The growth of TiO₂ Thin Layer using electrophoresis technique based on constant voltage method

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Abstract

Electrophoresis deposition technique is a simple method to grow a homogeneous layer. This method is suitable for TiO₂ thin film formation in dye-sensitized solar cell application. The aim of this paper is to study the growth of TiO₂ thin layer on ITO (indium-doped tin oxide) glass by the electrophoresis method in a constant voltage method. The experimental results show that the TiO₂ layer thickness rapidly increases at early time and then slowly increases with the increasing of the electrophoresis time. The layer thickness is found to be proportional to the root of the deposition time. In order to explain the experimental results, the simulation of TiO₂ film growth is performed. The simulation is based on the model of TiO₂ particles surrounded by positive ions moving to the cathode (ITO glass) due to an electric field, and subsequently the particles are attached to the cathode. Simulation results quantitatively agree with the experimental ones, indicating that the model can be used for the design of TiO₂ film growth using electrophoresis.

Keywords: electrophoresis; TiO₂ thin layer; constant voltage; simulation.

1. Introduction

Homogenous deposited TiO₂ is a main factor to obtain high performance in dye sensitized solar cell. Various methods have been carried out to obtain homogenous thin layer, such as slip casting [1], screen printing [2], sol gel [3], sputtering [4], spin coating [5], and electrophoresis deposition [6-8]. Previously, we have reported the deposition of TiO₂ into indium-doped tin oxide (ITO) glass using electrophoresis method [8, 9]. In this method, the charged particles in suspension move to the cathode due to the electric field and then attach there. The advantages of this method are a simple method and a cheap. We can also adjust applied voltage and deposition time to get an expected TiO₂ layer thickness [7].

Electrophoresis deposition has essentially two processes. First, the charged colloidal particles in the suspension migrate to the electrodes under an external load due to an electric field. Second, the migrated particles will be deposited on the substrate. Electrophoresis deposition can be conducted under constant current and constant voltage conditions.

The important parameters for the electrophoresis process are particle size, dielectric constant of the solution, solution viscosity, and zeta potential [10]. In our previous experiments [8], zeta potential became an important parameter in forming TiO₂ layer. Zeta potential value of the particle could be changed by adding the salt to the solution of these particles [10]. This value affects how fast the particles deposit on the substrate.

Although the experiment of TiO₂ thin layer growth using electrophoresis method has been carried out by many research groups, only a few study focused on the simulation point of view. This paper discusses the mathematical calculation compared to the experimental result of TiO₂ layer growth on ITO glass by the electrophoresis method on constant voltage condition.

2. Theoretical background

2.1. Constant voltage method

The mathematical formulation is based on the reference [7]. The formulation parameters are defined as shown in Fig. 1. Thickness of TiO₂ thin layer is \( d_1(t) \), while the distance between two electrodes is \( d_2(t) \). Because of \( d_2(t) \gg d_1(t) \), \( d_2(t) \) may be considered unchangeable.
with the time. Therefore, \( V_2(t) \) is not changed due to the time.

In this method, the voltage between electrodes in a function of time \( V_0(t) \) can be formulated as equation (1). The relationship between \( V_0(t) \), voltage on TiO\(_2\) thin layer \( V_1(t) \), voltage on TiO\(_2\) colloidal solution \( V_2(t) \), the current flows as a function of time \( I_0(t) \) and electric field on colloidal solution \( E_2(t) \) is as follows:

\[
V_0(t) = V_1(t) + V_2(t) = I_0(t)R_1(t) + d_2E_2(t) \tag{1}
\]

