Abstract—In this paper, we propose fabricating method of high quality titanium oxide (TiO$_2$) thin film for Dye-Sensitized Solar Cell (DSSC) by Electrophoresis Deposition (EPD). We focused on stirring time of TiO$_2$ solution, TiO$_2$ multilayer thin film and addition of EPD solution. Stirring time of TiO$_2$ solution was conducted for 1, 3, 6, 12, 24, 48 hours, and multilayer thin film was fabricated three types (single, double, four layer). Addition of EPD solution was adopted polyethylene glycol (PEG). The amount of PEG was conducted five types (0, 5, 15, 35 and 50 g/L). MK2 dye which is organic dye was used as photosensitizer. As a result, the highest conversion efficiency was obtained at 4.12% with stirring for 24 hours, four layers and 5g/L PEG.

Index Terms—Dye-sensitized solar cells (DSSC), electrophoresis deposition (EPD), MK2-dye, stirring time, multilayer TiO$_2$ thin film, polyethylene glycol (PEG).

I. INTRODUCTION

We have depended on fossil fuels for example petroleum, natural gas, coal and uranium. It is said that fossil fuels are getting dried up day by day. Using their material caused environmental problem such as global warming, abnormal weather, and scarcity of food. [1] because of these problems, clean energy must be used. Solar cells are useful device which convert light directly into electricity by photovoltaic effect. Solar cells are divided crystalline silicon solar cells, multi-crystalline silicon solar cells, dye-sensitized solar cells and organic solar cells. [2] Silicon solar cell is known because of high conversion efficiency than any other solar cells. However, silicon solar cell has problem its high material cost. Currently for third generation solar cell, dye-sensitized solar cell (DSSC) has been studied by world researchers.

DSSC was first published in 1991 by Michael Gratzel team. His team reported high conversion efficiency of DSSC about 13 %. [3] DSSC has attractive features that are simple structure, low cost and possibility of high conversion efficiency. [4], [5] Titanium oxide (TiO$_2$) is used in DSSC photoanode because of effectiveness, low price and useful multifunctional material. [6]

DSSC has anode electrode, dye, electrolyte and cathode electrode. The anode electrode is made of TiO$_2$-fluorine doped SnO$_2$ coated glassed (FTO). In theory of DSSC, when sunlight shines on dye-absorbed TiO$_2$ thin film, dye molecule absorbs visible light. Then the electrons in dye molecule are released. The electrons pass through TiO$_2$ thin film, conductive glass and external circuit. They reach counter electrode. An oxidation-reduction reaction occurs between counter electrode and electrolyte. Electrolyte helps preventing degradation of dye molecules by supplying back lost electrons to the dye. DSSC repeats these processes and creates current.

DSSC has merit of low cost, but major dye as photosensitizers ruthenium (cis-di(thiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylate)rut-henium(II), N719) are high cost material and not environmentally friendly photovoltaic systems. So, in order to improve these problems, researchers try experiment using natural dye for DSSC (achiote seeds, Hibiscus Sabdariffa, Rosa Damascene Flower and Monascus yellow, etc) [7]-[9]. But, DSSC using these natural dyes achieved low conversion efficiency, so it is important to develop inexpensive and ecological dye for DSSC. We used organic Dye sensitizer-MK2 substitute for N719 and natural dye. MK2 dye has some characteristics such as: rare metal free, short dyeing time and efficiency.

TiO$_2$ thin film has important role in DSSC. High conversion efficiency is achieved when TiO$_2$ thin film is good condition. Methods of fabricating TiO$_2$ thin film are doctor-blade [10], spin coating [11], sol-gel method [12] and sputtering method [13]. We adopted Electrophoretic deposition (EPD) method for fabricating TiO$_2$ thin film.

Electrophoresis deposition (EPD) charged particle in EPD solution positively or negatively. Particles move to cathode if particles are charged positively. In contrast, they move to anode if they are charged negatively. EPD method has advantages of low cost, short deposition time and high reproducibility. [14] EPD is usually used a biochemistry field. For example, separation of protein deoxyribonucleic acid (DNA). [15]

This study was performed to enhance TiO$_2$ thin film condition by stirring time, multilayer and addition. When we fabricated TiO$_2$ thin film, cracks occurred because of evaporation of EPD solvent. Cracks on the surface of TiO$_2$ thin film reduced conversion efficiency of DSSC. We checked that stirring time and multilayer effected TiO$_2$ thin film conditions. As an addition, we adopted Polyethylene glycol (PEG). It is said PEG made TiO$_2$ thin film porous condition. Porous TiO$_2$ thin film increases the amount of absorbed dye. So, PEG improved conversion efficiency of DSSC. We aimed high conversion efficiency of DSSC with...
the optimum stirring time, multilayer and PEG.

