Optik - International Journal for Light and Electron Optics 290 (2023) 171287

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.com/locate/ijleo

Investigation on short–circuit current density (J_{sc}) in the dye-sensitized solar cells by optimizing photoelectrode thickness

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ARTICLE INFO

Keywords:
Dye-sensitized solar cells
Short-circuit current density
Diffusion coefficient
Diffusion length

ABSTRACT

The photoelectrode of dye-sensitized solar cells (DSSC) is a vital part that loads the dye, transports the generated photoelectrons to the external load, and serves as an interface between the current collector and the dye. The performance of the DSSCs is highly influenced by the thickness of the photoelectrode. The short-circuit current density (J_{sc}) of the DSSC increases with thickness and reaches its maximum at a particular thickness, after which J_{sc} decreases and saturates. A theoretical approach is formulated, using which the optimal thickness required to obtain maximum J_{sc} for the DSSC is calculated. A novel analytical expression for optimal diffusion length (L_0), which is the electron diffusion length required to maximize J_{sc} is derived. The experimental validation of the simulated results is carried out with DSSCs of varying photoelectrode thickness. These validation results suggest that this theoretical approach to determine the optimal thickness of photoelectrodes enhances the efficiency of dye-sensitized solar cells.

1. Introduction

The energy crisis is becoming more severe than ever, and the developing world requires alternative energy sources other than conventional energy sources. The environmental impact of the greenhouse gases from these conventional sources is alarming, and hence the optimum utilization of renewable energy resources such as solar energy is the need of the hour.

In recent years, dye – sensitised solar cells (DSSC) have been highly researched owing to their easy manufacturing process and cost effectiveness. DSSC consists of the photoelectrode, the dye sensitizer, the electrolyte, and the counter electrode. When the incoming photon flux is incident on the DSSC, the dye molecules get excited, and the electrons are transferred to the conduction band of the photoelectrode. The electrons lost by the dye molecules are replaced by the electrolyte. The electrolyte receives the electrons from the counter electrode [1].

Various studies have revealed that surface area, roughness, thickness, crystallinity, structure, and morphology of the photoelectrode play a vital role in determining the solar cell performance [2–6]. The photoelectrode serves as the adsorbing medium for the dye, aids in the transport of the photoelectrons, and hence determines the charge collection efficiency. The porosity of the mesoporous photoanode determines the amount of dye loaded and hence affects the short-circuit current density (J_{sc}) [7,8]. Thus, the photoelectrode plays a vital role in generating photoelectricity.

The ideal photoanode should possess a high surface area to aid in better dye loading, good resilience to photo-corrosion, and

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https://doi.org/10.1016/j.ijleo.2023.171287
Received 23 November 2022; Received in revised form 25 March 2023; Accepted 8 August 2023
Available online 9 August 2023

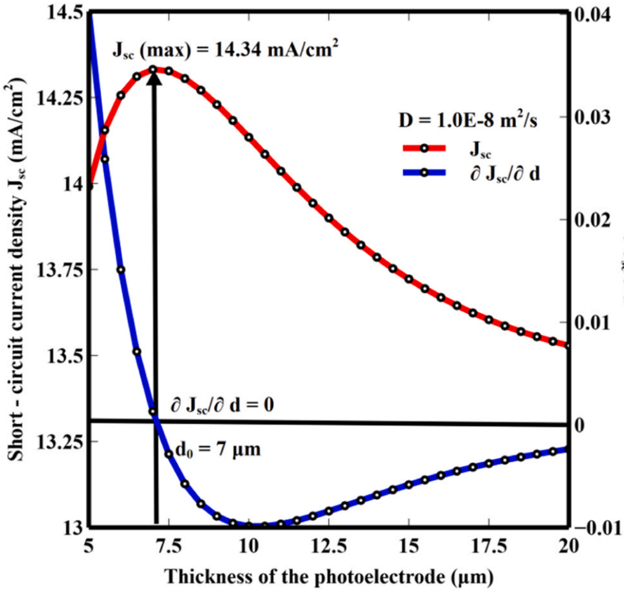

Fig. 1. J_{sc} as a function of thickness of the photoelectrode.

facilitate good interface contact with the dye molecules and with the FTO/ITO of the substrate. Hence, the structure and material of the photoanode determine the J-V characteristics of the solar cell, including the open-circuit voltage (V_{oc}), the short-circuit current density (J_{sc}), the amount of dye loading, and the fill factor (FF) of the solar cell [9,10].