Here, \( I_0(t) \) can be obtained by:

\[
I_0(t) = \frac{S_0E_2(t)}{\rho_2} \tag{2}
\]

where \( S_0 \) is electrode surface area and \( \rho_2 \) is TiO\(_2\) colloidal solution resistivity. The change in TiO\(_2\) thin layer resistance \( dR_1(t) \) between of TiO\(_2\) growth time between \( t \) and \( t + dt \) is:

\[
dR_1(t) = d\left(\frac{d_1(t)\rho_1}{S_0}\right) = \frac{dd_1(t)}{S_0} \rho_1, \tag{3}
\]

where \( \rho_1 \) is resistivity of TiO\(_2\) thin layer. Noted that \( dd_1(t) \) is the thickness change of TiO\(_2\) layer between interval \( t \) and \( t + dt \). Therefore, \( dd_1(t) \) value can be written as equation (4).

\[
dd_1(t) = \alpha_v(t)dt = A_vI_0(t)dt, \tag{4}
\]

where \( \alpha_v \) is TiO\(_2\) layer growth rate at constant voltage method. From equation (2-4), the equation (3) can be formulated as follows:

\[
dR_1(t) = \frac{\rho_1}{\rho_2} A_vE_2(t)dt \tag{5}
\]

After integration of both sides of equation (5), we obtain equation (6).

\[
R_1(t) = \frac{\rho_2}{\rho_1} A_v \int_0^t E_2(t)dt + d_2. \tag{6}
\]

From equations (2) and (6), equation (1) becomes:

\[
\frac{V_0(t)}{V_2(t)} = \frac{S_0}{\rho_2} \frac{\rho_1}{\rho_2} A_v \int_0^t E_2(t)dt + d_2 \tag{7}
\]

Both sides is integrated on \( t \), resulting in:

\[
\frac{dE_2(t)}{dt} = -\frac{S_0}{V_0\rho_2} \frac{\rho_1}{\rho_2} A_v E_2^3(t). \tag{8}
\]

Using initial condition,

\[
E_2(0) = \frac{V_0}{d_2} \tag{9}
\]

\( E_2(t) \) becomes:

\[
E_2(t) = \frac{1}{\left(\frac{d_2}{V_0} \frac{\rho_1}{\rho_2} A_v t\right)^\frac{1}{3}}. \tag{10}
\]

From equations (2) and (10), the current value \( I_0(t) \) becomes:

\[
I_0(t) = \frac{S_0}{\rho_2} \frac{1}{\left(\frac{d_2}{V_0} \frac{\rho_1}{\rho_2} A_v t\right)^\frac{1}{3}} \tag{11}
\]

Since the resistance of TiO\(_2\) layer is:

\[
R_1(t) = \frac{\rho_2}{\rho_1} d_1(t), \tag{12}
\]

and also equation (1), \( V_0(t) = I_0(t)R_1(t) + d_2E_2(t) \) becomes:

\[
V_0(t)\left(\frac{d_2}{V_0} \frac{\rho_1}{\rho_2} A_v t\right)^\frac{1}{3} = \frac{\rho_2}{\rho_1} d_1(t) + d_2 \tag{13}
\]

From above equation we can formulate:

\[
d_1(t) = \frac{\rho_1}{\rho_2} V_0 \left(\frac{d_2}{V_0} + \frac{2\rho_1 A_v}{\rho_2^2 V_0} t \right)^\frac{1}{3} - \frac{d_2}{V_0}. \tag{14}
\]

In initial condition, \( d_1(t) = 0 \) when \( t = 0 \). Using equation (4), the layer growth rate \( \alpha_v(t) \) can be obtained from differential of equation (14) to \( t \), as follow:

\[
\alpha_v(t) = \frac{d d_1(t)}{dt} = A_v \frac{S_0}{\rho_2} \frac{1}{\left(\frac{d_2}{V_0} \frac{\rho_1}{\rho_2} A_v t\right)^\frac{1}{3}} \tag{15}
\]

