IMPEDANCE SPECTROSCOPY AND TRANSPORT MECHANISMS OF TiO_2-BASED DYE SENSITIZED SOLAR CELL

W.A. FAROOQ[a], M. ATIF[a*], A. FATEHMULLA[a], F. YAKUPHANOGLU[b], I.S. YAHIA[c,d]

[a]*Department of Physics and Astronomy, College of Science, King Saud University, Riyadh 11451, Saudi Arabia*

[b]*Department of Physics, Faculty of Science, Fırat University, Elazığ Turkey.*

[c]*Nano-Science & Semiconductor Labs., Physics Department, Faculty of Education, Ain Shams University, Roxy, Cairo, Egypt.*

[d]*Department of Physics, Faculty of Science, King Khalid University P.O.Box 9004, Abha, Saudi Arabia*

Photoconduction mechanism and charge dynamics in the TiO_2-based DSSC were analyzed under dark and illumination conditions. The effects of high and low electric fields on charge dynamics in the solar cell were investigated by current- voltage characteristics. It was found that the charge dynamics of the solar cell was controlled by the thermionic emission (TEC) at lower voltage and followed by space charge limited current (SCLC) at the higher voltages. It is also observed that photoconduction mechanism is controlled by supralinear recombination mechanism while the charge dynamics is controlled by TEC and SCLC mechanisms. Spectroscopic parameters (capacitance, conductance and series resistance) at different biasing voltages and frequencies are also discussed.

(Received February 11, 2014; Accepted April 30, 2014)

Keywords: Spectroscopy, solar cell, space charge limited current (SCLC), Thermionic emission (TEC)

1. Introduction

A photovoltaic device considered to be an important device due to the fact of conversion of light energy into electrical energy. Since the beginning of the dye-sensitized solar cells (DSSCs) work in the early 1990s, a lot of attention in respect of their morphology and processes has been focused. The The dye-sensitized solar cell compared to conventional silicon solar cells has been studied extensively keeping in view its low fabrication process cost and higher efficiency [1-5]. Significant studies reported by Brian O'Regan and Michael Grätzel on the low cost TiO2-based DSSCs due to its suitable applications in the fulfillment of energy needs [4]. Grätzel's scientific investigations have provided a new prototype solar-energy conversion device to measure simultaneously placed molecular and nano science approaches on the map with conventional photovoltaic like silicon [6]. Spectral Sensitization study of TiO_2 nano crystalline electrodes with Cyanine Dyes was carried out by Ehret et. al in 2001 [7]. Puhong Wen et al. in 2012 investigated effect of the morphology and size of TiO_2 nano crystals with N719 Sensitizer in DSSC on UV-VIS and FT-IR spectra [8].

Research work carried out in the past regarding fabrication of dye-sensitized solar cell, makes it flexible, expedient and manageable. Since nano-crystalline TiO_2 electrode contacts have shown improved performance, new studies of fabrication with plastic substrates have been carried out on the flexible dye-sensitize solar cell [9-10].

[*]Corresponding author: atifhull@gmail.com

Photovoltaic devices posses two important steps to convert sunlight radiations into electrical energy as following: 1. Radiation absorption with electrical excitation. 2. Charge carriers separation. The way which radiation is absorbed and carriers are separated are two of the main differences between DSSCs and classical p-n junction [11]. DSSCs photovoltaic principle relies on differences in work functions between the electrodes of the cell in which photogenerated carriers could be separated. An asymmetry through cell is necessary to obtain electrical power. In classical p-n junction of solid state device the separation of photo-generated carriers relies on separation through depletion region built at p-n interface materials [11].

In this paper, we have discussed the problems encountered in photoconduction mechanism and charge dynamics. For the first time, the dielectric spectroscopic parameters (capacitance, conductance and series resistance) at different biasing voltages and frequencies were determined and discussed on the basis of the studied DSSC.

