA Switzerland. These glasses were cut into small pieces of 1 cm  $\times$  2 cm. Then FTO glasses were cleaned by sonicating in a solution of soap water for 60 °C in 30 min and rinsed with distilled water, and again washed with dilute 0.1M of HNO<sub>3</sub> and rinsed with distilled water. Finally, the glass plates were boiled for 5 minutes in aqueous ethanol and allowed to dry in air. Then to prevent the coating of TiO<sub>2</sub> in the area necessary for electrical contact scotch tape was applied to mask half of the FTO glass plate. TiO<sub>2</sub> slurry was prepared by grinding 0.5g of Degussa (Evonik) P25 TiO<sub>2</sub> powder (average particle size 21nm) with ~2 ml of HNO<sub>3</sub> (0.1M) for 30 minutes in an agate mortar. The spin coating speed was kept at 1000 r.p.m for the 1<sup>st</sup> layer preparation on the FTO glass substrate and then it was sintered at ~450 °C and allowed to cool to the room temperature. The procedure was repeated two more times in order to get 3 layered TiO<sub>2</sub> films.

#### 2.2 Preparation of electrolyte

The electrolyte sample was prepared by using Polyacrylonitrile (PAN) (Mw. 150,000) (0.100 g), ethylene carbonate (0.417g), propylene carbonate (0.385 g),4-tert-butylpyridine (4TBP)

(0.022 g), rubidium iodide (RbI) (0.048 g), tetrahexylammonium iodide (Hex<sub>4</sub>NI) (0.045 g), and 1-butyl-3-methylimidazolium iodide (BMII) (0.0126g). The molar ratio of the components in the gel polymer electrolyte was PAN: EC: PC:BMII: Hex<sub>4</sub>NI: RbI:4TBP:I<sub>2</sub> = 10:25:20:0.25:0.5:1.2:0.85:0.19. Therefore, the stoichiometric composition can be written as  $(PAN)_{10}(EC)_{25}(PC)_{20}(BMII)_{0.25}(Hex_4NI)_{0.5}(RbI)_{1.2}(I_2)_{0.19}$ .

For the sample preparation EC, PC and 4TBP were mixed in a closed glass bottle under continuous stirring. The relevant amount of iodides, RbI, Hex<sub>4</sub>NI, BMII were added to the mixture and stirred for a few more hours and then 0.1 g of PAN was added to the salt solution and stirred further to obtain a homogenous mixture. The resulting mixture was heated to ~100 °C under continuous stirring until the mixture became a homogenous and transparent slurry. The mixture was allowed to cool under continuous stirring. When the temperature dropped to ~50 °C, 0.0090g of iodine (I<sub>2</sub>) chips were also added to the slurry. The stirring continued until the slurry cooled down to room temperature. The resultant gel polymer electrolyte was used for the measurements and applications.

### 2.3 Assembly of DSSC and measurements

The prepared 3-layered TiO<sub>2</sub> photoelectrode was immersed in a saturated ethanol solution of N719, di-tetrabutylammonium cis-bis (isothiocyanato) bis (2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium (II). When the electrode was dipped in the dye solution the temperature of the dye solution and the electrode were kept at ~60 °C. The electrode was taken out from the dye solution after 24 hour dye adsorption at room temperature. Loosely bound dye molecules were washed away by rinsing with ethanol. The DSSC was assembled by sandwiching a thin film of gel polymer electrolyte between the photo-electrode and the platinum coated glass plate (counter electrode) by clipping them together.

The solar cells were irradiated by (1.5 AM) 1000  $\text{Wm}^{-2}$  using an ABET solar simulator. The area exposed to the light was 19 mm<sup>2</sup>. The *I-V* characteristics were measured by using an Autolab PGSTAT128N module with the help of NOVA software. The measurement scanning was done for the directions from forward bias (0.8 V) to reverse biased (-0.8 V) and from reverse bias (-0.8 V) to forward biased (0.8 V). The rates of scan was varied between 0.01-0.1 V s<sup>-1</sup> for the current voltage measurements.

