# CHAPTER V
# FABRICATION OF ZnO-NONI LEAVES DYE-SENSITIZED SOLAR CELL BY ELECTROPHORETIC DEPOSITION

## 5.1 Abstract

The electrophoretic deposition (EPD) was employed to prepare ZnO film for photoanode in dye-sensitized solar cell. The natural dye that extracted from noni leaves was used as a sensitizer on ZnO film. The effect of ZnO film thickness on the conversion efficiency of DSSC was investigated. The as-prepared ZnO films were smooth and uniform, and their thickness was increased with an increase in deposition voltage (from DC 15 V to 24 V) and deposition times (5 min to 20 min). The efficiency of converting sunlight into electricity of DSSC increased as the ZnO film thickness increased because of the increment of ZnO contents and dye loading. The ZnO film, which was fabricated by electrophoretic deposition method, had the thickness about 4 to 18 micrometers and exhibited the conversion efficiency of 3.7 to 22.9 milli-percents at the constant applied DC field of 15V and various deposition time of 5 to 20 min. Moreover, the ZnO film thickness about 4 to 7 micrometers exhibited the conversion efficiency of 3.7 to 14.1 milli-percents at the constant deposition time of 5 min and various applied voltage of 15 to 24V.

## 5.2 Introduction

Dye sensitized solar cell (DSSC) is an attractive photovoltaic device due to low cost and relatively simple fabrication process. The natural dye from noni leaves has been used as a sensitizer in this work because the synthetic dyes are very expensive and noni leaves dye exhibited the highest conversion efficiency in comparison to other dyes that used as sensitizer in chapter IV. The extracted noni leaves dye absorbed both visible and near-infrared wavelength regions, and then enhanced the efficiency of ZnO DSSC.

A semiconductor is one of components that used in DSSC photoanode. ZnO is one of the attractive semiconductor materials in solar energy conversion due to its stability against photocorrosion and photochemical properties similar to $TiO_2$. This material has a band gap similar to that of $TiO_2$ at 3.2 eV and higher electron mobility 115- 155 $cm^2/V\,s^2$ than that of $TiO_2$ (Chou et. al., 2007). There are various ZnO photoanode preparations, such as the doctor blade method, screen printing, sol-gel technique, and electrophoretic deposition (EPD) (Saito et al., 2008; Hara et al., 2000 and Redmond et al., 1994). The EPD is a useful method for the preparation of binder-free photoanode in a much shorter time, compared to the other coating techniques. It is especially attractive due to the low cost, simple equipment, formation of uniform layers of controlled thickness, and homogeneous microstructure (Grinis et al., 2008). The EPD is achieved via motion of charged particles in suspensions towards an electrode and deposit formation under an applied electric field (Li et al., 2010). Jarernboon et al. observed that the film thickness correlated with increase of the deposition voltage and deposition time in the preparation of $TiO_2$ nanoparticles on FTO substrates (Jarernboon et al., 2009).

The electrophoretic deposition method (EPD) is one of suitable techniques for fabricating photoanode film for DSSC because this method can control the film thickness of photoanode by changing the applied voltage and deposition time. The film thickness of photoelectrode is an essential factor which influenced the conversion efficiency of DSSC. Hara and co-workers prepared ZnO-DSSC using N719 as the sensitizer and obtained the conversion efficiency of 2.2%. In addition, using electrophoretic deposition method for ZnO-DSSC production on plastic substrate, the high efficiency of 4.17% was achieved (Yin et al., 2010).

In this study, The ZnO film was prepared via the electrophoretic deposition method and the noni leaves dye was used as the sensitizer. The applied voltage and deposition time are the electrophoretic deposition parameters that controlled the ZnO film thickness. The effect of ZnO film thickness on the efficiency of DSSC was investigated.

## 5.3 Experimental

### 5.3.1 Materials

Fresh noni leaves was purchased from Sam-Yan market, Bangkok, Thailand. Commercial ZnO nanoparticles (ZoNoP®, 99.93% ZnO) was purchase from Nano Materials Technology Co., Ltd., in Thailand. Acetylacetone ($\geq$ 99.5%) was purchased from Fluka. Lithium iodide beads (99%), 4-tert-butyl pyridine (96%) and hydrogen hexachloroplatinate (IV) hydrate (~38% Pt basis) were purchased from Aldrich. Iodine was purchase from Suksapan panit, Thailand. Fluorine-doped $SnO_2$ (FTO) glass (sheet resistance of 8 $\Omega/cm^2$) was purchased from Dyesol Company.

### 5.3.2 Preparation of natural dye sensitizers

Noni leaves were cut into very small pieces and then extracted in ethanol at room temperatue. Afterward, the solid residues were filtered out and the dye solution was evaporated. Finally, extracted dye was dissolved in ethanol to obtain concentration of 10 g/l before use.