When the thickness of a photoelectrode material rises, the interfacial surface area also grows, leading to higher dye loading. As a result, the short-circuit current density increases due to the excitation of more dye molecules [11]. Photoelectron generation reaches saturation if the photoelectrode's thickness exceeds the length of light's penetration. On the other hand, a thicker photoelectrode makes photoelectrons easier to recombine, which reduces J_{sc} [12]. The photoelectrode's thickness, thus, has an impact on J_{sc}.

Theoretical analysis of the effect of thickness of TiO_2 film on the efficiency of the DSSC revealed that the significant improvement in efficiency is observed when photoelectrode thickness is optimized [13–15]. From the theoretical studies carried out, it is inferred that even for the DSSCs with different dye sensitizers, the efficiency of the solar cell is dependent on the thickness of the working electrode [16–18].

Today, several studies are being carried out to determine how the dimensions of the TiO_2 nanorods affect the short-circuit current density. By optimizing the nanorod diameter, porosity of the photoelectrode can be tuned and hence the short-circuit current density is enhanced [19], [20]. The thickness of the photoelectrode is discovered to be the determining factor in the DSSC performance [21–24], even though the morphology of the photoelectrode material might vary as nanocrystalline, nanorods, and nanowire arrays. In the conversion of solar cell architecture from cell to module form, it is also found that the short-circuit current density (J_{sc}) depends mainly on photoelectrode thickness [25]. In this work, a theoretical approach to achieve the maximum J_{sc} by optimizing the thickness of the photoelectrode is formulated. Hence, the analytical expression for the optimal diffusion length (L_0) of electrons required to maximize J_{sc} is derived. The solar cell parameters, such as fill factor, efficiency, etc., are calculated and compared with experimental results available in the literature [26].

2. Theory and calculations

For attaining maximum J_{sc}, the DSSC parameters, such as thickness and diffusion length, should be optimized. Further, the increase in the short-circuit current density (J_{sc}) is estimated, and hence the efficiency of DSSC is calculated.

2.1. Calculation of the optimal thickness d_0

Soedergren et al., [27] have analytically solved the diffusion differential equation based on the electron diffusion in the porous photoelectrode and hence derived the expression for short-circuit current density, which is given by

$$J_{sc} = \frac{q\phi L\alpha}{1 - L^2\alpha^2}\left[- L\alpha + \tanh\left(\frac{d}{L}\right) + \frac{L\alpha \exp(- \alpha d)}{\cosh\left(\frac{d}{L}\right)}\right] \tag{1}$$

where q – Electronic charge; ϕ – the light density; L – diffusion length of the electrons; α – light absorption coefficient of the pho-

Table 1
Parameters of the dye-sensitized solar cell.

Parameters	Values
Electronic charge (q)	1.609E-19 C
Light Intensity (ϕ)	1.0E17 cm^{-2} s^{-1}[12]
Diffusion coefficient (L)	$L = \sqrt{D\tau}$ (m)
Diffusion Coefficient (D)	1.0E-6 m^2s^{-1}, 1.0E-7 m^2s^{-1}, 1.0E-8 m^2s^{-1} and 1.0E-9 m^2s^{-1}[26]
Mean Life time (τ)	5E-3 s,10E-3 s, 15E-3 s and 20E-3 s[12]
Light absorption coefficient (α)	5000 cm^{-1}[12]
Electron concentration – dark condition (n_0)	10^{17} cm^{-3} (assumed)
Ideality factor (m)	4.5[28],[29]
Temperature (T)	300 K
Boltzmann constant (k)	1.38E-23 J/K

