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Mathematical Modelling of Electron Transport Through the Anode (TiO₂) of a Standard Dye-sensitized Solar Cell

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ABSTRACT

In this study mathematical model of electron transport through the anode (TiO₂) of a standard dye-sensitized solar cell was developed. The modeling led to the generation of a set of differential equations and a linear equation. The linear equation relates the rates of electron emission, α from the sensitized Dye, rate of electron trapping, β by TiO₂ and the rate of electron diffusion, γ through the TiO₂. The linear equation was transformed such that it could compare the rate of electron trapping, β with the thickness, T of the TiO₂. The aim of the research was to determine the parameters of TiO₂ that influences its electron trapping. The specific objective was to look at the relationship between the rate of electron trapping by the anode and the thickness of the anode. The set of differential equations were solved jointly using two different methods: the Euler's method and the Runge-Kutta's method. Result showed that the size (thickness) of TiO₂ influences its electron trapping rate. And the solution to the system of differential equation showed that the thickness of the TiO₂ deteriorate with time. So from the result obtained, the recommendation is that the size of the anode use in the design of Dye-sensitized solar cell should be increased in order to improve the efficiency of the standard dye-sensitized solar cell. By improving electron transmission through the anode, we are invariably improving the efficiency of the solar cell.

Key words: Modeling, dye, solar cell, energy, efficiency

INTRODUCTION

The focus of this research is on solar source of energy through the use of solar cells. The solar cell of interest here is the standard dye-sensitized solar cell. It has been found that the sun delivers to the earth about 120,000 terawatts of energy per day, which is far more than what is obtained from burning of fossil fuel (Yu and Chen, 2009). This enormous energy is available for utilization of earth (Basu and Antia, 2008). If this energy is properly harnessed the world may not have need for fossil fuel any more. What this implies is that covering only 0.1% of the earth's surface with solar cells of 10% efficiency, this would satisfy the world's current energy need. But the challenge has been developing a device that can be able to convert this enormous energy into electricity for use by house hold and industries. The solar cells that have recorded the highest photon to current conversion efficiency are those based on single silicon crystal (Belfar and Mostefaoui, 2001) that have recorded efficiency of up to 18% (Yu and Chen, 2009). Such solar cells are known as first generation devices. The problem with the silicon solar cells is their high cost production and installation. The second-generation devices consisting of CuInGaSe₂ (CIGS) polycrystalline

semiconductor thin films can reduce the price significantly, but it does not reduce the challenge to make their efficiencies more practical. It is noteworthy to mention that a lot of researches have been carried out to improve the efficiency of the second generation solar cells. For example studies of Konan *et al.* (2007) and Tariq Bhatti *et al.* (2002). Now the third-generation solar cells, such as Dye-sensitized Solar Cells (DSSCs), bulk heterojunction cells and organic cells, are promising for inexpensive and large-scale solar energy conversion, but the challenge is that so far an efficiency of up to 10% has not been recorded (Yu and Chen, 2009; Reijnders, 2010).

The dye-sensitized solar cell is a new technology that mimics the photosynthesis process in its electricity generation from the sun. This technology has opened a new area of research interest for scientist (Zainudin *et al.*, 2011). Currently researchers are working to improve on the photon-to-current conversion efficiency of the dye-sensitized solar cell. Some researchers have varied the chemical composition of the Dye (Ruthenium complex) with the aim of improving the photo-to-current conversion efficiency (Kuang *et al.*, 2008). Some other researchers have also sampled various compounds for the cathode. Such compounds include: MgO, SnO₂, TiO₂, MgO + SnO₂, TiO₂ + SnO₂, SnO₂ + TiO₂ + MgO (Snaith and Duccati, 2010). Zainudin *et al.* (2011) used supercritical Anti-solvent Process to enhance the efficiency of dye-sensitized solar cell. Although they arrived at a positive result more work need to be done. It is worthy of note to mention that all these efforts are aimed at improving the efficiency of the Dye sensitized solar cell. It is believed that the anode (TiO₂) of the standard dye sensitized solar cell (Gratzel and Durrant, 2008) traps some of the electrons passing through it, thereby contributing in the reduction of the efficiency of the dye sensitized solar cell (Tachibana *et al.*, 2001; Hollister, 2010). The aim of this research was to develop a model that could analyze the process of electron transport through TiO₂ and from the analysis it is suggested that what could be done to improve the efficiency of the cell.