### **3. RESULTS AND DISCUSSION**

### 3.1 Forward bias to reverse bias

Fig. 2 shows the current density against cell potential curves obtained at the different scan rates (from 0.01-0.1V s<sup>-1</sup>). For this measurement the scanning was conducted from forward bias (0.8 V) to reverse biased (-0.8 V) direction. The scan direction is indicated by a solid line arrow in Fig.2. According to the curves in Fig.2 the current density values increase with increasing scan rate. Therefore, the highest current density is observed for the 0.1 V s<sup>-1</sup> scan rate. The can rate 0.01 V s<sup>-1</sup> gives the lowest current density value in this study. The change is very significant when the current density reaches close to short-circuit and this region is enlarged in the 1<sup>st</sup> inset of Fig 2 for clearer view. The region close to the  $V_{oc}$  is also enlarged in the second inset of Fig.2 to show the differences clearly.

The power density values are calculated by using the measured current-voltage data. The power density of the cell versus cell potential is shown in Fig 3 for different scan rates (from 0.01- $0.1 \text{ V s}^{-1}$ ). The power density values increase with increasing scan rate. The highest power density value is observed for the scan rate  $0.1 \text{ V s}^{-1}$ . With decreasing scan rate the power density gradually decreases. Therefore, according to the results, the power density of this TiO<sub>2</sub> multilayered quasi solid state DSSCs depends on the measurement scan rate.



Fig.2: The current density cell potential curves at different scan rate from  $0.1 - 0.01 \text{ V s}^{-1}$  in 3-layer of TiO<sub>2</sub> spin coated on the photo-electrode based DSSC. Scan direction is indicated using a solid line arrow.



Fig.3: The power density versus cell potential curves at different scan rate from  $0.1 - 0.01 \text{ V s}^{-1}$  in 3-layer of TiO<sub>2</sub> spin coated on the photo-electrode based DSSC. Scan direction is indicated using an arrow.

In order to investigate the influence on the DSSC parameters, the short circuit current density  $(J_{sc})$ , open circuit voltage  $(V_{oc})$  fill factor (*ff*) and efficiency  $(\eta\%)$  of the cells were calculated at different scan rates using *J-V* characteristic data. The values obtained are given in

Table 1. The  $J_{sc}$  values of the DSSC increase with the increasing measurement scan rate. Therefore, in this study the highest  $J_{sc}$  value of 21.25 mA cm<sup>-1</sup> is obtained for the 0.1 V s<sup>-1</sup> scan rate and the lowest 20.25mA cm<sup>-1</sup> for the 0.01 V s<sup>-1</sup> scan rate. Consequently, the highest efficiency, 5.63%, is shown for the 0.1 V s<sup>-1</sup> scan rate. The lowest efficiency of 5.21% is shown for the 0.01 V s<sup>-1</sup> scan rate. The dependence of cell parameters on the scan rate is possibly associated with relaxation effects of charge transfer at the two interfaces and mass transport in the electrolyte because these are the slowest processes as illustrated in Fig. 1. Therefore, the efficiency of the solar cell depends on the scan rate and thus, whenever DSSC results are presented it is important to mention the potential scan rate.

| Scan rate / V s <sup>-1</sup> | $J_{\rm sc}$ / mA cm <sup>-2</sup> | $V_{\rm oc}$ / mV | <i>ff</i> /% | Efficiency $(\eta)$ / % |
|-------------------------------|------------------------------------|-------------------|--------------|-------------------------|
| 0.01                          | 20.25                              | 700.84            | 37.42        | 5.21                    |
| 0.02                          | 20.37                              | 700.84            | 37.41        | 5.30                    |
| 0.04                          | 20.79                              | 704.80            | 36.58        | 5.40                    |
| 0.06                          | 21.06                              | 708.77            | 36.91        | 5.51                    |
| 0.08                          | 21.23                              | 712.74            | 36.74        | 5.56                    |
| 10                            | 21.31                              | 712.74            | 37.07        | 5.63                    |

Table 1: The short circuit current density  $(J_{sc})$ , open circuit voltage  $(V_{oc})$ , fill factor (ff), and the efficiency of the DSSCs prepared in this work under different measurement scan rate from 0.01 V s<sup>-1</sup> to 0.1 V s<sup>-1</sup>.

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Fig.4 shows the current density against cell potential curves obtained at the different scan rates (from 0.01-0.1 V s<sup>-1</sup>), for these measurements the scanning was conducted from reverse bias (-0.8 V) to forward biased (0.8 V) direction. The scan direction is indicated using an arrow in Fig. 4. The power density for different scan rates (from 0.1-0.01 V s<sup>-1</sup>) is shown in Fig 5 as a function of cell potential. For this scan direction the power density values increase with decreasing scan rate. Therefore, the trend has reversed when the scan direction changes. Consequently, the highest power density value is observed for the scan rate 0.01 V s<sup>-1</sup> and the lowest is shown for 0.1 V s<sup>-1</sup>.



