One and Two Dimensional Models of Dye Adsorption for application in Dye Sensitized Solar Cells

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Abstract. The dye sensitized solar cells are currently the subject of intense research in the field of renewable energy as a low-cost photovoltaic device. The light adsorption occurs in dye molecules adsorbed on a highly porous structure of titanium dioxide (TiO_2) porous film. The progress in the efficiency and stability of these solar cells is very low, due to many fundamental aspects of their operation that are still unknown. One process, for which there is limited information, is the time taken to upload the dye on the TiO_2 nanoporous film which acts as a semiconductor. Dye molecule is adsorbed onto a TiO_2 working electrode by dipping it into the dye solution for periods of several hours to several days. However, such long dipping times are not economical for industrial production of DSSCs. The factors controlling this process are not yet fully understood. We have developed a 1D and 2D models based on the Langmuir isotherms to study and understand the diffusion and adsorption of the dye molecules in TiO_2 nanotube films. Our modelling results show that the adsorption of dye into the TiO_2 nanotubes is controlled by the diffusion coefficient, the adsorption-desorption ratio and the initial dye concentration.

1. Introduction

With increasing worldwide energy demand, the need to adopt the renewable energy technologies as an alternative energy sources is very important to developing countries. Among all the renewable energy technologies solar energy is one of the potential candidate to satisfy the global energy needs. One promising photovoltaic technology is the dye sensitized solar cells, which are regarded as a low cost solar cell with high light to energy conversion efficiency [1-2]. Currently the DSSCs based on the TiO_2 nanoparticles films sensitized with ruthenium (Ru) dyes have been reported to achieve a light to energy conversion efficiency of more than 12 %. The dye molecules adsorbed on the TiO_2 surface act as the photon absorber. Thus the dye molecules adsorbed on the TiO_2 working electrode are of importance during the photon absorption and the overall efficiency of the solar cells.

The adsorption of organic and inorganic molecules for the functionalization of titanium surfaces is of particular interest for number of technological applications like photovoltaic, biosensors, water filter, etc. The interaction between the TiO_2 semiconductor surfaces with dye molecules or other molecules in particular has attracted more attention in the field of renewable energy as application on dye sensitized, Perovskites and quantum dots solar cells [1-3]. In dye sensitized solar cells (DSSCs), the adsorption of dye molecules like ruthenium dye onto the TiO_2 surfaces has relevance in understanding the surface interaction and photon absorption in these types of solar cells. The formation of strong bonds and surface coverage between the dye molecules as light sensitizer and TiO_2 semiconductor is an important factor for allowing efficient charge transfer between the two materials in DSSCs. In DSSCs the experimental procedure used for the adsorption of ruthenium dye molecules on the surface of the TiO_2 is by dipping in the solution of dye molecules, usually the ruthenium complex dye. This experiment is sometimes done in several hours or days [3, 4]. The optimum adsorption time is an extremely important factor during the experiment. It is well known that the time taken during the dye uptake experiment has an impact on the efficiency of the solar cells [4]

2. Computational Method

The present model is intended to simulate the formation of a monolayer on the surface of the TiO_2 film (a general case in which the dye molecules are adsorbed on the surface of TiO_2 film to form a mono layer) and understand the factor controlling this process. The model is based on the Langmuir adsorption isotherm, which uses active site concept in adsorption expression in order to address the reduction of its rate with the coverage of the wall. The model assumes that [4-6]:

(a) Adsorption of dye molecules is controlled by transient diffusion along the film,
(b) The dye molecules stick to the surface of the film and only a monolayer is formed and
(c) There is a constant number of molecules of the adsorbate even after the adsorption.

The concentration of dye molecules inside the film can be calculated using Fick′s second law for cartesian (one dimensional) and cylindrical (two dimensional) [4]. We solved one and two dimensional diffusion equation for dye molecules concentration $c(r, z, t)$, where z is the distance from the second end of the TiO_2 working electrode, r is the radius of the nanotubes and t is the time, for two dimensional models given by [4, 6]:

$$\frac{\partial c}{\partial t} = D\nabla^2 c = D\left[\frac{1}{r}\frac{\partial}{\partial r}\left(\frac{\partial c}{\partial r}\right)\right] + D\frac{\partial c}{\partial z}, \tag{1}$$

Where D is the diffusion coefficient, c is the concentration, r is the distance from the centre of the pore and z is the distance along the pore from the extracting electrode as illustrated on Fig.(1).