FORMULATION OF THE MODEL

Before the mathematical model, a compartmental model of the scheme was first presented (Fig. 1). The scheme was presented to portray the absorbed photons, the sensitized Dye, the emitted

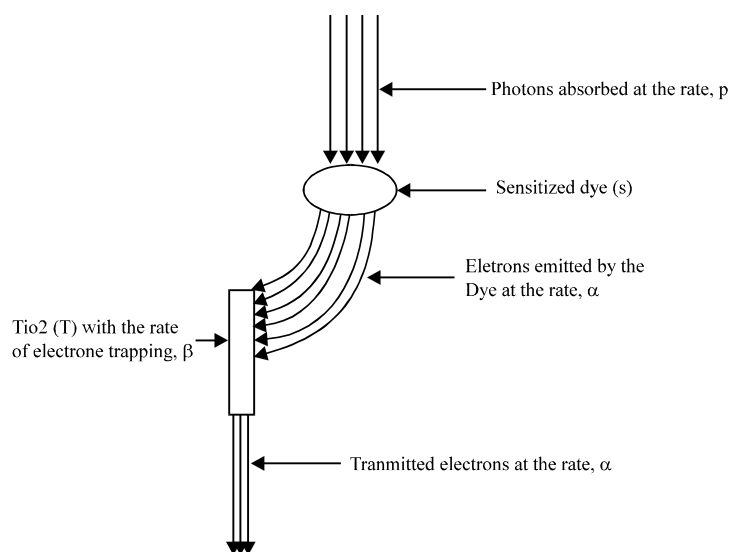


Fig. 1: Compartmental model of electron emission by the sensitized dye and the corresponding transport through TiO₂

electrons from the Dye, the TiO_2 anode and the transmitted electrons from the anode, in that order. The whole system was considered to be dynamic (Glazier *et al.*, 2003). To formulate the model and set up the related differential equations (Mlyashimbi *et al.*, 2011), we make the following deductions:

Let:

- $s(t)$ = thickness of the sensitized Dye (which depends on time, t)
- $T(t)$ = thickness of TiO_2 (which depends on time, t)
- p = rate of photon absorption by the Dye
- α = rate of electron emission by the sensitized Dye
- β = rate of electron absorption by the TiO_2 anode
- γ = rate of electron transmission/diffusion by TiO_2 anode

With these the model was formulated. The kinetics of the whole process is represented by the below system of differential equations:

$$\frac{ds}{dt} = p(t) - \alpha s(t) - \beta T(t)s(t) - \gamma T(t)s(t) \quad (1)$$

$$\frac{dT}{dt} = \beta T(t)s(t) - \gamma T(t)s(t) \quad (2)$$

Eq. 1 and 2 reduce to:

$$\frac{ds}{dt} = (p - \alpha)s(t) - (\beta - \gamma)T(t)s(t) \quad (3)$$

$$\frac{dT}{dt} = (\beta - \gamma)T(t)s(t) \quad (4)$$

Let $q = p - \alpha$ and $r = \beta - \gamma$. Eq. 3 and 4 reduce to:

$$\frac{ds}{dt} = qs(t) - rT(t)s(t) \quad (5)$$

$$\frac{dT}{dt} = rT(t)s(t) \quad (6)$$

Intuitively, we can say that the quantity of electrons diffused through the anode is equal to the quantity released by the sensitized dye minus the quantity trapped by the anode.