2.2. Calculation of layer growth rate

To calculate the layer growth rate, we need to define that the number of attached positive ion on a TiO\(_2\) particle is \( n^+ \), so that the number of charge that carries a TiO\(_2\) particle is \( n^+q \). Value of \( n^+q \) is also zeta potential value. So, we can calculate attached TiO\(_2\) particle on ITO glass at interval \( dt \) as much as \( I_0(t)dt/n^+q \). The number of TiO\(_2\)
particle in one layer is \( S_0/\pi a^2 \). Here, it is assumed that the diameter of TiO\(_2\) particle is \( a \) and the particles attach on ITO glass with no space each other, and the area of ITO surface is \( S_0 \). Thus, the number of formed layer at time interval \( dt \) is \( \pi a^2 I_0(t) dt/S_0 \) layer. Therefore, in time interval \( dt \), TiO\(_2\) layer thickness change \( dd_1(t) \) will be

\[
dd_1(t) = \frac{2\pi a^3}{S_0 n^\gamma} I_0(t) dt
\]  

(16)

In constant current condition, the deposited TiO\(_2\) particles on electrode at certain time will be constant. So that the thickness \( d_1(t) \) will be proportional to electrophoresis time \( t \) as equation (17).

\[
d_1(t) = \alpha_i t = A_i I_0 t
\]  

(17)

Here, \( A_i \) is constant and \( \alpha_i \) is TiO\(_2\) layer growth rate at constant current method. Using equation (17), we obtain,

\[
dd_1(t) = \alpha_i dt
\]  

(18)

Because in constant current \( I_0(t) = I_0 \), layer growth rate can be formulated as,

\[
\alpha_i = \frac{2\pi a^3}{S_0 n^\gamma} I_0.
\]  

(19)

Considering condition of attached positive ion on TiO\(_2\), i.e., by inserting equation (19) into equation (17), it will be obtained equation (20).

\[
n^+ = \frac{2\pi a^3 \alpha_i t}{d_1 S_0 q}
\]  

(20)

Next, we obtain equation (21) from equations (4) and (20),

\[
A_v = \frac{2\pi a^3}{n^\gamma S_0 q}
\]  

(21)

Finally, from equations (15) and (21), for constant voltage method, the rate of layer growth can be formulated as follows,

\[
\alpha_v(t) = \frac{2\pi a^3}{n^\gamma \rho^2 q} \left( \frac{1}{\sqrt{\frac{d_1^2}{\rho^2} + \frac{4\rho^3 a^3}{\rho^2 n^\gamma q}}}ight)^2
\]  

(22)

3. Electrophoresis experimental

Electrophoresis deposition process was set-up as shown in Fig. 1. ITO glass (12 Ohm, Sigma Aldrich) was used as the cathode and carbon as the anode. The distance between the anode and cathode was fixed at 4 cm. Electrophoresis is performed after the condition of TiO\(_2\) solution is found to be stable. Stable solution occurs if the interaction force among TiO\(_2\) particles is balance, and then the particles do not move to the bottom by the gravitation force. In our experimental, the electrophoresis solution is made from TiO\(_2\) particles and isopropyl alcohol. Salt Mg(NO\(_3\))\(_2\) is added in order to obtain the stable solution. The detail procedure can be seen in reference [8]. TiO\(_2\) particles with the diameter of about 400 nm were deposited on the ITO glass under the following conditions; constant applied voltage of 50 V, and various time depositions.

4. Results and discussions

The experiment results are shown in Fig. 2 and Fig. 3. Figure 2 shows the relationship between TiO\(_2\) layer thickness and electrophoresis time. It can be found that TiO\(_2\) layer thickness rapidly grows at early time and then slowly increases with the time. In other words, the increase of the layer thickness is proportional to the root of deposition time. Figure 3 shows the growth rate of TiO\(_2\) layer versus time at constant voltage of 50 V. The layer growth rate decreases as the electrophoresis time increases. The results in Figs. 2 and 3 occur because the resistance of formed TiO\(_2\) layer increases as thickness of TiO\(_2\) layer increases. Consequently, electric field of TiO\(_2\) colloidal solution decreases, resulting in slow deposition of TiO\(_2\) on the substrate.
The experimental results above can be explained by simulation results in Figs. 4 and 5. The detail of simulation parameters is listed in Table 1. Simulation was done using MATLAB software. Figure 4 shows that the layer thickness is plotted as a function of the electrophoresis time for applied voltage of 50 V. The data of experimental results (Fig. 2) are also plotted in the figure. We can find that the increasing of layer is proportional to the root of the deposition time, reflecting the result of the equation (14).