### 5.3.3 Electrophoretic deposition (EPD)

A commercial nanocrystalline ZnO powder was dispersed well in ethanol (5 g/L) with 250 µl of acetylacetone and ultrasonicated for 2 h. After ultrasonication, the suspension was put in a container for electrophoresis. The electrophoretic cell contained two FTO glasses and the distance between electrodes was 1 cm. The EPD was performed at a DC electric field. After EPD, the residual solvent on the as-deposited film was evaporated in air at ambient temperature and calcined at 500 °C for 1 h in ambient conditions. The 1 ml of noni leaves dye solution were dropped on the post heated electrodes in at room temperature and the excess dye molecules were washed out with water and ethanol and keep in dry and dark container.

### 5.3.4 Cell assembly

To assemble the DSSC cells, the 127 µm-thick transparent parafilm® was used to make a narrow empty space inside the cell and the Pt cathode film prepared from spreading 7 mM hexachloroplatinic acid in 2-propanol on FTO glasses and calcining at

450 °C for 30 min. The electrolyte solution was composed of 0.025 M of iodine ($I_2$), 0.5 M of lithium iodide (LiI) and 0.2 M of *tert*-butyl pyridine that was dissolved in acetonitrile. Then, the electrolyte was injected to spread thoroughly in the as-prepared space between the two electrodes.

### 5.3.5 Characterizations

The crystal structure of the ZnO/FTO electrode (area 1cm x 1 cm) which was fabricated by doctor blading and electrophoretic deposition method were examined by X-ray diffractometer (XRD) with 2 theta ($2\theta$) 20-60 degree.

The surface and cross-section morphologies of ZnO, ZnO/dye and ZnO/dye/polythiophene which were deposited on FTO glass were studied by field emission scanning electron microscope (FE-SEM) with 2k, 5k, 50k and 100k magnification.

The thicknesses of ZnO which were deposited on FTO glass were measured by using a profilometer (Veeco Dektak 150) with force 3 mg.

The optical absorption of extracted natural dyes (0.25 g/L) was measured by a UV-Visible spectrophotometer (UV-1800).

The optical absorption of ZnO and ZnO/ noni leaves dye (area 1.5cm x 2.5cm) which were deposited on FTO glass were measure by a UV-Visible spectrophotometer (UV-2550).

The photovoltaic properties of the prepared DSSC, i.e. short circuit current (Jsc, mA/cm2), open circuit voltage (Voc, V), fill factor (FF) and efficiency ($\eta$, %) were determined from the I-V curve obtained by using digital Keithley 236 multimeter under an irradiation of white light from 100 mW/cm$^2$ halogen-tungsten lamp.
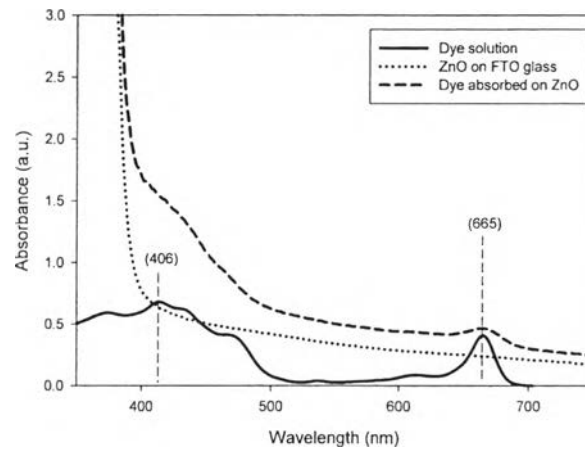
## 5.4 Results and discussion



**Figure 5.1** The absorption spectra of noni leaves dye, ZnO and its absorption on ZnO.

Figure 5.1 shows the absorption spectra of noni leaves dye solution and its absorption on the ZnO films with the thickness of 4 micrometers. The extracted dye from noni leaves has chlorophyll pigment as main component (Chang *et al.,* 2010) which absorbed at wavelength of 406 and 665 nm. The ZnO film does not generally absorb the visible light. However, the noni leave pigment absorbed on ZnO film shows its visible light absorption.
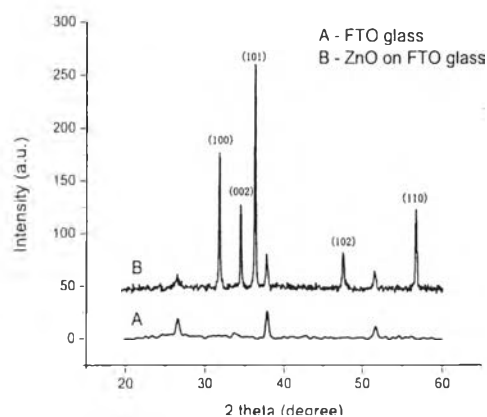