That is:

$$\gamma T(t)s(t) = \alpha s(t) - \beta T(t)s(t) \quad (7)$$

$$\gamma T(t) = \alpha - \beta T(t) \quad (8)$$

$$(\gamma + \beta)T(t) = \alpha \quad (9)$$

Equation 9 shows that a linear relationship exists between the rate of electron emission by the sensitized dye and sum of the rates of electron trapping and diffusion by and through the anode. Looking at Eq. 9, we observe that if the graph of the function is plotted at varying values of T , a straight line graph will be obtained with $(\gamma + \beta)$ as the slope and α as the intercept along $F(T)$ axis. It is not easy to determine from here how β varies with T since for a straight line graph the slope remains the same at any two given point along the line. In order to find out how β relates with T , we introduce a parameter say ξ that defines the material nature of the anode (TiO_2). So with this, we can say that the rate of diffusion of electrons by TiO_2 approaches the difference between the rate of electron emission by the sensitized dye and the rate of electron trapping by TiO_2 .

That is:

$$\gamma = \alpha - \xi\beta \quad (10)$$

Substituting Eq. 10 into 9:

$$(\alpha - \xi\beta + \beta)T - \alpha = 0 \quad (11)$$

This implies:

$$[\alpha + (1 - \xi)\beta]T - \alpha = 0 \quad (12)$$

The cell is not so inefficient that the material of TiO_2 will absorb all the electrons coming to it. Since this is not the case, it implies that: $1 - \xi > 0$. This means that the term $(1 - \xi)$ can take any value that is greater than zero but not more than one.

Let $v = 1 - \xi$. And by making β the subject of the formula in Eq. 12, we obtain:

$$\beta = -\alpha[T - 1] / vT \quad (13)$$

We try to plot the graph of β against T to see how they vary with each other. With this a matlab programme was written to plot the graph (Knight, 2000). Here we had assumed that the Dye is emitting the whole of its electrons such that $\alpha = 1$. The value of ' v ' was taken to be 0.1, since ' v ' can take any value greater than zero but not more than one. The range of the sizes of TiO_2 was taken from 0 to 10, in step of 1. The values of v and α were supplied for each matlab prompt.

SOLUTION TO THE SYSTEM OF DIFFERENTIAL EQUATIONS (EQ. 5, 6)

Next we try to solve the system of differential equations given by Eq. 5 and 6. This is a form of boundary value problem since we have assumed that the sensitized dye is a perfect one. If this is the case it shows that the dye needs little photon to produce more electrons.

Thus: $q = p - \alpha = \text{negative value}$. This implies that, $q < 0$. Here -3 were chosen as the value of q .

Next we make another assumption. For the cell to be inefficient (owing to electron trapping by the anode) it means $\beta > \gamma$. This implies that, $r = \beta - \gamma > 0$. We have assumed that the sensitized dye is a perfect one such that, its rate of electron emission is equal to 1. This implies that if electron did not pass through any other substance or channel, but only through the anode, then, $\beta + \gamma \approx 1$.

This implies that, $\beta \approx 1 - \gamma$. By substitution, we find that: $\gamma < 0.5$. So in this work the value of γ was taken to be 0.4 and that of $r = 0.2$. First of all we try to find out how the thickness of TiO_2 changes over a small time lag (between 0.1×10^{-9} and 0, in time step of 0.05×10^{-9}) in nanoscale.

Two different methods were used in matlab to solve the system of differential equations and plot the graph of T against time. The two methods were the Euler's method and the Runge-Kutta's method.

The solution to the system of differential equation as given by Euler takes the form:

$$Y_{i+1} = y_i + \Delta t \cdot f(t_i, y_i) \quad (14)$$

While that of Runge-Kutta's method takes the form:

$$Y_{i+1} = y_i + 1/6 (k_1 + k_2 + k_3 + k_4) \quad (15)$$

Where:

$$\begin{aligned} k_1 &= \Delta t \cdot f(t_i, y_i) \\ k_2 &= \Delta t \cdot f(t_i + \Delta t/2, y_i + k_1/2) \\ k_3 &= \Delta t \cdot f(t_i + \Delta t/2, y_i + k_2/2) \\ k_4 &= \Delta t \cdot f(t_i + \Delta t, y_i + k_3) \end{aligned}$$

The system of differential equations (Eq. 5 and 6) were re-written to suit the forms of solutions we have here. Thus we obtain:

$$\frac{dy(1)}{dt} = qy(1) - ry(2)y(1) \quad (16)$$

$$\frac{dy(2)}{dt} = ry(2)y(1) \quad (17)$$

A matlab programme was afterwards written to solve the two equations (Eq. 16, 17) and a graph of T against time, t plotted.