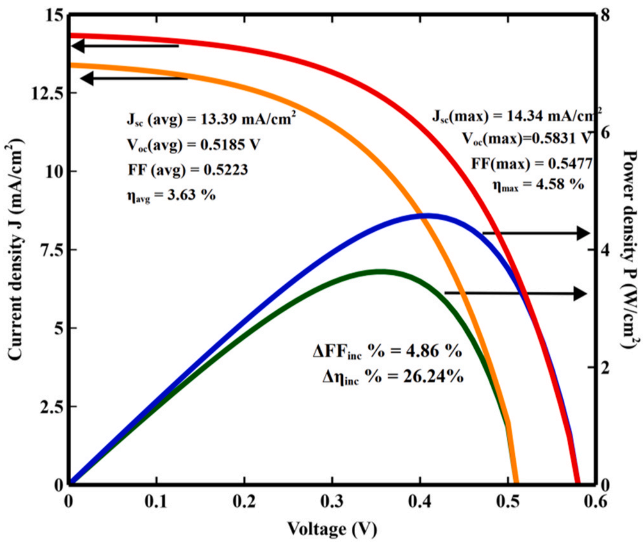

Fig. 2. J-V plots showing the improvement in performance of DSSC with optimized photoelectrode thickness (d_0).

toelectrode; d – thickness of the electrode.

When first order derivative of J_{sc} with respect to d, $\frac{\partial J_{sc}}{\partial d}$is equated to zero, the optimal thickness 'd_0' can be calculated. At this optimal thickness 'd_0', J_{sc} can attain maxima or minima, and this can be determined by substituting 'd_0' in the second order derivative of J_{sc} with respect to d, i.e., $\frac{\partial^2 J_{sc}}{\partial d^2}$.

$$\frac{\partial Jsc}{\partial d} = \frac{q\phi L\alpha}{1 - L^2\alpha^2}\left\{\frac{1}{L}\mathrm{sech}^2\left(\frac{d}{L}\right) - \alpha\exp\left(-\alpha d\right)\mathrm{sech}\left(\frac{d}{L}\right)tanh\left(\frac{d}{L}\right) - L\alpha^2\exp\left(-\alpha d\right)\mathrm{sech}\left(\frac{d}{L}\right)\right\} \tag{2}$$

$$\frac{\partial^2 J_{sc}}{\partial d^2} = \frac{q\phi L\alpha}{1 - L^2\alpha^2}\left\{\left[2\mathrm{sech}\left(\frac{d}{L}\right)tanh\left(\frac{d}{L}\right)\left(-\frac{1}{L^2}\mathrm{sech}\left(\frac{d}{L}\right) + \alpha^2 e^{-\alpha d}\right)\right] + \left[\frac{\alpha e^{-\alpha d}}{L}\left(\mathrm{sech}\left(\frac{d}{L}\right)tanh^2\left(\frac{d}{L}\right) - \mathrm{sech}^3\left(\frac{d}{L}\right)\right)\right] + L\alpha^3 e^{-\alpha d}\mathrm{sech}\left(\frac{d}{L}\right)\right\} \tag{3}$$

As shown in Fig. 1, the J_{sc} graph clearly depicts that when the first derivative is zero the optimal thickness of the photoelectrode, d_0 is found to be 7 μm. At this point, J_{sc} attains a maximum of 14.34 mA/cm^2 when the diffusion coefficient (D) and the mean life time (τ) of electrons in the photoanode is 1.0E-8 m^2/s and 10E-3 s respectively.

