Dye Sensitized Solar Cells with Low Cost Carbon Nanotubes Electrodes

F. M. Al-Marzouki, S. Abdalla, and S. Al-Ameer

Department of Physics, Faculty of Science, King Abdulaziz University Jeddah, P.O. Box 80203, Jeddah 21589, Saudi Arabia

Correspondence should be addressed to S. Abdalla; smabdullah@kau.edu.sa

Received 20 October 2015; Revised 24 December 2015; Accepted 3 January 2016

Academic Editor: Gonzalo Martínez-Barrera

Copyright © 2016 F. M. Al-Marzouki et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Dye sensitized solar cells (DSSCs) are very sensitive to electrodes, due to either high cost or easy corrosion problems. To minimize these factors, we present DSSCs with cheap carbon nanotubes as counter electrodes. In addition, we suggest replacing the electrolyte (in typical DSSCs) with a solid film of powdered CsSnI$_3$. The electrical behavior (I-V characteristics) of the proposed device has been measured for different shading conditions. In the light of a theoretical model based on the presence of two diodes, the experimental data have been explained, taking into account a new equivalent circuit for the DSSC. These DSSCs may receive different levels of sun radiation, which stimulates the study of partial shading; so, we have studied the effect of different shadow rates on the solar conversion efficiency of a unit of 4-W-connected DSSCs. The validity of the present model has been examined by fitting it into I-V characteristics at different shading rates.

1. Introduction

Due to the enormous acceleration of modern civilization and the developments in all domains all over the world, the increase in the rate of energy consumption is a characteristic of this civilization, and a dire need for energy is always present. However, the exhausted energy sources, such as mineral and animal traces, are inevitably disappearing, and solar energy has become an increasingly hot topic, particularly over the recent years. For example, an enormous quantity of energy is supplied each second, to the earth’s surface (about $9.5 \times 10^{16}$ Joule/second [1]). In their pioneer work, O’Regan and Grätzel [2] have initiated the principals of dye sensitized solar cells (DSSCs). Since 1990s, DSSCs have continuously augmented by time as it is illustrated in Figure 1. In this figure, the number of publications of CNTs has been reported and CNTs have been extensively used as counter electrode. Due to the high rate of publications, several huge companies have commercialized these solar cells. As a consequence, the fabrication methods for CNT films and photovoltaic materials have been developed. Table 1 shows the different fabrication methods of DSSCs.

Grätzel has reported that this quantity of energy is ten thousand times more than mankind needs, nowadays.

This means that only a slim part of the global surface area, which is about 0.1%, with a solar efficiency of about 10%, would be totally enough to cover our energy needs. Consequently, the solar energy cells have received increasing attention over the last three decades. They have passed through several substantial steps, starting with simple solar cell [3], to a second main step, solar cells based on thin film solar cells (SCs) [4, 5] and the present third generation which uses organic-SC and dye sensitized solar cells [5–8]. In addition, the third generation has more compatibility with flexible substrate and relatively low cost of basic materials.

Furthermore, nanotechnology launches several axes of research, particularly in nanoenergy. For example, it is now easy to prepare a suitable nanomaterial with different nanostructures, using the dye sensitized solar cells to get the optimum converted energy. Moreover, one can paint a glass slide with carbon nanotubes (CNTs) and consider it as an active electrode (working electrode), which is placed against another similar glass slide which represents a counter electrode. This is illustrated in Figure 2, where the space
CNTs used in photoanode of DSSC, 2004. Taking these points into account, this research work will deal with the elaboration of an alternative (and cheaper) to these techniques and materials has been offered. These tubes are highly conductive, photoactive, and mechanically strong, if well-prepared using different methods. For example, CNTs prepared by CVD are photoactive, and mechanically strong, if well-prepared using different methods. For example, CNTs prepared by CVD are chemically inactive. CNTs show favorable features as counter electrodes [16].

Despite offering relatively high conversion efficiency, serious problems of life duration are strongly associated with the use of typical dye sensitized solar cells. First, problems associated with the electrodes result from the use of organic liquids ionic solutions with I$_2$, which reacts with the electrode leading to strong corrosion, in addition to the problems of solution loss by leakage process. Second, DSSCs should not rely on dyes, because they are weakened by time (bleaching effect of time), which limits the technical use of this technology. Third, platinum, which is often used as a counter electrode, has been inconvenient for use as a noble metal.

This largely inhibits the use of DSSCs on a commercial scale. Fourth, the rare indium is an undesired metal on the commercial scale. So, to minimize or even to overcome these factors that resist the large application of DSSCs, in this research work, we suggest that the extraordinary properties of carbon nanotubes should be used to build a commercial solar cell with relatively high conversion efficiency. In addition, we suggest replacing the electrolyte with a solid film of powdered CsSnI$_3$ "diffused" into TiO$_2$ (below the painted glass), as shown in Section 2. This replacement will eliminate the problem of using electrolyte as iodine ions.