2. Experimental details

In order to develop a TiO2-based DSSC, TiO2 film of thickness 3-5 µm was deposited on commercially available FTO glass substrate. Then it was sintered at 450 ^{0}C in air for 40 min. Later on we dip this in an N-methyl-N- butyl imidazolium iodide (MBII) dye. For washing we used anhydrous ethanol and for drying moisture-free air is used. For sputtering on FTO A platinum counter electrode for the cell was used and mixed with an iodide electrolyte solution (0.5 M lithium iodide mixed with 0.05 M iodine in water-free acetonitrile) for the cell. Figure 1 shows the schematic diagram of the prepared solar cell.

To measure current–voltage characteristics a KEITHLEY SC- 4200 semiconductor characterization system and a Class- BBA Solar Simulator was used.

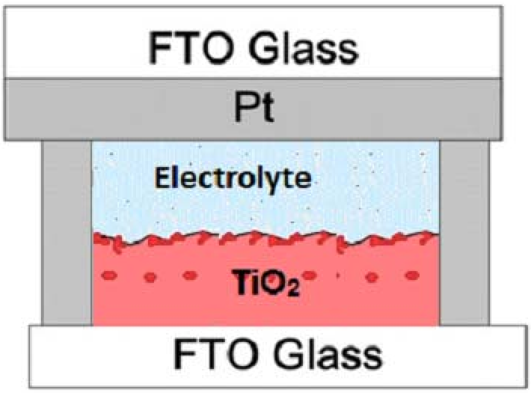

Fig.1: Schematic structure of studied dye-sensitized solar cell.

The surface micrographs of the nanostructure TiO_2 photo-electrode and their grain size were investigated by atomic force microscope (AFM, Park System, XE100) using a non-contact mode. A PARK system XEI software programming attached to AFM was used to analysis the obtained scanned morphology.

3. Results and discussions

3.1 Structure characterization of TiO_2/FTO

The surface morphology and the grain size of TiO_2/FTO photo-electrode were investigated by means of Atomic force miscopy (AFM). Fig.2 represents the 3D morphology of TiO_2/FTO in scanned area 5x5 µm2. It is clear that TiO_2 has nano-clusters and the mean vale of the clusters size equal 152.86 nm and the film roughness equals 117.11 nm.

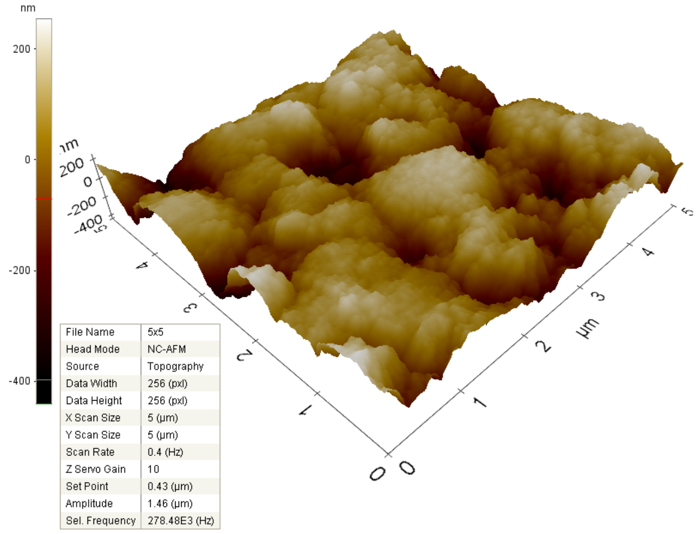

Fig.2: AFM 3D micrograph of TiO2/FTO of scanned area 5x5 µm2.

3.2 Photovoltaic characteristics of the solar cell

Figure 3 represents the current-voltage characteristics of the DSSC at different illuminations. The value of the solar cell short-circuit current density (I_{SC}) and an open- circuit voltage (V_{OC}) is shown in figure 3.