II. EXPERIMENTAL METHOD

A. Electrophoresis Deposition for TiO₂ Thin Film

For DSSC anode electrode, P-25 TiO₂ powder (JAPAN AEROSIL), ethanol (Wako) were used in preparing anode electrode. We measured 0.2g TiO₂ powder with electronic balance (ITX-120, ASONE) and stirred it with 40ml ethanol in a plastic vessel by magnetic stirrer. The EPD anode was Aluminum plate (20×20×1mm), cathode was FTO (20×20×1.8mm). They were placed into the fabricated TiO₂ solution with 10mm distance between anode and cathode. EPD current was set at 0.12mA from current source (ADVANTEST, R6144), and EPD time was set for 100 seconds. After EPD, TiO₂ thin film was sintered at 450°C for 60 minutes. The experimental set up is shown in Fig. 1.

1) Stirring time for TiO₂ solution

Rotation per minute (rpm) of magnetic stirrer was set to be 700rpm. Stirring times were set to be 1hour, 3hours, 6hours, 12hours, 24hours or 48hours.

2) Multilayer TiO₂ thin film

We used EPD method and drying process to fabricate multilayer thin film. Single layer thin film has cracks on the surface of thin film. Fabricating multilayer reduces cracks. We made double layers and four layers thin film. To make double layers thin film, firstly we conducted 50 seconds EPD. After EPD, thin film with silicon take out from solution and conduct drying process for 60 seconds with drying oven (DO-450 iuchi). Drying temperature was set at 60 degrees. EPD was conducted for 50 seconds after drying process. These processes completed double layers thin film. Four layers needed four times 25 seconds EPD and three times drying as shown in Fig. 2.

3) Polyethylen glycol (PEG)

Experiment of A.1 and A.2 did not have binder. This experiment studied polyethylene glycol (PEG) as binder. PEG is known non-ionic surfactant. It has characteristics of burnout and good solubility in water and ethanol. [16]

In this experiment, 0.2g TiO₂ powder, 40ml ethanol and PEG (Wako, average molecular 1500) were mixed with magnetic stirrer. The amount of PEG was 0, 5, 15, 35 or 50 g/L. Each amount of PEG was added to the TiO₂ solution.

B. Electrophoresis Deposition for Cathode Electrode

We used carbon nanotube (CNT, CNT dispersion KJ, X7006L) electrode with Poly (diallyl dimethylammonium chloride) (PDDA, sigma Aldrich, 20wt%) for cathode electrode of DSSC. PDDA has a strong electron withdrawing ability from CNT [17]. In DSSC, Pt is usually used for cathode electrode, but it is high cost and rare material. We used CNT/PDDA cathode electrode for substitution for Pt. Fig. 3 depicts experimental set up for EPD to make CNT/PDDA electrode. Firstly, we mixed 0.5mL of PDDA solution and 9.5mL of deionized water, so 1wt% PDDA solution was made. Afterward, we blended CNT solution with 1wt% PDDA solution in proportion of 10:1 (CNT/PDDA). Then we obtained CNT/PDDA solution for using. With EPD, CNT/PDDA cathode electrode was fabricated. Distance between anode (FTO 40×20×1.8mm) and cathode (Aluminum plate 40×20×1mm) was set 10 mm with silicon. EPD time was set to 90 seconds and EPD voltage was set 3 V. After EPD, it was dried at air temperature for 24 hours. The electrode average thickness is around 15μm.