Till now, only few papers have dealt with data concerning solar illumination, with different shadow rates on DSSCs conversion efficiency. In these papers, the forward bias electrical I-V characteristics are shown, taking into account the charge neutrality (via the continuity equation), through the semiconductors of the cell. But, on the contrary, the well known model of Butler-Volmer (BVM) takes into consideration the reverse bias, when polarizing the solar cell. Moreover, BVM was adopted by Chen et al. [17] and De Marco et al. [18]; however, the experimental data of partially or totally shadowed I-V characteristics are not completely fitted with one of these two models or even by some accord between these two models. Taking these points into account, this research work will deal with the elaboration of an
Table 1: Developments of different fabrication methods of DSSCs.

<table>
<thead>
<tr>
<th>Production method</th>
<th>Advantage</th>
<th>Disadvantage</th>
<th>Year</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerosol depositing (Wet Route)</td>
<td>Performance films and mass production</td>
<td>High cost, high temperature, complicated processes</td>
<td>2011</td>
<td>[26]</td>
</tr>
<tr>
<td>Array-drawing (Wet Route)</td>
<td>High efficient cells</td>
<td>Small production and difficult to control</td>
<td>2010</td>
<td>[27]</td>
</tr>
<tr>
<td>Transfer printing (Dry Route)</td>
<td>High performance, low cost, and simple method</td>
<td>Limitation of film size, limitation to control the manufacturing method</td>
<td>2006</td>
<td>[28]</td>
</tr>
<tr>
<td>Dip-coating (Dry Route)</td>
<td>Cheap and simple method</td>
<td>Hard to control film thickness</td>
<td>2012</td>
<td>[29]</td>
</tr>
<tr>
<td>Spin-coating (Dry Route)</td>
<td>Mass production, cheap and simple method</td>
<td>Loss of CNTs through fabrication and creation of inhomogeneous films</td>
<td>2010</td>
<td>[30]</td>
</tr>
<tr>
<td>Spray-coating (Dry Route)</td>
<td>Rapid process, mass production, cheap and simple method</td>
<td>Creation of rude surfaces with possible aggregation of CNTs</td>
<td>2010</td>
<td>[31]</td>
</tr>
<tr>
<td>EPD (Dry Route)</td>
<td>Cheap, rapid, and large area films</td>
<td>Hard to control the film thickness and limited substrate</td>
<td>2008</td>
<td>[32]</td>
</tr>
<tr>
<td>Printing (Dry Route)</td>
<td>Possibility of using different substrates, simple and fast</td>
<td>Hard to control the film thickness</td>
<td>2009</td>
<td>[33]</td>
</tr>
<tr>
<td>Brush painting (Dry Route)</td>
<td>Mass production, cheap and rapid deposition</td>
<td>Hard to control the film thickness</td>
<td>2014</td>
<td>[34]</td>
</tr>
</tbody>
</table>

An adequate model to explain clearly the electrical behavior and I-V characteristics of DSSCs with partly or completely shadowing conditions. So, we will modify the well known one-diode model of a photovoltaic cell, using another diode. Thus, the cell will be represented by two diodes: one accounts for the forward bias and the other accounts for the reverse bias. The presented model is, thus, adopted to investigate the different illumination effects on a DSSC, made of 4 series-connected elements.

Finally, Slonczewski and Weiss [19] compared the ratio of energy produced per dollar, to the cost of installation and manufacturing, and they discovered that the use of graphite was an excellent solution in producing low cost cells [19] with relatively high efficiency which we took into account when we replaced them with CNTs, instead of graphite.

The literature is not poor in the application of CNTs as the counter component of the counter electrode of DSSCs [20–23]. Mixing aerosol with chemical evaporation deposition, Aitola et al. [21] have produced single-walled carbon nanotubes and have deposited film on polyethylene terephthalate substrate. Their plastic films have surface electrical resistance about 60 ohms $\text{sq}^{-1}$ when using CNT film as transparent conducting film (TCF) for DSSC. Their data have given 0.74% solar conversion efficiency at an intensity 100 mW/cm$^2$ which is by far inferior to the reference cell (4.4%). Experimental data [24] have improved the efficiency of DSSCs using Pt-free and transparent conductive oxide-free counter electrode and N-doped CNTs. The use of this doping on carbon nanotubes creates an extra free electron which can be used in reduction of electrolyte at high rate leading to increase of the efficiency. This efficiency has been improved to reach 1.5% [21]. Carbon nanotubes have been, also, used as an alternative to transparent conducting oxide materials in the Pt-based counter electrode of DSSC [25].

2. Materials and Methods

2.1. Cell Assembling (Figure 3). First, a comparison between the structure of a typical DSSC and a solid dye sensitized solar cell with carbon nanotubes is suggested. The enriched carbon nanotube solar cell (CNTSC) consists of the following:

1. A mixture of 90% semiconducting nanotubes and 10% metallic nanotubes, “South/West Nano Technologies,” with a length of about 2.4 $\mu$m and diameter of about 1.5 nm was used.

2. A thick film of powdered CsSnI$_3$ “diffused” into TiO$_2$ (below the painted glass). This thick film was prepared, using the method described by Chung et al. [35]. The advantage of using CsSnI$_3$ was the diffusion of SC into nanoporous TiO$_2$ and it could be stabilized at a solid phase inside TiO$_2$ [35]. In their
method, there were no by-products and consequently the compound was not only stable against high temperatures, but also strong against chemical reactions, in contrast to the most known solar cells [35]. This study showed that carbon nanotubes (CNTs) could replace the counter electrode. This presented it as a useful utility because the CNTs were chemically inert and corrosion of electrodes was very difficult with these tubes.

