Dependence of Temperature and Wavelength on the Current-Voltage Characteristics of a Dye Sensitized Solar Cell

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Abstract—The dye sensitized solar cell mimics the process of photosynthesis which occurs in green plant, to produce electrical energy by harnessing the photon energy from the sun. The DSSC has dye adhered to the wide bandgap semiconductor material like TiO₂, ZnO etc and works as a photo electrochemical cell. In this research work, the processes occurring at the 3 interfaces of the DSSC (FTO/TiO₂, TiO₂/dye/electrolyte and electrolyte/Pt-FTO) have been studied with the help of the two diode model and the relevant equations. For these processes, the effect of temperature and Solar Insolation on the current density - voltage characteristics is studied making use of the MATLAB Graphical User Interface. MATLAB GUI makes use of the interface to create software which inputs the user values for temperature in Kelvin and Solar Insolation in kW/m² and generates a plot between current density and voltage of the solar cell.

1. INTRODUCTION

Dye Sensitized Solar Cells DSSCs have emerged as a new class of low cost energy conversion with simple manufacturing devices as compared to the conventional solar cells. In semiconductor p-n junction solar cell charge separation is taken care by the junction built in electric field, while in dye sensitized solar cell charge separation is by the kinetic process as it takes place during photosynthesis (M. Spath, 2003). The key to developing this different kind of solar cell was the incorporation of the dye molecules in some wide bandgap semiconductor electrodes. (Nazeeruddin MK, 2011)

The front electrode of a DSSC is a transparent conductive oxide glass (TCO) coated with nanoporous TiO_2 covered with a monolayer of the ruthenium-complex dye while the counter electrode is a TCO glass coated with a thin layer of platinum (around 5 nm). The gap between the two electrodes is filled by an electrolyte containing an iodide/tri-iodide ($I^{T}I_3^{-}$) redox couple. (Brian O'Regan)

When analysing the DSSC parameters, almost in all the cases only the illumination level is taken into consideration irrespective of other important parameters which also play a key role in the overall efficiency of the cell. External parameters like temperature and wavelength which strongly influences the cell limiting parameters are yet to be fully evaluated.

In this research work, we make use of the Graphical User Interface of the MATLAB software to evaluate the effect of temperature and wavelength on the current-voltage characteristics. A graphical user interface (GUI) is a graphical display in one or more windows containing controls, called *components*, that enable a user to perform interactive tasks. The user of the GUI does not have to create a script or type commands at the command line to accomplish the tasks. Unlike coding programs to accomplish tasks, the user of a GUI need not understand the details of how the tasks are performed.

GUI components can include menus, toolbars, push buttons, radio buttons, list boxes, and sliders—just to name a few. GUIs created using MATLAB tools can also perform any type of computation, read and write data files, communicate with other GUIs, and display data as tables or as plots. (MATLAB)

2. OPERATING PRINCIPLE

A schematic presentation of the operating principles of DSCs is given in Fig. 1.



Fig. 1: Working of DSSC

The sunlight which strikes in the form of photons when absorbed by the dye molecules excites them from the highest occupied molecular orbitals (HOMO) to the lowest unoccupied molecular orbital (LUMO) states as shown schematically in the Fig. 1. This process is represented by Eq. 1(Robertson, 2006). The dye molecule becomes oxidized when an electron is injected into the conduction band of the wide bandgap semiconductor nanostructured TiO₂ film, (Equation 2) (H. Tian, 2005). The injected electron is transported between the TiO₂ nanoparticles and then extracted by a load circuit or device where the work done is delivered as an electrical energy, (Equation 3). I^{-}/I_{3}^{-} redox ions present in the electrolytes act as an electron mediator between the TiO_2 photoelectrode and the carbon coated counter electrode (H.J. Snaith, 2007). Consequently, regeneration of the oxidized dye molecules (photosensitizer) takes place on receiving the electrons from the I⁻ ion redox mediator that get oxidized to I₃⁻ (Tri-iodide ions). This process is represented by Eq. 4. The I_3^{-1} substitutes the internally donated electron with the help of the one from the external load and therefore gets reduced back to Γ ion, (Equation 5). The movement of the electrons in the conduction band of the wide bandgap nanostructured semiconductor is accompanied by the diffusion of chargecompensating cations in the electrolyte layer close to the nanoparticles surface (Gratzel, 2006).

Therefore, there is no permanent chemical change or transformation in DSSC because of the generation of electrical power.