![Fig. 3. Experimental set up for EPD to make CNT/PDDA electrode](image-url)
C. Electrolyte and Dye Solution

The electrolyte was composed of 0.6M of 1,2-dimethyl-3-propylimidazolium iodide (Wako), 0.1M of lithium iodide (Lil sigma Aldrich), 0.2M of iodide (sigma Aldrich), 0.5 M of 4-tert-butylpyridine (sigma Aldrich) and 10mL of acetonitrile (Wako). The dye solution was composed of 10mg of (2-Cyano-3-[5'''-(9-ethyl-9H-carbazol-3-yl)-3',3''',3''',4-tetra - n - hexyl - [2, 2', 5', 2', 5', 2'']-quarterthiophen - 5-yl] acrylic acid) (MK2 dye, sigma Aldrich) and 108ml of toluene (Wako). Prepared thin film was soaked in dye solution for 3 hours at 25 degrees. After the thin film was absorbed the dye, its surface was rinsed by toluene and deionized water continuously to remove any dye that had not adsorbed on the surface of thin film.

D. Making DSSC and Measurements

Prepared TiO2 thin film with dye, cathode electrode and blended electrolyte were assembled, so DSSC was completed. The thickness of TiO2 thin film and cathode electrode were measured by step gauge (BRUKER DektakXT), and surface of TiO2 thin film was observed by metallurgical microscope (OLYMPUS BX60M). Absorption spectrum of dye adsorbed TiO2 thin film was measured by spectrophotometer (SHIMADZU, UV-3600). The open-circuit voltage Voc(V), short-circuit current density Jsc (mA/cm^2), fill factor (%) and efficiency conversion (%) of DSSC was measured with solar simulator (OAI, TriSOL) by simulating the Sunlight (AM1.5, 100mW/cm^2).

III. RESULT AND DISCUSSION

The TiO2 thin film was formed on FTO-glass with EPD method. Fig. 4 shows images of surface of TiO2 thin film with metallurgical microscope. The images when stirring time was for 1, 6, 24, or 48 hours, respectively, were shown in this paper.

Fig. 4 (a) (b) (c) (d) of TiO2 thin film shows in case of 1, 6, 24, or 48 hours stirring time with single layer. Single layer with short or long stirring time has many cracks on the surface of TiO2 thin film. It is assumed that increasing stirring time don’t affect reducing cracks.

Fig. 4 (e) (f) (g) (h) show the images of double layers TiO2 thin film that has 1, 6, 24, or 48 hours stirring time. In double layers, cracks on the surface of TiO2 thin film are finer than compared with case of single layer. Double layer has good condition than case of single layer. Fig. 4 (i) (j) (k) (l) show the images of four layers TiO2 thin film that has 1, 6, 24, or 48 hours stirring time. In four layers, small cracks or no cracks exists on TiO2 thin film. It is assumed that multilayer reduced cracks on the film.

Only four layers with 1 hour stirring time has small cracks. For 1 hour stirring time was too short for TiO2 thin film. In multilayer process, we conducted drying process. Drying process volatilized ethanol in the TiO2 film. Volatilizing ethanol each layer reduced cracks of TiO2 thin film. Cracks reduce the amount of absorbed dye in TiO2 thin film and impact on conversion efficiency of DSSC. We measured absorption spectra of dye absorbed in TiO2 thin film with spectrophotometer. The absorption spectra of absorbed dye are shown in Fig. 5 (a) single layer (b) double layer (c) four layer with different stirring time. It was revealed the absorbed amount of dye rises in the range of about 400-600 nm if the TiO2 thin film has multilayer. The maximum adsorption wavelength of MK2 dye is 480 nm. It is considered that the amount of the dye in TiO2 thin film increased by decreasing cracks, so dye absorbed much light. It is shown the high absorption spectra stirring for 24 hours (single layer), for 48 hours (double layers), for 24 hours (four layers) in this experiment. Long stirring time did not affect cracks on the film, but improve absorption ability.

![Fig. 4. The microscope images of different layers](image-url)
Fig. 5. Absorption spectra of absorbed dye different TiO$_2$ films and stirring time of TiO$_2$ solution; (a) single layer, (b) double layer, (c) four layer.

Fig. 6. Absorption spectra of absorbed dye with different amount of PEG.

Next, we added Polyethylene glycol (PEG) to TiO$_2$ solution for EPD as binder. In this experiment, TiO$_2$ thin film has single layer and 1 hour stirring time. Fig. 6 shows the absorption spectra of adsorbed dye, and Table 1 shows result of measurement of DSSC (single layer, 1 hour stirring time). From Table 1, the highest conversion efficiency is 1.25% with four layers, 24 hours stirring time and PEG of 5g/L. If the amount of PEG increases more than 5g/L, conversion efficiency and short-circuit current density achieve low values. TiO$_2$ thin film with four layers and 24 hours stirring time generated higher value than in case of having single layer and 1 hour stirring time. Compared with measurement result of single layer and 1 hour stirring time, each short circuit current and conversion efficiency values were achieved higher data. In this result, it is assumed that stirring time and multilayer affected DSSC performance. In Fig. 7, TiO$_2$ thin film with amount of 5g/L PEG is the best absorption spectra (orange line) in agreement with single layer and 1 hour stirring time.