(3) A film of semiconducting nanotubes (instead of the indium oxide in DSSCs) was used.

(4) A film of CsSnI₃ with a porous TiO₂ paste (instead of the electrolyte in DSSCs) was used.

(5) For photovoltaics, semiconducting carbon nanotubes were used (instead of the dye in DSSCs).

(6) A film of Mixed Carbon Nanotubes (MCNTs) was used as a counter electrode (instead of the platinum electrode in DSSCs), "South/West Nano Technologies," with a length of about 2.4 μm and diameter of about 1.5 nm.

(7) MCNTs were composed of mixtures of 66% semiconducting nanotubes and 33% metallic nanotubes (Carbon Nanotechnologies, "UNIDYM® Inc.").

Dispersion of CNTs was carried out, using ultrasound agitation in 1,2-dichloroethane for about one hour for the regular mixture and for about four hours for the enriched mixture. Using spray paint technique, the dispersion was dyed (using a technique of airbrush) onto a glass substrate. In a regular manner, the painted glass slides were rotated while spraying, in order to obtain a homogeneous painting. The glass slides were heated on a hot plate, in order to get rid of what they might present to the solvents. The exposed surface area of about 4.8 mm² resulted from the obtained solar cell, with an interelectrode distance of about 2.5 mm. The glass slides were about one mm thick.

2.2. Production of Solar Energy. The cell was connected to a resistor (R_L). The latter varied in the range of 0 < R_L < 10 MΩ and was connected to a current amplifier. The current I (and the voltage V across R_L) was measured, as a function of the load resistor R_L. The cell was subjected to solar radiation with
an average flux of about 890 W/m². We used a vast range of CNTs concentrations to build up DSSCs.

3. Model

3.1. Theoretical Aspects. The driving forces acting on the photogenerated electrons transportation in TiO₂ occur due to the diffusion mechanism, rather than due to the action of the electric field [37] (the same applies to the holes in the paste). In fact, the miniscule volume of TiO₂ nanoparticles (from 20 nm to 70 nm) creates an important space charge layer. Also, O’Regan et al. [38] and Grätzel [39] have shown that the sintered particles are usually surrounded by an excess of charges from the paste that screens any electric field in the region. Södergren et al. [40] used the recombination, generation, and electron transport rates, to estimate the electron collection efficiency of the nanostructured photoactive electrode. While developing our model, their model [40] was taken into account.

Here, one can describe the neutrality of charges as

\[
\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2} - \frac{n - n_0}{\tau} + g, \tag{1}
\]

where \(n\) is the free electron density, \(\tau\) is the electron lifetime, \(D\) is the diffusion coefficient, \(g\) is the generation rate of electrons, and \(n_0\) is the electron density in an equilibrium state in a dark condition. Consider the following boundary conditions:

\[
n|_{x=0} = n_0 \exp \left( \frac{qV}{mkT} \right), \tag{2}
\]

\[
\frac{\partial n}{\partial x} = 0, \tag{3}
\]

where \(V\) represents the photoelectrode potential, which is related to the energy variation between the electrode potential and Fermi energy (Fermi level), \(E_F\). Consequently, the current density equation is given as

\[
j = j_{SC} - j_0 \exp \left( \frac{qV}{mkT} - 1 \right). \tag{4}
\]

It is important to note that an ideality factor \(m\) is considered, when applying (2). Bashahu and Nkundakura [41] identified a value of \(m\) to be about 22, from experimental data that considered only one set of current-voltage experimental data. Due to the inevitable presence of a parasitic resistance \(R_s\), only the last equation cannot describe the electric I-V characteristics data. This resistance should be introduced as series resistance \(R_s\) to get an exact estimation of the current-voltage characteristics. In addition, this parasitic resistance \(R_s\) contains the resistive effects of the metallic contacts. Another parasitic resistance \(R_{sh}\) should also be considered, due to the presence of a parallel electric field, which is present due to the leakage path across the interface between TiO₂ and the paste. In order to understand the I-V characteristics and to simulate an equivalent circuit that described the electrical characteristics of DSSC, Halm et al. [42] developed the classic “one-diode” model (Figure 1) that sufficiently described the following I-V characteristics:

\[
I = I_{ph} - I_0 \left[ \exp \left( \frac{q(V + I_R)}{mkT} \right) - 1 \right] - \frac{V + I_R}{R_{sh}}, \tag{5}
\]

where \(I_0\) is the current density at saturation-reversed conditions, \(I_{ph}\) is the photocurrent density of the diode as a current source, \(q\) is the electron charge, \(k\) is Boltzmann constant, \(T\) is the absolute temperature, and \(R_{sh}\) is a parallel electric resistance connected to the cell. Considering this with \(I = 0\), the open circuit voltage \(V_{OC}\) can be given as

\[
V_{OC} = \frac{mkT}{q} \ln \left( \frac{l_{ph}}{l_0} + 1 \right). \tag{6}
\]

This last equation gives the reason why \(V_{OC}\) corresponds with the high growing current of the short circuit. But the finely built current of the dye cells is not too simple to be described by only one diode, because it will be poorly described and it cannot be used to explain the electrical behavior of DSSC. Another important factor is that the parasitic resistances \(R_s\) and \(R_{sh}\) are considered to be independent of the voltage, which is not the real case. However, these fitting parameters represent an effective tool that is used to have a first sight interpretation of the characteristic behavior of the I-V [43].