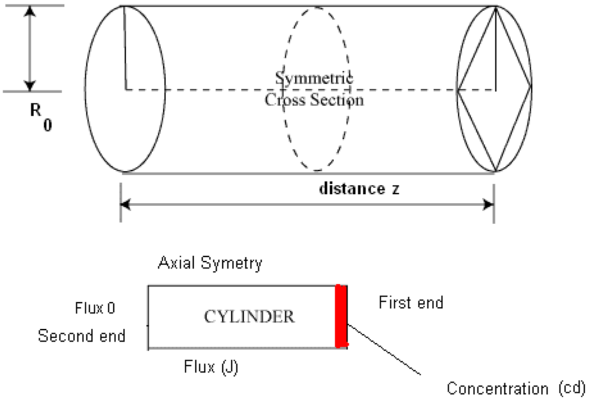

Figure 1. The TiO_2 nanotube represented by a cylinder penetrating the entire TiO_2 film with a bulk concentration of dye molecules at the right hand end of the nanotube.

As defined by Kimmish and Nestle [6] we consider an effective diffusion coefficient which depends on the value of the sticking or material coefficient (k) as

$$D_{eff} = \frac{D}{1+k}. \tag{2}$$

To find the net flux of dye molecules $J(z,t)$ moving towards the pore surface

$$J = -D\frac{\partial c}{\partial z}. \tag{3}$$

We consider the molecules flowing onto the surface and being adsorbed onto to it less the desorbed molecules to give a fractional surface coverage (θ), given by,

$$\theta(z,t) = \frac{\Gamma(z,t)}{\Gamma_{max}}. \tag{4}$$

Where $\Gamma(z,t)$ is the surface coverage a distance z from the electron extracting electrode and Γ_{max} is the maximum surface coverage of the TiO_2 nanotube film. If all molecules a distance l_{mol} out of the surface are adsorbed, where l_{mol} is the length of the dye molecules,

$$\Gamma_{max}\frac{\partial\theta}{\partial t} = k_{ads}\cdot l_{mol}(1-\theta(z,t))c - k_{des}\Gamma(z,t), \tag{5}$$

where k_{ads} and k_{des} are the adsorption and desorption rate of dye molecules respectively.

We assume a quasi-static equilibrium, i.e., the adsorption and desorption take place quickly compared to time taken for the dye molecules to diffuse to the surface, thus the left hand side of the above equation (Eq.(5)) is set to zero. Hence, if $k = \frac{k_{ads}}{k_{des}}$, then

$$k_{ads}\cdot l_{mol}(1-\theta(z,t))c - k_{des}\Gamma(z,t) = 0, \tag{6}$$

So that we have

$$\theta(z,t) = 1 - \frac{1}{1+\frac{c}{c_{con}}} \tag{7}$$

where c_{con} is the constant for Langmuir isotherm given by,

$$c_{con} = \frac{\Gamma(z,t)}{k\ l_{mol}} \tag{8}$$

The total number of dye molecules on the surface can be written as,

$$N_{surf} = 2\pi\Gamma_{max}\int_0^d \theta(z,t)dz \tag{9}$$

The boundary conditions at the curved surface (radial axis) at all times t is given by

$$J(r=R_0,r) = -D\frac{\partial c}{\partial r} \tag{10}$$

In order to achieve this modelling analysis we have employed this model using the MATLAB programing software.

3. Results and discussion

The adsorption process is a complex phenomenon which comprises of the different steps like diffusion of dye molecules and adsorption of the molecules on the surface of the pore. This involves the interaction between the dye molecules and active sites of the adsorptance. Fig.(2) shows the time variation due to the diffusion coefficient. It is clear that the time variation depends on the diffusion coefficient. But if we scale our graph by the characteristic time ($t_z = \frac{d^2}{D}$) where d is the length of the film and D is the diffusion coefficient, the variation of dye uptake on the pore surface at the end is the same as illustrated on Fig.(1). As illustrated by Fig.(3), along the pore the diffusion takes place slower and takes longer than the characteristic time ($t_z = \frac{d^2}{D}$). Diffusion along the pore is slowed down by the adsorption of dye molecules at the pore surface.