Figure 5 shows the simulation of growth rate for TiO2 layer versus the time, obtained from equation (22). We can obtain that the growth rate rapidly decreases at the early time and then slowly decreases with time. The simulation results in Figs. 4 and 5 reproduce quantitatively the experimental results in Figs. 2 and 3, respectively. Such results are found by the assumptions that the TiO2 layer growth rate at constant current $\alpha_i$ is 0.0005 and the resistivity of TiO2 colloidal solution $\rho_2$ is 625 Ohm-cm. The constant value of $\alpha_i$ is obtained from equation (19) by inserting the following parameters: the number of attached positive ion on a TiO2 particle $n^+$ is $1.4 \times 10^9$ and the current constant $I_0$ is 1.25 V. It is noted that the value of $\alpha_i$ used here is 20 times lower than that of the reference [7], while the $\rho_2$ is 10 times smaller than that of the one [7]. Such different values are reasonable due to different size of TiO2 particles, where the diameter of TiO2 particles in reference [7] is about 25 nm.

In order to understand how the simulations explain the experimental results, let’s consider the relation between resistance of TiO2 layer $R_1$ and $d_1$ in equation (12), i.e., $R_1 = \rho_1 d_1/S_0$. This relationship indicates that the resistance of the layer $R_1$ will increase when the thickness of TiO2 layer $d_1$ increases. Consequently, because the applied voltage $V_0$ is kept to be constant, the electric field $E_2$ in equation (10) decreases, and finally the growth rate in equation (22) also decreases, resulting in Fig. 5. The decrease of the growth rate automatically influences the growth of TiO2 thickness, resulting in TiO2 layer thickness rapidly grows at early time and then slowly increases with the time, as shown in Fig. 4. Therefore, the model used here can be applied for the design of TiO2 film growth using electrophoresis.

5. Conclusion

The growth of TiO2 layer by electrophoresis method has been studied experimentally and numerically in constant voltage. The experimental results show that the TiO2 layer thickness rapidly grows at early time and then slowly increases with the time. Such result is also reflected by the relation between the growth rate and the electrophoresis time, where the layer growth rate decreases as the electrophoresis time increases. Our simulation results also agree quantitatively with experimental results, indicating that such simulation is useful for understanding phenomenon that occurs in electrophoresis process.

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Table 1
Parameters used in our simulation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average of TiO2 particle radius (nm)</td>
<td>$a$</td>
<td>500</td>
</tr>
<tr>
<td>Distance between electrodes (cm)</td>
<td>$d_2$</td>
<td>4</td>
</tr>
<tr>
<td>Surface area of the electrode (cm$^2$)</td>
<td>$S_0$</td>
<td>5</td>
</tr>
<tr>
<td>Elemental charge (Coulomb)</td>
<td>$q$</td>
<td>$1.602 \times 10^{-19}$</td>
</tr>
<tr>
<td>TiO2 layer growth rate at constant current</td>
<td>$\alpha_i$</td>
<td>0.0005</td>
</tr>
<tr>
<td>Resistivity of TiO2 layer (MOhm-cm)</td>
<td>$\rho_1$</td>
<td>200</td>
</tr>
<tr>
<td>Resistivity of TiO2 colloidal (Ohm-cm)</td>
<td>$\rho_2$</td>
<td>625</td>
</tr>
<tr>
<td>Number of attached positive ion on a TiO2 particle</td>
<td>$n^+$</td>
<td>$1.4 \times 10^9$</td>
</tr>
</tbody>
</table>

Fig. 4. Simulation result of TiO2 thickness versus deposition time for applied voltage of 50 V

Fig. 5. Simulation result of layer growth rate versus deposition time
References