3.2. Reverse Behavior through Dye Sensitized Solar Cells. Sastrawan et al. [44] and Chen et al. [17] have shown that the generated photocurrent produced when cells are collected together makes the shaded cell operate in reverse bias. The counter electrode (platinum or else) supplies electrons to the paste, which facilitates possible and easier ways of injecting electrons from the paste, and thus the charges will transfer from the corresponding electrode (\(\Gamma\)) directly to the porous TiO₂, and the oxidation of the electrode (\(\Gamma\)) allows one to consider the reverse current passage making a possible introduction to a reverse diode, in addition to the forward one (Figure 3).

Wolf and Rauschenbach [45] have shown that the charge transfer is mainly due to a reduction in the oxidation reaction (in the shadowed cell), and the recombination via the substrate. Following this, the net flow of charges yielded a current given by BVM and it was written in terms of overvoltage as

\[
j = j_0 \left[ \exp \left( \frac{\beta (qn)V}{kT} \right) - \exp \left( - \frac{(1 - \beta)(qn)V}{kT} \right) \right], \tag{7}
\]

where \(\beta\) is the cathodic transfer coefficient, \(j_0\) is the exchange current density, and \(n\) is the number of transferred electrons. Both (\(\Gamma\)) and (\(\Gamma\)), affected the current density (which was going to the cathode) via the concentrations and the reaction area. Here, the first term, in (7), is a linear function of the current, but the other term is a linear function of the current going to the anode. Moreover, the direct relationship between the two currents going to the anode and cathode resulted in the exchange current \(j_0\). In fact, BVM gave the reasons about the homogeneity of the electric field around the electrodes.
Some limitations, however, arose, because of a small correction of the overpotential at the counter electrode, which was essential for fitting current-voltage characteristics in an effective way [47]. Chen et al. [17] introduced the idea of $R_s$ of the transparent conductive oxide layers of the BVM, which improved the fitting process of the cell's electrical characteristics.

3.3. Electrical Behavior of DSSC. In the equivalent circuit, the rectification behavior of the diode explained the electrical behavior of DSS at the reverse polarization conditions. We proposed another parallel-diode with the current generator, in order to represent the rectifying behavior. The presence of the second diode prevented the recourse of the electrochemical variables, when the transfer of charges occurred at the paste. We schematically present the two-diode model in Figure 3. Applying the conservation of energy principal (via Kirchhoff equation), the characteristic equation of the circuit in Figure 3 can be described as

$$I = I_{ph} - I_{0, For} \left[ \exp \left( \frac{q (V + I R_s)}{m_{For} kT} \right) - 1 \right]$$

$$+ I_{0, rev} \left[ \exp \left( \frac{-q (V + I R_s)}{m_{rev} kT} \right) - 1 \right] - \frac{V + IR_s}{R_{sh}}. \quad (8)$$

In dark conditions, it can be understood that, at reverse polarization, only the third term in (8) remained, while in the illumination conditions with forward polarization, the “one-diode” based model was equivalent to the two-diode based model. The values of $R_s$ were taken to be constant in our model, in both forward and reverse bias. As a first approximation, we considered $R_s$ = $R_{sh}$; that is, we considered the fact that they would have the same magnitude in both conditions. On the contrary, the physical meaning of the exponential term was controlled by the ideality-factor value, which depended on the operative conditions and was not equal. This means that the difference between the ideality factors in forward and reverse bias is a function of the condition of active working (temperature, illumination intensity, effective surface area, etc.).

4. Results

4.1. Characterization of Obtained Cell

4.1.1. Raman Scattering Spectra. At different excitation light, 514.5 nanometers, 676.4 nanometers, and 1064.0 nanometers, the main surface enhanced Raman scattering spectra characteristics of carbon nanotubes have been taken and are illustrated in Figure 4.

This figure shows characteristics of samples with different nanoropes of about 18 up to 99 separated CNTs which are in good agreement with published data [48]. As seen, the spectra of ropes are strongly depending on the excitation wavelength.

4.1.2. XPS Spectra. XPS spectra have been taken with SSX-100 ESCA spectrometer using 1486.6 eV Al-K$_\alpha$ radiation. Figure 5 illustrates XPS spectra with two different resolutions: (a) low and (b) high. The high resolution illustration shows the presence of C-C bond at 285 eV, in addition to some carbonyl moiety in harmony with carboxylated groups at 288 eV. The low-resolution XPS spectrum shows a net peak at 284.8 eV which is due to carbon 1s.