Fig.4: The current density cell potential curves at different scan rate from 0.1 - 0.01 V s<sup>-1</sup> in 3-layer of  $TiO_2$  spin coated on the photo-electrode based DSSC. Scan direction is indicated using a solid line arrow.



Fig. 5: The power density versus cell potential curves at different scan rate from 0.1 - 0.01 V s<sup>-1</sup> in 3-layer of TiO<sub>2</sub> spin coated on the photo-electrode based DSSC. Scan direction is indicated using an arrow.

The calculated  $J_{sc}$ ,  $V_{oc}$ , ff,  $\eta\%$  of the cell measured at different scan rates are given in Table 1 for the scan direction from reverse bias to forward bias. The  $J_{sc}$  values increase from 20.23 to 20.63mA cm<sup>-2</sup> with increasing the scan rate. However, the trend of  $V_{oc}$  and  $\eta$  variation shows a completely opposite behavior with the change of scan direction. Therefore, the highest  $V_{oc}$  and  $\eta$  of 687.3mV and 5.68% are shown for the 0.01 V s<sup>-1</sup> scan rate. This trend can be attributed to the effect of reverse biasing and the relaxation behavior of the charge transport.

| Scan rate / V s <sup>-1</sup> | $J_{\rm sc}$ / mA cm <sup>-2</sup> | $V_{\rm oc}$ / mV | <i>ff</i> /% | Efficiency $(\eta)$ / % |
|-------------------------------|------------------------------------|-------------------|--------------|-------------------------|
| 0.01                          | 20.23                              | 687.3             | 40.85        | 5.68                    |
| 0.02                          | 20.32                              | 686.3             | 39.73        | 5.54                    |
| 0.04                          | 20.47                              | 681.4             | 38.50        | 5.37                    |
| 0.06                          | 20.53                              | 676.4             | 37.81        | 5.25                    |
| 0.08                          | 20.58                              | 672.7             | 37.34        | 5.17                    |
| 0.10                          | 20.63                              | 670.5             | 36.80        | 5.09                    |

Table 2: The short circuit current density (*Jsc*), open circuit voltage (*Voc*), fill factor (*ff*) and the efficiency of the under different measurement scan rate from  $0.01 \text{ V s}^{-1}$  to  $0.1 \text{ V s}^{-1}$ . The scan direction is from reverse bias to forward bias.

The investigation of the scan rate dependence of the cell performance can be further continued by analyzing capacitances of the cell interfaces, namely, the electrolyte/photo-electrode and the electrolyte/counter-electrode interfaces. According to the all the above results it can be concluded that the potential scan rate is a very important parameter to mention when presenting DSSC performances. The measured efficiency of the solar cell is directly related with the scan rate, therefore, in order to remove measurement artifacts from solar cells parameter results, researchers in the field might come to an agreement to use a fixed scan rate and direction for the I-V characterization when potentiostats are used for the measurements.

The dependence of solar cell parameters on the scan rate of the potential used for the current-voltage (*I-V*) measurements has been investigated. *I-V* measurement were conducted by varying the scan rate and the direction (from forward bias to reverse bias and reverse bias to forward bias) for cells under 1000 W m<sup>-2</sup> irradiation. The scan rate of the potentials was varied from 0.01 to  $0.1 \text{ V s}^{-1}$ . The  $J_{sc}$  of the cells increased from 20.2 to21.3 mA cm<sup>-2</sup> whereas the energy conversion efficiency increased from 5.21 to5.63 mA cm<sup>-2</sup> with the increase of the scan rate when the scanning is done from forward bias to reverse bias direction. The cell efficiency has increased by 5.4% merely due to the increase of scan rate from 0.01 to 0.1 V s<sup>-1</sup> for this scan direction. Two different trends of efficiency variation is observed when the scanning direction is altered. The study of scan rate dependence of cell performance will be further continued by analyzing capacitances of the cell interfaces. According to all the above results it can be concluded that the potential scan rate is a very important parameter to mention when presenting the DSSCs performance.

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