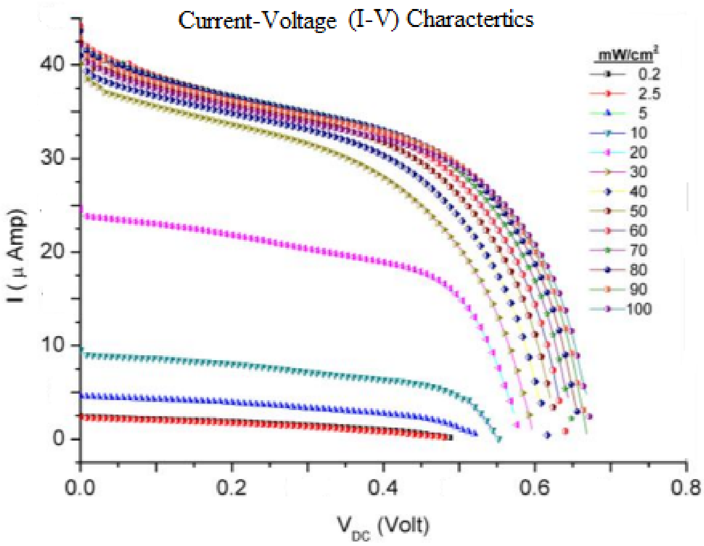

Fig.3: Current-voltage (I-V) characteristics of the studied solar cell.

We observe the photocurrent created via injection of electrons into conduction band of TiO_2 as the incident light falls on the sensitized dye in DSSC [12]. The values of the short-circuit current density (I_{SC}), the open-circuit voltage (V_{OC}) and the maximum power output (P_{max}) is clearly demonstrated by the I-V curves. At different illuminations I-V characteristics of the solar cell are observed and are shown in figure 3. It shows an increasing trend of the photocurrent of the solar cell with increasing illumination. Therefore it is concluded that the solar exhibits a photovoltaic behavior. Figure 4 shows the output power at different illuminations of the solar cell.

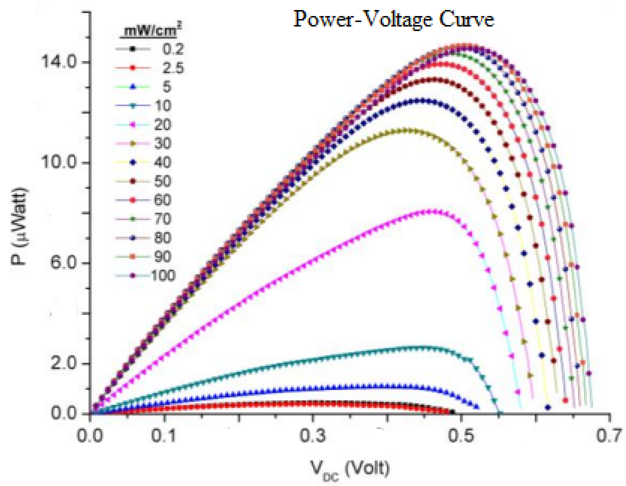

Fig.4: Power-voltage curves of the studied solar cell.

The experimental results shown in figure 4 depict an increasing trend of the power of the solar cell with increasing illuminations which is an indication of the solar cell response to stimulating light illumination. In figure 5 the variation of Voc against intensity of incident light are shown. . It was found that the values of the Isc and Voc values are increasing with increasing illumination until it reaches to a critical value of illumination where the Isc trend become constant. For the analyzation of the photoconduction mechanism of the solar cell the value of Isc was plotted against illumination intensity to show its dependence (Figure 6). Figure 6 clearly shows Isc vs. lnL indicating two regions. The first region is found to be linear where the illumination varies from 0 to 20 mW/cm^2 but for second region the value of Isc reaches to critical region. It is evident from the experimental observations that the first region possesses the carriers having high mobility and field-enhanced dissociation of excitons [12]. The change in the value of Isc from linear region to saturation region is observed due to the change in their charge recombination rate.