VARIATION OF TIME

When the time was set between 0.1×10^{-9} and 0, in time step 0.05, Fig. 1 and 2 were obtained. When the time was set between 0 and 10, in time step of 0.5, Fig. 4 was obtained. When the time step was varied from 0.1 to 0.6, significant changes in the thickness of TiO_2 were minimal. But as from time step of 0.7 up to 1, there were significant changes. At time step of 0.7, Fig. 5 was obtained. At time step of 0.8, Fig. 6 was obtained. At time step of 0.9, Fig. 7 was obtained. And at time step of 1, Fig. 8 was obtained.

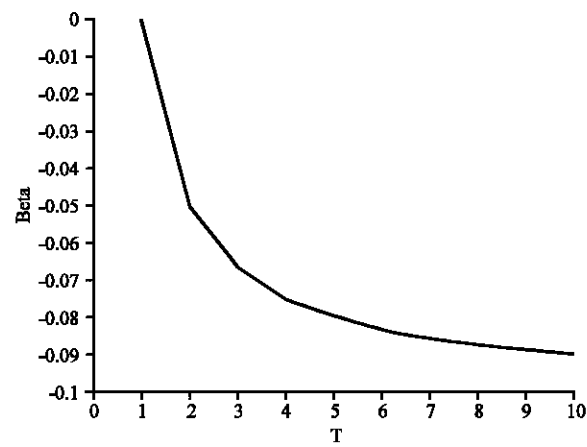


Fig. 2: Graph of Beta against T

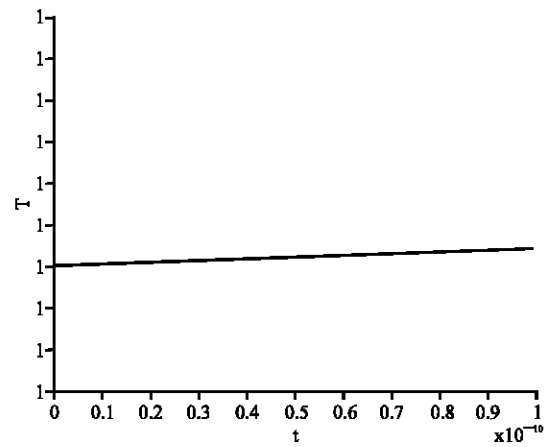


Fig. 3: Solution obtained using the Euler's Method

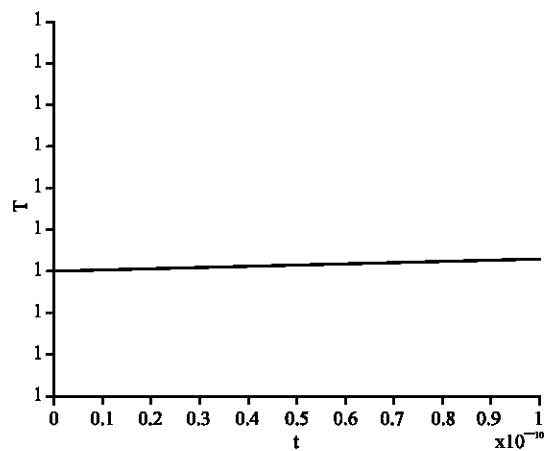


Fig. 4: Solution obtained using the Runge-Kutta's method

RESULTS

The graph generated by the Matlab programme for the plot of the rate of electron absorption (Beta) against titanium oxide thickness is shown in Fig. 2. Figure 2 shows that an increase in “T” leads to a decrease in “Beta”. This implies that increasing the thickness of the anode will lead to reducing the electron trapping rate of the anode. Again, the result of the Matlab programme for the solution to the system of differential equations that resulted from the model is shown in Fig. 3 and 4. Figure 3 and 4 showed that over a give short time frame the thickness of the titanium dioxide remains unchanged. Figure 5-7 showed that at increased time step, the thickness of the anode begins vary. Figure 5 showed a slight variation up to a little above the mark 1.06 while Fig. 6 showed a little variation up to the mark 1.04 and remained at that level over time. As the time step was further increased, there was noticed a significant deterioration in thickness of the anode up to the mark 0.3 as seen in Fig. 7. As the time step was further increased, the thickness of the anode reduced to zero and remained there as seen from Fig. 8 and 9. The result showed that the thickness of TiO_2 influences its electron absorption rate. And the plot of T against time, t following both Euler’s solution and Runge-Kutta’s solution showed that within the short period of

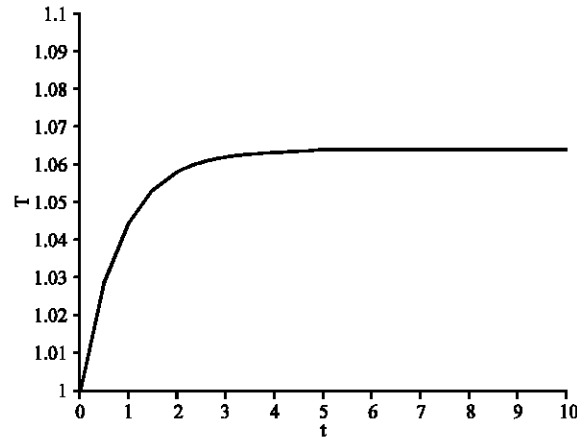


Fig. 5: Result obtained for plot of T against t for time between 0 and 10 in time step 0.5