2.2. Improving the efficiency of the DSSC by maximizing J_{sc}

The relationship between the current density (J) and voltage (V) of the DSSC is given by [28], [29].

$$J = J_{sc} - \frac{qDn_0}{L}\tanh\left(\frac{d}{L}\right)\left[\exp\left(\frac{qV}{kTm}\right) - 1\right] \tag{4}$$

where, k – Boltzmann constant; T – Temperature; m – Ideality factor; J_{sc} – Short-circuit current density; J – current density; D –

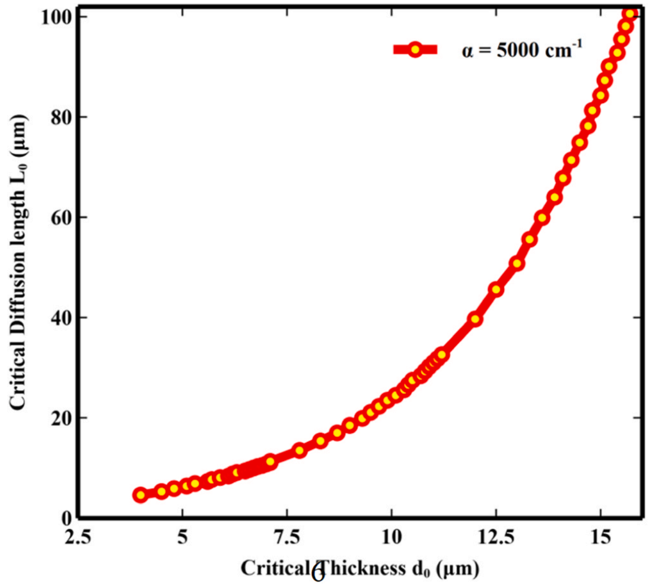

Fig. 3. Variation of optimal diffusion length (L_0) with optimal photoelectrode thickness (d_0).

Diffusion coefficient of the electrons in the photoelectrode; n_0 – Electron concentration under dark conditions; d – Film thickness of the photoelectrode; L – Diffusion Length of the electrons in the photoelectrode.

Using the J-V plots, the performance of the DSSC can be estimated effectively. The Eq. (4) is utilized to draw the J-V plots and the key parameters such as the open-circuit voltage (V_{oc}), the fill factor (FF) and the efficiency (η) can be calculated using the Eqs. (5) to (7). The parameters involved in calculating in the efficiency are given in Table 1.

The open – circuit voltage (V_{oc}) of the solar cell can be given by

$$V_{oc} = \frac{kTm}{q} \ln\left[\frac{LJ_{sc}}{qDn_0 \tanh\left(\frac{d}{L}\right)} + 1\right] \tag{5}$$

The Fill Factor and the Efficiency of the solar cell is given by

$$FF = \frac{J_{mp} \times V_{mp}}{J_{sc} \times V_{oc}} \tag{6}$$

$$\eta = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}} \times 100\% \tag{7}$$

By optimizing the thickness of the photoelectrode, maximum J_{sc} can be obtained, which leads to improved efficiency. The increase in the fill factor ($\Delta FF_{inc}\%$) and increase in the efficiency ($\Delta\eta_{inc}\%$) can be calculated using the Eqs. (8) and (9). and is shown in Fig. 2.

$$\Delta\eta_{inc}\% = \frac{\eta_{\max} - \eta_{avg}}{\eta_{avg}} \times 100\ \% \tag{8}$$

$$\Delta FFinc\ \% = \frac{FF_{\max} - FF_{avg}}{FF_{avg}} \times 100\% \tag{9}$$

The average short-circuit current density (J_{sc}(avg)) is the value of saturated J_{sc} of the DSSC. From J_{sc}(avg) the average efficiency (η_{avg}%) is calculated, while the maximum efficiency (η_{max}%) of the DSSC is calculated from J_{sc}(max).

2.3. Analytical derivation of optimal diffusion length (L_0)

The optimal diffusion length (L_0) is the diffusion length of the electrons required in order to attain the maximum J_{sc}. The analytical expression for the "optimal diffusion length (L_0)" is derived by equating the first order derivative of J_{sc} with respect to'd′ to zero.

$$\left.\frac{\partial Jsc}{\partial d}\right|_{d=d_0;\ \ L=L_0} = 0; \tag{10}$$