Next, we conducted experiment to aim high conversion efficiency using three technics. TiO$_2$ thin film has four layers structure, 24 hours stirring time and different amount of PEG. Fig. 7 shows absorption spectra of adsorbed dye with three types (0g/L, 5g/L or 50g/L) and Table II shows result of measurement of DSSC (four layers, 24 hours stirring time). From Table II, the highest conversion efficiency is 4.12% with four layers, 24 hours stirring time and PEG of 5g/L. If the amount of PEG increases more than 5g/L, conversion efficiency and short-circuit current density achieve low values. TiO$_2$ thin film with four layers and 24 hours stirring time generated higher value than in case of having single layer and 1 hour stirring time. Compared with measurement result of single layer and 1 hour stirring time, each short circuit current and conversion efficiency values were achieved higher data. In this result, it is assumed that stirring time and multilayer affected DSSC performance. In Fig. 7, TiO$_2$ thin film with amount of 5g/L PEG is the best absorption spectra (orange line) in agreement with single layer and 1 hour stirring time.

TABLE I: MEASUREMENT RESULT (SINGLE LAYER, 1 HOUR STIRRING TIME)

<table>
<thead>
<tr>
<th>PEG (g/L)</th>
<th>Jsc(mA/cm2)</th>
<th>Voc(V)</th>
<th>FF(%)</th>
<th>η(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.36</td>
<td>0.64</td>
<td>44.8</td>
<td>1.25</td>
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<tr>
<td>5</td>
<td>9.81</td>
<td>0.67</td>
<td>41.6</td>
<td>2.75</td>
</tr>
<tr>
<td>15</td>
<td>8.02</td>
<td>0.65</td>
<td>43.4</td>
<td>2.26</td>
</tr>
<tr>
<td>35</td>
<td>6.75</td>
<td>0.68</td>
<td>41.8</td>
<td>1.92</td>
</tr>
<tr>
<td>50</td>
<td>7.64</td>
<td>0.61</td>
<td>39.4</td>
<td>1.83</td>
</tr>
</tbody>
</table>

TABLE II: MEASUREMENT RESULT (FOUR LAYER, 24 HOUR STIRRING TIME)

<table>
<thead>
<tr>
<th>PEG (g/L)</th>
<th>Jsc(mA/cm2)</th>
<th>Voc(V)</th>
<th>FF(%)</th>
<th>η(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
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<td>0.66</td>
<td>42.9</td>
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</tr>
<tr>
<td>5</td>
<td>12.8</td>
<td>0.71</td>
<td>45.6</td>
<td>4.12</td>
</tr>
<tr>
<td>15</td>
<td>12.20</td>
<td>0.66</td>
<td>40.7</td>
<td>3.30</td>
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<tr>
<td>35</td>
<td>10.46</td>
<td>0.66</td>
<td>41.8</td>
<td>2.87</td>
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<tr>
<td>50</td>
<td>8.02</td>
<td>0.67</td>
<td>40.3</td>
<td>2.16</td>
</tr>
</tbody>
</table>
Fig. 8 is the data that blue line shows single layer and 1 hour stirring time, red line shows four layers and 24 hour stirring time, which have some amount of PEG from Table I. Red line and blue line have peak value in the 5g/L PEG.

Fig. 9 shows the relation between multilayer and conversion efficiency. There are three types conditions (blue: No PEG and 1h stirring, red: 5g/L PEG and 1h stirring, gray: 5g/L PEG and 24h stirring). DSSC with single layer, 1 hour stirring time no PEG got 1.25% conversion efficiency. With same conditions (no PEG and 1 hour stirring time), double layer and four layers produces 2.15%, 2.73% conversion efficiency respectively. From this result, multilayer raised conversion efficiency of 1.25%. DSSC with four layers, 24 hours stirring time and 5g/L PEG achieved 4.12%. Optimum three factors raised conversion efficiency about 220%.

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REFERENCE


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