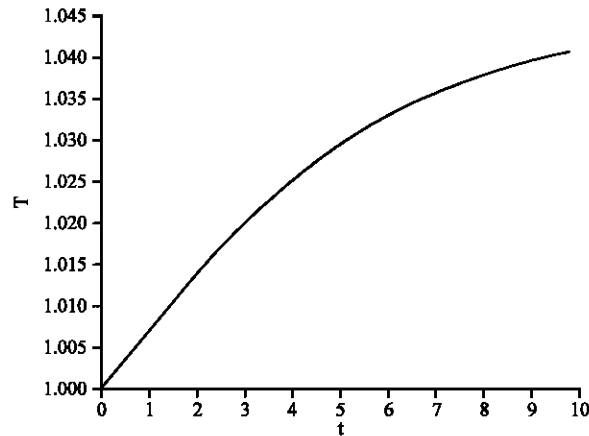


Fig. 6: Result obtained when the time step was set at 0.7

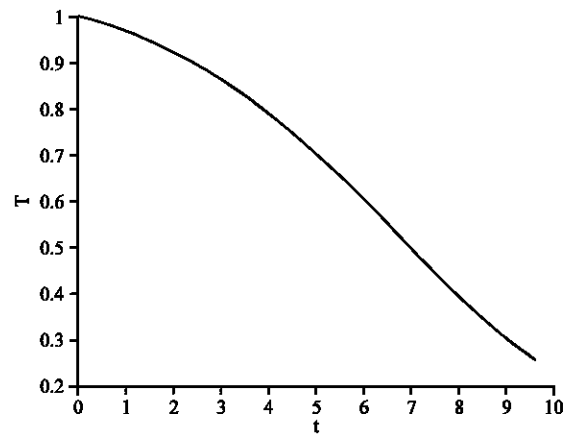


Fig. 7: Result obtained when the time step was set at 0.8

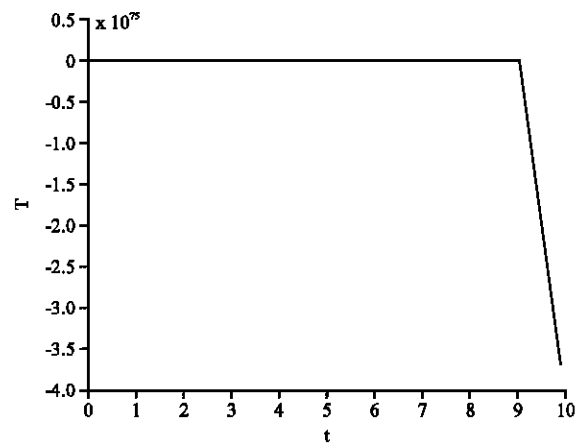


Fig. 8: Result obtained at increase time step of 0.9

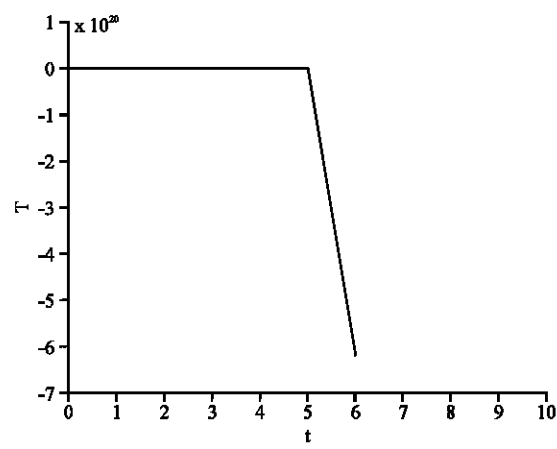


Fig. 9: Result obtained at time step of 1

electron kinetics through the anode, the thickness of the anode was not affected. Increase in the thickness of TiO_2 was seen to reduce the rate at which the crystal traps electrons looking at Fig 1. This has a positive effect on the efficiency of the solar cell.

DISCUSSION

Result from Fig. 4 shows that between 0 and 10, as the time step of increases, the thickness of TiO_2 increases. In Fig. 4, the increase in the thickness of TiO_2 got up to 1.063 mark and remained at that mark over time. At time step of 0.7 the thickness reduces to 1.041. As the time step increase up to 0.8, the thickness of TiO_2 hit the mark 1. As the time step was further increased up to 0.9, the thickness of TiO_2 came to the zero mark. At further increment in the time step, the thickness did not leave the zero mark. This shows that over time, the thickness of titanium dioxide in the dye sensitized solar cell reduces. It will get to a point in time when the thickness becomes zero. At that point the efficiency of the solar cell will be said to be zero, because no current will be found at the output terminal. There is need to increase the thickness of TiO_2 in the standard dye sensitized cell, since we have earlier established that the rate of electron trapping by TiO_2 reduces with increasing TiO_2 thickness. And more over, we have seen that over time, the thickness is affected negatively. So the more the thickness, the better it is for the cell. Peter and Wijayantham (2000) agrees that electron trapping affect the diffusion of electron through the anode. In their relation, they obtained that the rate of electron diffusion through the anode is inversely proportional to the rate of electron trapping by the anode. The result obtained in this work also agrees with that obtained by Beermann *et al.