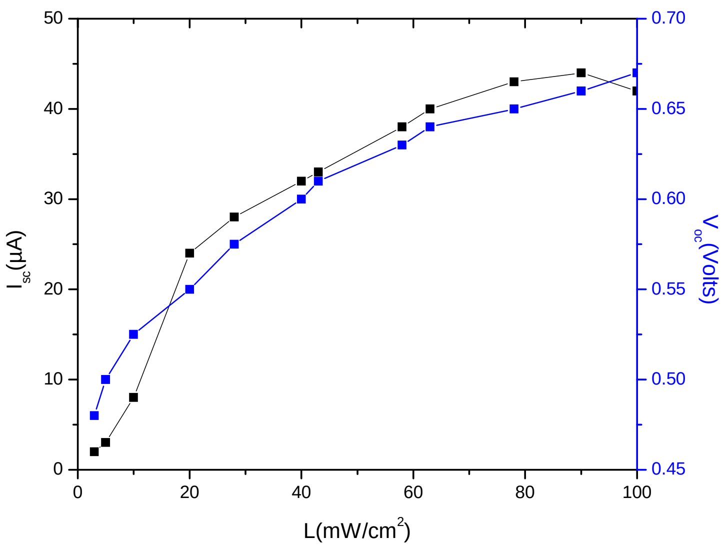

Fig.5: Plots of I_{SC} vs L of the studied solar cell.

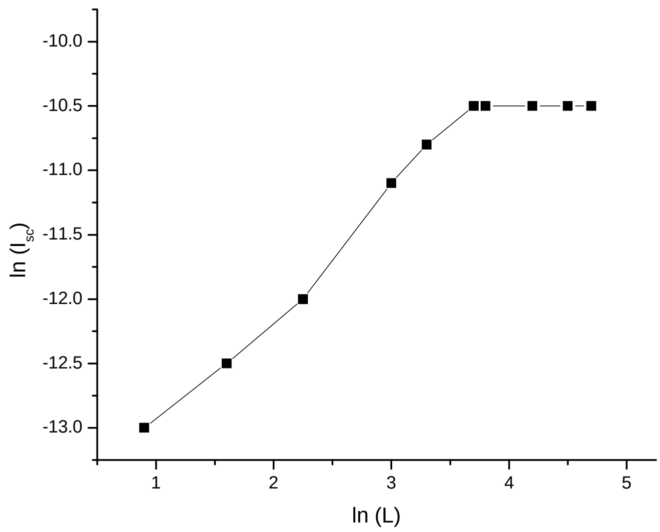

Fig.6: Illumination dependence of the short circuit current Isc for the DSSC.

3.3. Capacitance–voltage characteristics of the DSSC.

The capacitance–voltage (C–V) curves are shown in Fig.7. The capacitance values are decreased with increase of frequency. As seen in Fig.7, after 100 kHz, the capacitance of the solar cell is changed from the positive capacitance to the negative capacitance.

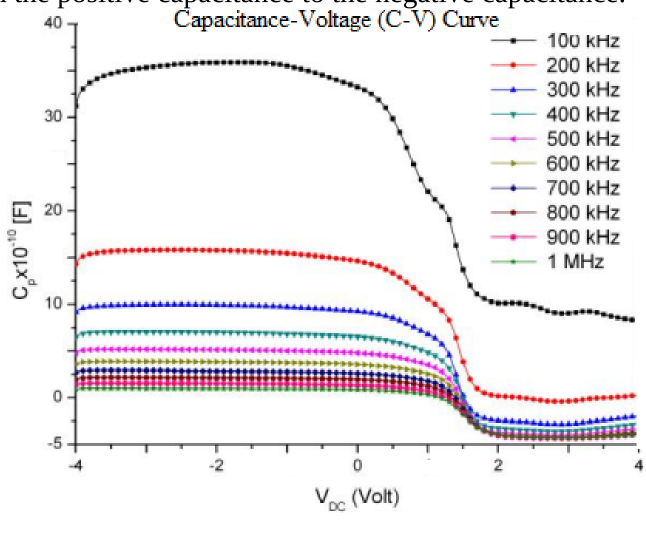

Fig.7: Capacitance–voltage (C–V) curves at different frequencies.