Mialhe et al. [49] and Ishibashi et al. [50] have shown that studying the effect of each variable on the different parts of the current-voltage curves (where some of these parameters could be neglected at certain parts of the I-V characteristics) is the best way to understand the electrical behavior of the DSSCs. Models with one diode can be used to get an accurate estimation of the DSSCs physical parameters; that is, the application of (8) to the experimental data can give the cell parameters when extrapolating numerical calculations which could be obtained either from extrapolating experimental results [51] or from using the spectral and electrochemical studies with the help of a suitable equivalent circuit of DSSC (single cell). We carried out our analysis in two successive steps. First, an initial group of fitting parameters were extracted using experimental data; then, second, they were, iteratively, refined out using “Levenberg Marquardt,” an algorithmic procedure that is used for nonlinear curve fitting [52]. In the analysis, we reported a detailed procedure for the estimation of the initial parameters:

(a) $I_{ph}$ was considered to be coincident with the short circuit photocurrent, $I_c$.

(b) From the slope of current-voltage curves, we were able to estimate the shunt resistant $R_{sh}$ when $I = I_{sc}$:

$$- \frac{dV}{dI} \bigg|_{I=I_{sc}} = R_{sh}. \quad (9)$$

The value of $R_{sh}$, in our device, was about $1.1 \times 10^5 \Omega$, which was a remarkably high value. Accordingly, when we took into account the photocurrent values of about some milliampere, then, we can consider $R_{sh}$ to tend to infinite values. Moreover, O’Regan et al. [53] reported that rash usually
increased, when illumination decreased. Thus, we kept it as a constant factor.

(c) Following Han et al. [36], in forward bias, the series resistance $R_{s\text{,for}}$ could be obtained by direct application of the well known curves of $e^x - e^y$ because of the addition of several different resistances: contact resistance, substrate sheet resistance, electrical resistance of the paste, and resistance of all wires of the cell.

(d) Then, we were able to estimate the exact potential through the cell $V_F$, by using the forward bias resistance, $R_{s\text{,for}}$ as

$$V_F = V_{\text{app}} - V_s = V_{\text{app}} - IR_{s\text{,for}}. \quad (10)$$

(e) The value of the recombination resistance was then estimated from the analysis of the different spectra of electrochemical impedance spectroscopy in the middle frequency region [42]:

$$R_{\text{rec}} = \frac{kT}{q\beta I_{0\text{,for}}} \exp\left(\frac{-q\beta V_F}{kT}\right). \quad (11)$$

(f) We were able to estimate the value of the ideality factor in forward bias, using the semilog curve of the recombination resistance $R_{\text{rec}}$ versus the potential at the SC electrode, $V_F$, where $m_{\text{for}} = 1/\beta$ and $I_{0\text{,for}}$.

With regard to the reverse-bias term in (8), the best fitting parameters of current-voltage curves could be used to estimate several parameters of the DSSC: the reverse series resistance $R_{s\text{,rev}}$, the reverse series resistance $R_{s\text{,rev}}$, and the ideality factor $m_{\text{rev}}$. Here, one can easily neglect both $R_{s\text{,rev}}$ and the current generator.

(g) The value of recombination resistance is, then, estimated from analysis of the different spectra of electrochemical impedance spectroscopy in middle frequency region [42]:

$$R_{\text{rec}} = \frac{kT}{q\beta I_{0\text{,for}}} \exp\left(\frac{-q\beta V_F}{kT}\right). \quad (12)$$

(h) The value of the ideality factor, in forward bias, could be estimated using semilog curve of recombination resistance $R_{\text{rec}}$ versus the potential at the SC electrode, $V_F$, where $m_{\text{for}} = 1/\beta$ and $I_{0\text{,for}}$.

In regard to the reverse-bias term in (8), the best fitting parameters of current-voltage curves could be used to estimate several parameters of the DSSC: the reverse series resistance $R_{s\text{,rev}}$, the reverse series resistance $R_{s\text{,rev}}$, and the ideality factor $m_{\text{rev}}$. Here, one can easily neglect both $R_{s\text{,rev}}$ and the current generator.

At elevated negative voltages, with the best nonlinear square fitting processes, we estimated $I_0\text{,rev}$-values from its current value at zero voltage. Also, we found $R_{s\text{,rev}}$ from the slope of the current-voltage curves, particularly, at the straight line of the current-voltage curves. The initial value of $m_{\text{rev}}$ was considered as 1.5, to be in the range $1 < m_{\text{rev}} < 2$. Since we used the same series resistance, we assumed that $R_{s\text{,rev}} > R_{s\text{,for}}$. Systematically, the estimated $R_{s\text{,for}}$ was highly affected by the illumination intensity (or shadow rate). Figure 6 illustrates a steep decrease of the short circuit current with a shadowing rate. The open circuit voltage decreased also, at a high shadow rate, which could be predicted from (6). But a minor increase of the fill factor was as a result of the high shadow rate. We attributed this decrease of $R_s$ to the effect of photocurrent. The strong reduction in the $R_s$ value was a function of the produced photocurrent.

The magnitudes of $R_{s\text{,for}}$, at 1 sun illumination, ranged as 20 $\Omega$ (complete illumination) $< R_{s\text{,for}} < 21$ $\Omega$ (0.75 of the complete illumination). Consequently, $R_{s\text{,for}}$ was nearly not affected by the extent of the shaded photovoltaic region, and the values of $R_{s\text{,for}}$ were taken as $R_{s\text{,rev}}$. Table 1 shows the information about the numerical coefficients.