Dye + photon \rightarrow Dye*	(1) Excitation process
$Dye^* + TiO_2 \rightarrow e_{(TiO2)} + Dye^+$	(2) Injection process
$e^{-}_{(TiO2)} + C.E. \rightarrow TiO_2 + e^{-}_{(C.E)} + e^{-}_{Energy generation}$	electrical energy (3)

$Dye^{+} + 3/2(I^{-}) \rightarrow Dye + \frac{1}{2}(I_{3}^{-})$	(4) Regeneration of dye
$\frac{1}{2}(I_3) + e_{(C.E.)} \rightarrow 3/2 (I) + C.E.$	(5) e ⁻ Recapture reaction

3. METHODOLOGY

3.1 Dependence of temperature and wavelength on DSSC characteristics

An operating DSSC is fundamentally governed by the relative kinetic rates of several charge transfer steps. The charge transfer process which takes place from the excited dye to TiO_2 nanoparticles, from the electrolyte to the dye and from TiO_2 to the load terminals all play a very important task in the performance of DSSC. Thus, it is very essential to understand all the electronic processes taking place at the TiO_2 nanoparticle level, as well as the dynamics of charge separation and charge transport at the metal/oxide interface.

The oxidized dye must be regenerated by the redox couple at the speed of ns to kinetically compete with the metal oxide electrons for subsequent electron injection as well as to prevent the recombination, which depends on the energetics of metal oxide/dye/electrolyte interface. Interface is the region formed when two phases (systems) are in contact through which the intensive properties of one phase transfer to the other. Energetic interface is the region produced when layering or interpenetrating of two or more materials of different valence and conduction bands or with dissimilar molecular energy levels, i.e. highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) (V. Thavasi, 2009).

A study of the interfaces kinetics of the DSSC shows that interactions are modulated by the different distribution of interacting sites at the solid surface and powder aggregation (Fattori A1, 2014).

Under a steady-state condition of DSSC under illuminated condition, the following electron diffusion differential equation can be used to describe the electron injection from the excited dye molecules, transport in the mesoporous semiconductor (TiO2) thin film, and recombination with electrolyte at the TiO2/electrolyte interface (Sodergren S., 1994) (Roberto Gómez, 2005):

$$D\frac{\partial^2 n(x)}{\partial x^2} - \frac{n(x) - n_o}{\tau} + \Phi_o \alpha \exp(-\alpha x) = 0$$
Eqn. 1

where n(x) is the excess electron concentration at position x inside the mesoporous TiO₂ thin layer; n_o is the electron concentration under dark conditions. T is the lifetime of the conduction band free electrons; ϕ_o is the incident irradiation intensity; α is the light absorption coefficient of the mesoporous TiO₂ thin layer; and D is the electron diffusion coefficient (Yasuteru Saito, 2004).

A standard DSSC consists of three interfaces formed by FTO/TiO_2 , $TiO_2/dye/electrolyte$, and electrolyte/Pt-FTO represented by an equivalent circuit shown in Fig. 2(Yong, 2008).



Fig. 2: Equivalent Circuit of the DSSC

The interfacial charge transfer at the TiO₂/dye/electrolyte is depicted by a combination of the rectifying diode D_i and a double layer capacitance C. A recombination diode D_r with an ideality factor, m is employed to denote the interfacial charge recombination losses to both the dye cation and the redox electrolyte. All parallel resistive losses across the photovoltaic device, including the leakage current is best represented in the diode model with the help of a shunt resistance R_{sh} .

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The charge transfer resistance and interfacial capacitance at the FTO electrode and electrolyte/Pt-FTO interface are characterized by R_E and C_E , and RCE and CCE, respectively. The photo-generated current J_{ph} is in parallel with the rectifying diode. An inductive recombination pathway due to charge-transfer current is incorporated into the circuit, consisting of a recombination resistance (Rrec) in series with an inductance (L). The Warburg impedance (W) is used to represent the Nernst diffusion of the carrier transport by ions. A resistance element Rs represents the bulk and contact resistive losses present in a DSSC, such as the sheet resistance of the FTO glass. The general solution of Eq. (1) in terms of current density–voltage (J–V) relationship, with short-circuit current and open-circuit voltage boundary conditions, can be expressed as below:

$$J = J_{ph} - J_i \left\{ \exp\left(\frac{q(V+JZ)}{nk_B T_C}\right) - 1 \right\}$$
$$-J_r \left\{ \exp\left(\frac{q(V+JZ)}{mk_B T_C}\right) - 1 \right\} - \left(\frac{V+JZ}{R_{sh}}\right)$$
$$J_{sc} = [1 - r(\lambda)]q\phi_o L_n \alpha$$
$$\left[\frac{-L_n \alpha \cosh\left(\frac{d}{L_n}\right) + \sinh\left(\frac{d}{L_n}\right) + L_n \alpha \exp(-d\alpha)}{(1 - L_n^2 \alpha^2) \cosh\left(\frac{d}{L_n}\right)} \right]$$
$$Z = \frac{1}{\frac{1}{R_{rec}}} + \frac{1}{Z_s}} + R_s$$
$$Z_s = R_E + R_{CE}$$

where J_{ph} is the photo-generated current density, j depicts the complex number, k is the incident solar insolation in kW/m², J_{SC} is the cell's short -circuit current density at 25°C and 1 kW/m², K_I is the cell's short-circuit current temperature coefficient, n and m represent the diode ideality factor of the first and second diode respectively, Φ_0 represents the number of photons incident on the solar cell per unit area (#photons/cm2), $r(\lambda)$ represents the reflection losses, J_i and J_r are the saturation current density of the rectifying and recombination diodes, respectively, k_B is the Boltzmann constant, T_C is the cell temperature and T_{Ref} is the reference temperature (298.14 K) (Ryer, 1997).