A negative capacitance phenomenon (or inductive behaviour) has been observed in different electronic devices such as polymer light-emitting diodes, and dye-sensitized solar cells. The analysis with equivalent circuit models indicates that negative capacitance reveals a major failure of the operation in photovoltaic devices, due to some dynamic effect that prevents the accumulation of photo generated carriers [13].

The obtained result is in agreement with the results obtained earlier by L.M. Peter in 2007 [12]. The C-V characteristics were analyzed by the following relation [12]:

$$\frac{1}{C_{sc}^2} = \left(\frac{2}{\varepsilon\varepsilon_o N_d e}\right)\left(V - V_{fb} - \frac{kT}{e}\right)$$

where C_{sc} is the space-charge capacitance of semiconductor electrode, ε is the dielectric constant of the semiconductor, ε_o is the permittivity of free space, N_d is the dopant density, V is the applied potential, and V_{fb} is the flat band potential. The curves of $1/C^2$ versus V at 5 kHz, 10 kHz, 50 kHz, and 100 kHz were plotted. The built-in potential V_{bi} was obtained from the plotted of $1/C^2$ versus V curves [14]. The V_{bi} values decrease with increasing frequency in this case (from 0.84 eV at 5 kHz to 0.30 eV at 100 kHz). The highest value of Vbi was found for 5 kHz.

4. Conclusions

The charge dynamics and photoconduction mechanisms of the solar cell were analyzed using current -voltage and capacitance-voltage characteristics. It was found that the charge transport mechanism is controlled by TEC and SCLC mechanisms, while photoconduction is controlled by supralinear recombination mechanism. The results of the studied solar cell showed that this new kind of the dye solar cell structure can provide a new perspective in the application of low-cost solar cell module

Acknowledgements

The authors would like to extend their sincere appreciation to the Deanship of Scientific Research at King Saud University for its funding of this research through the Research Group Project No. RGP-VPP-293.

References

[1] M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humpbry-Baker, E. Miiller, P. Liska, N. Vlachopoulos, M. Gratzel, Journal of American Chemistry Society, **115**, 6382 (1993).
[2] A. Hagfeldt, M. Gratzel, Accounts of Chemical Research **33**, 269 (2000).
[3] T. Yoshida, K. Terada, D. Schlettwein, T. Oekermann, T. Sugiura, H. Minoura, Advanced Materials (Weinheim Ger.) **12**, 1214, (2000).
[4] B. O'Regan, M. Gratzel, Nature **353**, 737 (1991).
[5] G. Smestad, Solar Energy Mater Solar Cells **32**, 259 (1994).
[6] M. Gratzel, Nature **414**, 338 (2001).
[7]A. Ehret, L. Stuhl, and M. T. Spitler J. Phys. Chem. B **105**, 9960 (2001).
[8] P. Wen, Y. Han, and W. Zhao, International Journal of Photoenergy, Article ID 906198, 7 pages (2012)
[9] A.F. Nogueria, C. Longo, M.-A.Depaoli, Coord. Chem. Rev. **248**, 1455 (2004).
[10] M. Gratzel, J. Photochem. Photobiol. C: Rev. **4**, 145 (2003).
[11] Donald Neamen, Semiconductor Physics and Devices, Second Edition, Mc Graw Hill, pp.130 (1997).
[12] L.M. Peter, Phys. Chem. Chem. Phys. **9**, 2630 (2007).
[13] J. Bisquert, G. Garcia-Belmonte, A. Pitarch, and H. Bolink, Chem. Phys. Lett. **422**,184 (2006)
[14] I.S. Yahia, H. S. Hafez, F. Yakuphanoglu, B. F. Senkal, M. S. A. Abdel Mottaleb, Synth. Met. **161**, 1299 (2011).