To examine quantitatively the accuracy (including its validity) of our model for the different shadowing rates, we used “PSice” with the proposed model including the EC. By using this technique, the output power was accurately estimated after I-V characteristics data. First, and for simplicity, at a complete shaded rate, we considered the module to be composed of only one single element, which would
Table 2: Methods to estimate the numerical parameters used to fit experimental data to (8).

| Symbol | $I_{ph}$ | $I_0$ | $m$ | $R_s$ | $R_{sh}$ | $\frac{dV}{dI}|_{I=I_{sc}}$ |
|--------|---------|-------|-----|-------|--------|-----------------------------|
| Forward direction | $\approx I_1$ | Using EIS analysis | Using EIS | Using EIS | When $-(dV/dI)|_{I=I_{sc}}$ |
| Reverse direction | Using (8) | Using (8) | Using (8) | Using (8) | — |

Table 2 shows the magnitudes of the physical parameters which have best fitted the experimental data to the model.

Using the principal of charge conservation, Sastrawan et al. [44] derived an expression that described the $I$-$V$ characteristics of the cell in forward bias; their fitting values were not very far from ours, whereas the BVM ([7]) explained the reverse-biased behavior conduction in DSSC. One writes

$$I = I_{ph} I_{rr} \beta - A \frac{qDn_0 d}{L^2} \left[ \exp \left( \frac{q (V + IR_s)}{m_F kT} \right) - 1 \right] \beta$$

$$- A j_0 \left[ \exp \left( \frac{an (V + IR_s)}{kT} \right) \right] - \exp \left( \frac{-(1-\alpha)n (V + IR_s)}{kT} \right) - \left( \frac{V + IR_s}{R_{sh}} \right).$$

(15)

$I_{ph}$ is the photocurrent, $I_{rr}$ is the constant correlated with the irradiance parameter, $\beta$ is the shading rate, $D$ is the diffusion length of the electron, $j_0$ is the exchange current density, $\alpha$ is the cathodic transfer coefficient, $n$ is the number of electrons transferred, and $A$ is the surface of the area cell.

Equation (15) could be approximated, in reverse bias, where the first quantity could be neglected, but the second quantity has no real effect on the current density in the forward bias. The different physical parameters, described by (14), of the DSSC are reported in Table 3. Noting that $I_{ph}$ is taken to be coincident with $I_{sc}$, just like Halm et al. [42],

Figure 6: Series resistance as a function of light intensity for different shading rates.

Figure 7: Experimental data of $I$-$V$ characteristics of a four-cell module with one fully shadowed cell.
Table 3: Best fitting parameters and experimental values to fit experimental data to (8).

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_{sc}$</td>
<td>Short circuit current</td>
<td>2.4</td>
<td>mA</td>
</tr>
<tr>
<td>$R_{s,For}$</td>
<td>Series resistance</td>
<td>20</td>
<td>Ω</td>
</tr>
<tr>
<td>$R_{s,rev}$</td>
<td>Series resistance</td>
<td>23</td>
<td>Ω</td>
</tr>
<tr>
<td>$I_0,rev$</td>
<td>Irradiance factor</td>
<td>$2.3 \times 10^{-5}$</td>
<td>mA</td>
</tr>
<tr>
<td>$d$</td>
<td>Film thickness</td>
<td>$7 \times 10^{-6}$</td>
<td>m</td>
</tr>
<tr>
<td>$m_{rev}$</td>
<td>Diode ideality factor</td>
<td>1.1</td>
<td>—</td>
</tr>
<tr>
<td>$m_{For}$</td>
<td>Diode ideality factor</td>
<td>1.5</td>
<td>—</td>
</tr>
<tr>
<td>$A$</td>
<td>Area of dye sensitized solar cell</td>
<td>0.28</td>
<td>cm$^2$</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
<td>300</td>
<td>K</td>
</tr>
</tbody>
</table>

we have used the following equations to deduce the values of $D$ and $L$:

$$D = \frac{d^2}{R_tC\mu},$$

$$\tau = R_{rec}C\mu,$$

$$L = \sqrt{DR_T} = d\sqrt{\frac{R_{rec}}{R_{CT}}}.$$ (16)

Moreover, just like Sastrawan et al. [44], we have calculated the cathodic transfer coefficient $\alpha$ and we have, also, used the work of Van De Lagemaat and Frank [52], to estimate the electron density, $n_0$.

Figure 7 shows the electrical behavior of the conduction mechanism, which is a direct reflection of (15). However, the fit between the experimental data and model is not quite well demonstrated. This is because one has used the single independent measurements, to describe different physical parameters; so, some of the cell parameters have to be kept constant at certain conditions. For example, Wang et al. [54] have shown that the diffusion length $L$ depends on the potential. The fitting parameters $\beta$ and $I_{irr}$ could be estimated, when varying the shadowing conditions of the cell. The simulated curve estimated after (8) fits the experimental data well. Thus, our model allows us to predict the values of the recombination rates (current), by following the interface between the paste and the transparent conductive oxide layer, which leads to a corresponding potential decrease, due to photovoltage drop $V_{\text{bump}}$. Figure 8 shows the measured and simulated current-voltage curves with the complete shadowing rate.