* (2002). Related the diffusion coefficient, γ of electrons to the thickness, T of the film of TiO_2 , they established the relationship connecting these as:

$$\gamma = T^2/6t_{\text{peak}} \text{ (where } t_{\text{peak}} = \text{peak time)}$$

The above shows that as thickness increases the rate of electron diffusion also increases.

It is logical if we reason in this way: the aim of research in the area of dye sensitized solar cell is to find a substitute to the burning of fossil fuel, which posses environmental challenges. In order to achieve this we should look out for dye-sensitized solar cells that could output relatively high voltages (talking about dye-sensitized solar cells of improved efficiency). So far the maximum open circuit voltage that has been recorded for a dye-sensitized solar cell is: 800 mV (Snaith and Ducati, 2010). And the target is to develop dye-sensitized solar that could attain an open circuit voltage of at least 24 V, so that through rectification a desired voltage of up to 240 V could be obtained. At the present nanosize of the anode we are getting open circuit voltage of 800 mV(maximum). This could be due to the inability of the majority of the electrons to pass through the pores in the anode, leading to more electron trappings and losses. Assuming a thicker anode is used more electrons will pass through thereby reducing the rate of electron trapping by the anode. And when more electrons pass through at relatively low resistance, greater open circuit voltage would be obtained, since voltage is proportional to current following Ohm's law.

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