IMPEDANCE SPECTROSCOPY AND TRANSPORT MECHANISMS OF TiO$_2$-BASED DYE SENSITIZED SOLAR CELL

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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.

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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 TiO$_2$-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].

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Photovoltaic devices possess 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 °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.

![Image](image.png)

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

The surface micrographs of the nanostructure TiO2 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 TiO2/FTO

The surface morphology and the grain size of TiO2/FTO photo-electrode were investigated by means of Atomic force microscopy (AFM). Fig.2 represents the 3D morphology of TiO2/FTO in scanned area 5x5 µm2. It is clear that TiO2 has nano-clusters and the mean vale of the clusters size equal 152.86 nm and the film roughness equals 117.11 nm.
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.

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.
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/cm² 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.
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.

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]:

\[
\frac{1}{C_{sc}^2} = \frac{2}{ee_o N_a e} \left( V - V_{fb} - \frac{kT}{e} \right)
\]
where $C_{sc}$ is the space-charge capacitance of semiconductor electrode, $\varepsilon$ is the dielectric constant of the semiconductor, $\varepsilon_0$ 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 $V_{bi}$ 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.

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