The presented model (two-diode model) fits well for all the 4 shadowing rates, which are seen from the simulation plots. The value of $V_{\text{bump}}$ is doubled, when comparing it with a single cell. This is well shown after (13), when all the parameters are doubled. Similar electric results are shown with a complete shadowing rate, and with a multiplication factor of 3. This explanation is only applied, when the four elements composed of cells with different electrical parameters, $V_{\text{rev}}$ and $V_{\text{OC}}$, are determined for all the cells with different shadow rates which makes it possible to put the second term in (13) as a sum product.

Figure 9 shows that good simulation plots obtained when considering a two-diode model fit nearly perfectly for all the experimental current-voltage curves. In this figure, the simulation plots obtained by application of a 2-diode model fit nearly perfectly to the experimental data concerning all the considered shadowing rates. The reverse current passing the diode will induce the DSSC to operate as a load under potentials over 1.45 volts, if only one quart of the effective surface of

![Figure 8: I-V characteristics experimental data for different shading rates illustrated as symbols and one shaded cell, two shaded cells, and fully illuminated module.](image)

![Figure 9: I-V characteristics experimental data for different shading rates illustrated as symbols.](image)
the photoelectrode is put in the dark. Consequently, the step is added to the I-V characteristics because the reverse diode is turned on suddenly. When half of the active area is shaded, the electric current arising from recombination increases more than the current generated by the photoexcitation at the unshaded photoelectrode; thus, the net output current will decrease which is shown by a plateau when reaching the critical short circuit value of the shaded cell, keeping the value of $V_{\text{bump}}$ constant. The $x$-axis extension of the area lies under the influence of the photocurrent drop $V_{\text{bump}}$ and it does not get affected by the factor relating the illuminating active area of the photoelectrode to the obscured one as it is expected from (13).

When half of the active area is shaded, the electric current arising from recombination increases more than the current generated by the photoexcitation at the unshaded photoelectrode electrode; thus, the net output current will decrease which is shown by a plateau when reaching the critical short circuit value of the shaded cell, keeping the value of $V_{\text{bump}}$ constant. The $x$-axis extension of the area lying under the influence of the photocurrent drop $V_{\text{bump}}$ does not get affected by the factor relating illuminating active area of the photoelectrode to the obscured one as it is expected from (13). The carbon nanotubes in the present study were double-walled which are conductive materials. They can reduce the contact resistance which decreases in turn the charge transfer $R_{CT}$ resistance with the DSSC due to fast transfer kinetics of electric charges (Table 4).

Lee et al. [55] have used carbon nanotubes as counter electrodes in DSSC and found a photovoltaic efficiency of 7.67% and the values of $R_{CT}$ of their cell were 0.82 ohms cm$^2$. Interestingly, their efficiency is comparable to the typical Pt-DSSC photovoltaic efficiency (7.83%). Experimental measurements of the present work have led to an efficiency of 5.7% and one can attribute the low value of efficiency to the nature of the impurities in the commercial carbon nanotubes and the effect of defect-rich edge planes in the bamboo-structured carbon nanotubes.

In addition, the measurements data of the present work have given relatively low values of the charge transfer resistance, about 1.05 ohms cm$^2$ which is lower than that of typical Pt-electrode (1.8 ohms cm$^2$). Our data are summarized in Table 5.

The function of DSSC is very sensitive to the number of walls of carbon nanotubes. In general, these nanotubes can be classified into single-walled carbon nanotubes, double-walled carbon nanotubes, and multiwalled carbon nanotubes. Zhang et al. [56] have compared the photovoltaic efficiency of three different DSSCs based on single-walled carbon nanotubes, double-walled carbon nanotubes, and multiwalled carbon nanotubes. They have found that the efficiencies vary in the range, 8.03% for double-walled carbon nanotubes, 7.61% for single-walled carbon nanotubes, and 7.06% for multiwalled carbon nanotubes. These efficiencies have been well matched with the charge transfer resistance; that is, $R_{CT} = 3.13$ ohms cm$^2$ for double-walled carbon nanotubes, $R_{CT} = 6.72$ ohms cm$^2$ for single-walled carbon nanotubes, and $R_{CT} = 10$ for multiwalled carbon nanotubes.

The double-walled carbon nanotubes have larger “inner surface area” that can easily activate the charge transfer between them. However, the bamboo structure of multiwalled carbon nanotubes has more complicated “inner surface area” that strongly decrease the charge mobility and increase the corresponding charge transfer resistance. Consequently, this decreases the photovoltaic efficiency.

Carbon nanofibers have large surface area, high density of surface defects, and very thin filament size. These characteristics lead to an efficient DSSC due to their thinner thickness. As is well known, the electrical resistance of the counter electrode decreases as it gets thinner: Electrical resistance ($R$) = resistivity ($\rho$) × length (l)/area (A). For example, as the counter electrode increases from 5 micrometers, 10 micrometers, and 15 micrometers, to 20 micrometers, the net DSSC series resistance increases from 6.9 ohms cm$^2$, 9.9 ohms cm$^2$, 10.6 ohms cm$^2$, and 11.9 ohms cm$^2$. Because all factors are constant and only the counter electrode thickness decreases with the carbon nanofibers structure, the overall efficiency of DSSC with carbon nanofiber increases as a result of the reduction of counter electrode area. Table 6 shows the photovoltaic efficiency as a function of counter electrode thickness.