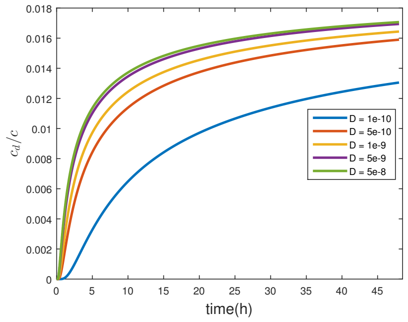

Figure 2. Dependence of surface coverage on different values of diffusion coefficient. The values used in simulation are $k = 1 \times 10^3$, $c_d = 6 \times 10^{21}\text{m}^{-3}$ and $d = 15\mu\text{m}$

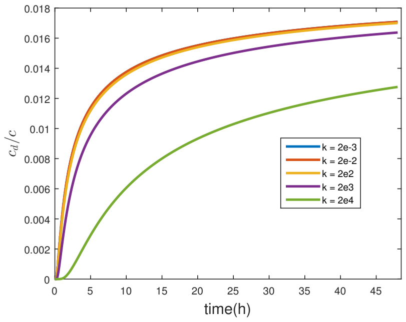

Figure 3. Dependence of surface coverage on different values of material constant. The simulation values are $D = 5 \times 10^{-9}\text{m}^2\text{s}^{-1}$, $c_d = 6 \times 10^{21}\text{m}^{-3}$ and $d = 15\mu\text{m}$

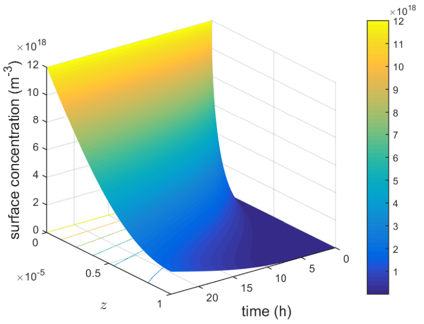

Figure 4. Surface concentrations on the TiO_2 film for 24 hours simulated time. The values used in simulation are $k = 1 \times 10^3$, $D = 6 \times 10^{-9}\text{m}^2\text{s}^{-1}$ and $d = 15\mu\text{m}$

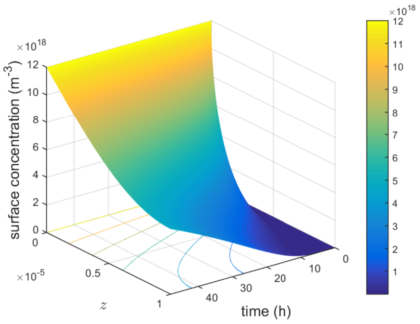

Figure 5. Surface concentrations on the TiO_2 film for 48 hours simulated time. The values used in simulation are $k = 1 \times 10^3$, $D = 6 \times 10^{-9}\text{m}^2\text{s}^{-1}$ and $d = 15\mu\text{m}$

This delay is seen more clearly for large k values. This illustrates the importance of understanding the value of the material sticking coefficient. The duration of the dye loading plays an important role on the surface coverage. It has been reported experimentally that the longer duration for dye loading affects the efficiency of the solar cells [5, 8]. As illustrated in

Fig.(4) and (5), it can be observed that the time of dye loading plays an important role on the surface coverage. The time effect is also observed for the higher values of the material coefficient (k), due to the fact that a higher value of k in our models shows that the dye molecules which interact with the surface will stick on the surface.

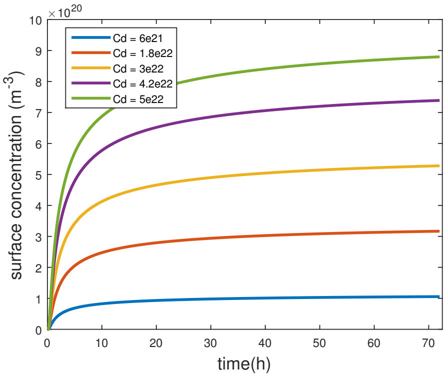

Figure 6. Dependence of surface coverage on different initial dye concentration. The simulation values are $k = 1 \times 10^3$, $D = 5 \times 10^{-9}\mathrm{m}^2\mathrm{s}^{-1}$, and film thickness $d = 15\mu\mathrm{m}$

Since there are interactions between the dye molecules and the surface, the process will be much slower compared to smaller values of k. This delay is not needed in this experiment as it affects the overall efficiency of the solar cells and it's not good for economical production of these solar cells. The effect of increasing the initial dye concentration (c_d) on the surface coverage and its saturation time is illustrated on Fig.(6). It can be observed from Fig.(6) that the surface coverage increases with increase initial dye concentration. When we increase the initial dye concentration we are increasing the probability of more dye molecules to diffuse into the film and hence reducing the saturation time. Similar effect was also reported and observed experimentally by Chou et al. [5].

4. Conclusion

Our model demonstrates that dye molecules can easily take few hours to be fully adsorbed onto the surface of the pore in the nanotube TiO_2 film. The model shows that the time depends on the ratio of adsorption to desorption rates (k). The time scale for diffusion along the pore radius is given by simple expression $t_z = \frac{d^2}{D}$. The initial dye concentration plays an important role on the surface coverage and the dye uploading time.

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