The photocurrent density (J_{ph}) mainly depends on the solar insolation and on the operating temperature of the cell. The saturation current of a solar cell varies with the cell temperature, which is given below:

$$\boldsymbol{J}_{i} = \boldsymbol{J}_{RS1} \left(\frac{\boldsymbol{T}_{C}}{\boldsymbol{T}_{REF}} \right)^{3} \exp \left[\frac{\boldsymbol{q} \boldsymbol{E}_{g} \left(\frac{1}{\boldsymbol{T}_{REF}} - \frac{1}{\boldsymbol{T}_{C}} \right)}{\boldsymbol{n} \boldsymbol{k}_{B}} \right]$$
$$\boldsymbol{J}_{r} = \boldsymbol{J}_{RS2} \left(\frac{\boldsymbol{T}_{C}}{\boldsymbol{T}_{REF}} \right)^{3/2} \exp \left[\frac{\boldsymbol{q} \boldsymbol{E}_{g} \left(\frac{1}{\boldsymbol{T}_{REF}} - \frac{1}{\boldsymbol{T}_{C}} \right)}{\boldsymbol{m} \boldsymbol{k}_{B}} \right]$$

where Eg represents the band-gap of the N719 dye molecule (1.6 eV). The reverse saturation current of the cell at a reference temperature depends on the open-circuit voltage (V_{OC}) (Tsai, 2008) and can be approximately obtained by following equation as given by

$$J_{RS1} = J_{SC} / \left[\exp(qV_{OC} / k_B nT_C) - 1 \right]$$
$$J_{RS2} = J_{SC} / \left[\exp(qV_{OC} / k_B mT_C) - 1 \right]$$

3.2 Software Used

The software used for the simulation work is MATLAB. A Graphical User Interface has been created which inputs values for temperature and wavelength and generates a plot of current density versus voltage with the help of callback functions which makes use of programming of the equations based on the dependence of the above said parameters on cell characteristics.

The effect of variation of temperature and illumination is studied for the operating characteristics of the DSSC. The interface works like a software which depends on the user for the input values and generates a J-V plot in accordance to the values. A screenshot of the GUI DSSC Simulator is shown below:



Fig. 3: MATLAB GUI-DSSC Simulator

3.3 Values used for the simulation of the model

The different parameters used for the simulation have been assigned values according to the generalized DSSC configuration and has been listed in the Table below.

Table 1: Value of parameters used for the simulation of	
J-V curve for the DSSC	

	Characteristics	Value
1.	Electron Charge, q	1.6x10-19C
2.	Electron diffusion length, Ln	1.56x10-3cm
3.	Light absorption coefficient, α	3975.3cm-1
4.	Light intensity, Φo	5.125x1016 cm-2s-1
5.	Film thickness, d	12µm
6.	Ideality Factor, n and m	1.45 and 2.9
7.	Boltzmann Constant, Kb	1.38x10-23
8.	Bandgap of dye molecule, Eg	1.6eV
9.	Impedance, Zs	286.51

4. RESULTS AND DISCUSSIONS

The DSSC model is simulated using the equations mentioned in Section 3 and a strong dependence of the cell characteristics on the illumination and temperature values is obtained. The different parameters such as V_{OC} , J_{SC} , J_{RS} etc have been estimated assuming the parameters in the Table 1 according to the DSSC configuration.

Fig 4. shows the dependence of illumination on the J-V characteristics of the cell. The dependence of the illumination value is a logarithmic function as V_{oc} varies logarithmically in accordance to the variation in the illumination and linearly for photocurrent J_{sc} .



Fig. 4: Effect of Illumination on J-V Characteristics

Fig. 5 shows the variation in the J-V characteristics of the cell for the variation in the cell temperature value from 298K to 323K. The increase in the DSSC working temperature can influence the charge transfer and the recombination kinetics, resulting into change in V_{OC} and J_{SC} . The increase in photocurrent is due to reduction in the gap between Fermi-

level of TiO_2 and redox potential which causes enhanced electron transfer from LUMO state to the conduction band of the semiconductor.



Fig. 5: Effect on Temperature on J-V Characteristics

5. CONCLUSION

A detailed study of the current density voltage characteristics, electronic and ionic processes and dynamic response of a TiO_2 based dye sensitized solar cell (DSSC). Effect of the variation in temperature and illumination has been studied using a graphical user interface application of the MATLAB software.

It is found that the saturation current of the rectifying diode and the saturation current of the recombination diode are responsible for the recombination losses and have the major impact on the overall conversion efficiency.

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