Comparing the experimental data recently published by Elboly et al. [57] to the typical Pt- counter electrodes or carbon nanotubes counter electrodes, the carbon fiber SDDC has higher electrocatalytic efficiency and photovoltaic performance. This is attributed to its low electrical resistance of charge transfer and to high interfacial area. This also leads to accelerating mobility of charges which will reduce

<table>
<thead>
<tr>
<th>Table 4: Best fitting parameters and experimental values to fit experimental data to (15).</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symbol</td>
</tr>
<tr>
<td>$R_{sh}$</td>
</tr>
<tr>
<td>$R_{s}$</td>
</tr>
<tr>
<td>$I_{ph}$</td>
</tr>
<tr>
<td>$d$</td>
</tr>
<tr>
<td>$\beta$</td>
</tr>
<tr>
<td>$D$</td>
</tr>
<tr>
<td>$n_0$</td>
</tr>
<tr>
<td>$D$</td>
</tr>
<tr>
<td>$j_0$</td>
</tr>
<tr>
<td>$\alpha$</td>
</tr>
<tr>
<td>$m$</td>
</tr>
<tr>
<td>$m$</td>
</tr>
<tr>
<td>$A$</td>
</tr>
<tr>
<td>$T$</td>
</tr>
</tbody>
</table>
Table 5: Current-voltage characteristics of DSSC with carbon nanotubes as counter electrode: measurements have been carried out under 0.75 sun illumination.

<table>
<thead>
<tr>
<th>Counter electrode</th>
<th>( R_{CT} ) (ohms cm(^2)) ±0.4</th>
<th>( J_{SC} ) (mA cm(^2)) ±0.1</th>
<th>( V_{OC} ): open circuit voltage</th>
<th>FF ±0.02</th>
<th>Efficiency% ±0.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNTs</td>
<td>1.05</td>
<td>8.2</td>
<td>0.32</td>
<td>0.32</td>
<td>5.7</td>
</tr>
<tr>
<td>Pt</td>
<td>1.8</td>
<td>13.4</td>
<td>0.81</td>
<td>0.64</td>
<td>6.9</td>
</tr>
<tr>
<td>Bare FTO</td>
<td>—</td>
<td>1.7</td>
<td>0.82</td>
<td>0.04</td>
<td>0.06</td>
</tr>
</tbody>
</table>

\( R_{CT} \): charge transfer resistance, \( J_{SC} \): short circuit current, \( V_{OC} \): open circuit voltage, and FF: fill factor. Active area of the device is 0.25 cm\(^2\).

Table 6: DSSC parameters as a function of counter electrode thickness.

<table>
<thead>
<tr>
<th>Thickness, µm</th>
<th>( R_{CT} ) (ohms cm(^2))</th>
<th>( J_{SC} ) (mA cm(^2))</th>
<th>( V_{OC} ): open circuit voltage</th>
<th>FF ± 0.02</th>
<th>Efficiency% ±0.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>6.9</td>
<td>18.7 ± 0.1</td>
<td>0.78 ± 0.007</td>
<td>67</td>
<td>9.77 ± 0.14</td>
</tr>
<tr>
<td>10</td>
<td>9.9</td>
<td>18.41 ± 0.12</td>
<td>0.78 ± 0.005</td>
<td>63</td>
<td>9.05 ± 0.12</td>
</tr>
<tr>
<td>15</td>
<td>10.6</td>
<td>17.837 ± 0.18</td>
<td>0.78 ± 0.005</td>
<td>60</td>
<td>8.34 ± 0.14</td>
</tr>
<tr>
<td>20</td>
<td>11.9</td>
<td>17.1 ± 0.1</td>
<td>0.78 ± 0.005</td>
<td>57</td>
<td>7.63 ± 0.09</td>
</tr>
</tbody>
</table>

the rate of reduction and increases the performance. More studies of counter electrode thickness and charge transfer resistance will give huge steps to improving the efficiency of solar conversion.

5. Conclusions

It has been demonstrated that the addition of a second diode to the equivalent circuit explains quite well the reverse behavior of the shaded elements; and this addition fits well the forward bias I-V characteristics of the experimental data, when working in several shading conditions. It has, also, been shown that different rates of shadow affect the efficiency of a dye synthesized solar cell. When applying the 2-diode model, we found very close matching between the experimental values of the 2-diode model, we found very close matching between the curve and the simulation curves and the simulation data. Our approaches used a few amounts of fitting factors compared to the previously proposed models, which makes this model relatively flexible, effective, and more reliable.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

This project was funded by the Deanship of Scientific Research (DSR), King Abdulaziz University, Jeddah, under Grant no. G-1436-130-35. The authors, therefore, acknowledge with thanks DSR technical and financial support.

References


Submit your manuscripts at http://www.hindawi.com