**Figure 5.2** XRD pattern of ZnO film prepared by electro deposition method.

Figure 5.2 shows the XRD pattern of ZnO on FTO glass that fabricated by electro deposition method. The XRD pattern corresponds to the hexagonal ZnO structure (wurzite) (JCPDS database card No. 36-1451) with the diffraction peaks of (100), (002), (101), (102) and (110) crystal plane. For the diffraction peaks at scattering angle 26.61, 37.85 and 51.62 degree correspond to FTO (fluorine doped tin oxide) glass (JCPDS database card No. 46-1088). (Liao *et al.*, 2005)
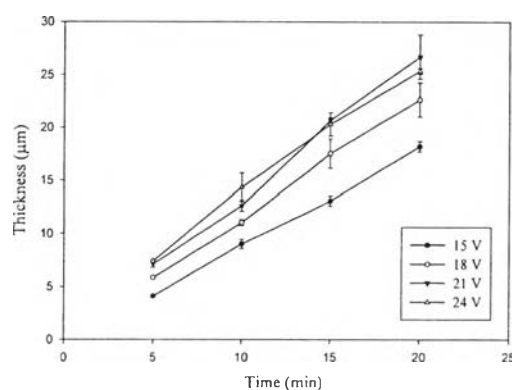


**Figure 5.3** The thickness of ZnO films with different time and voltage for deposition.

**Table 5.1** The thickness of ZnO films with different time and voltage for deposition

| Time \ Voltage | 5 min | 10 min | 15 min | 20 min |
|---|---|---|---|---|
| 15 V | 4.11341 | 9.04784 | 13.08445 | 18.22066 |
| 18 V | 5.865367 | 11.05816 | 17.55968 | 23.63513 |
| 21 V | 7.143073 | 12.64163 | 20.69878 | 26.69572 |
| 24 V | 7.42923 | 14.36604 | 20.31833 | 25.35041 |

As shown in figure 5.3 and table 5.1, the thickness of ZnO films was significantly increased with increasing voltage and time for deposition. The thickness of

ZnO films was proportional to applied voltage for deposition due to the high electrophoretic mobility of the ZnO particles. When comparing the thickness of films between 21V and 24V at 20 minutes, both films are not different in thickness. This result can be explained that the electric field influencing electrophoresis decreases with prolonged deposition time due to the formation of the ZnO insulating layer on the conducting glass surface (Besra *et al.*, 2007).
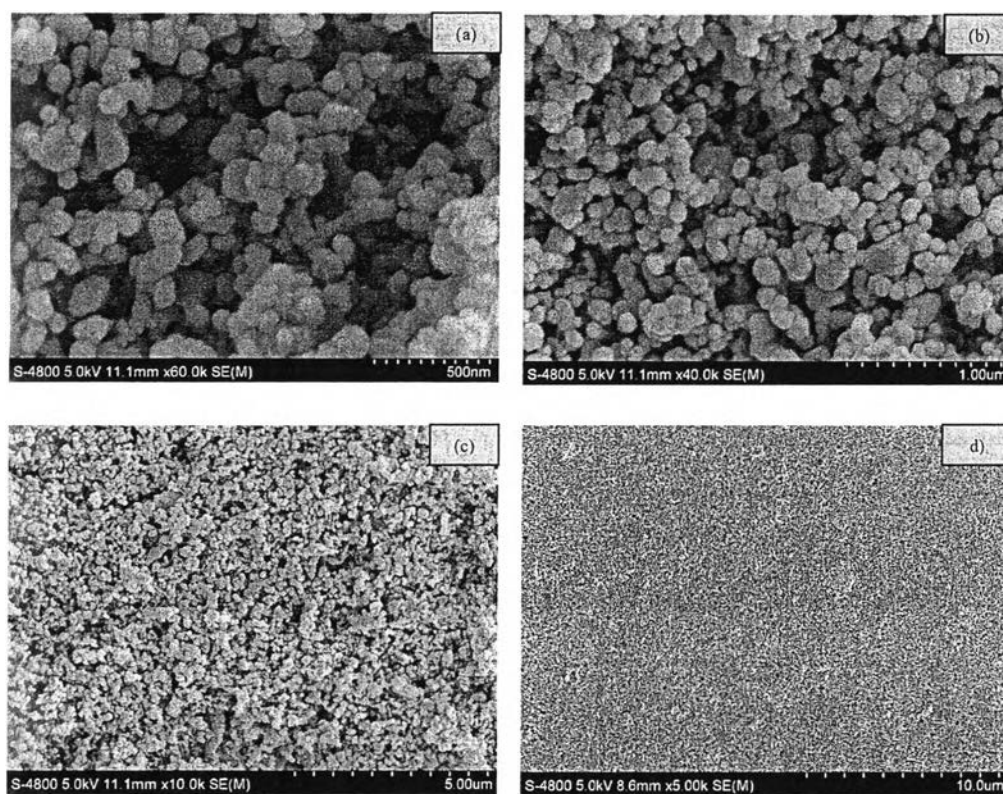


**Figure 5.4** Top view FE-SEM images of ZnO film prepared by electrodeposition at 15V for 5 min; magnifaication of 60k (a), 40k (b), 10k (c) abd 5k (d).

Figure 5.4 shows the surface images of ZnO films that were fabricated by the EPD at 15V for 5 min. Their surface is uniform and smooth. From the image, the film consists of a porous structure with the particle size ranging in between 50 – 200 nm. The

thickness of ZnO films increased with deposition voltage and time for deposition as shown in figure 5.5 and 5.6.
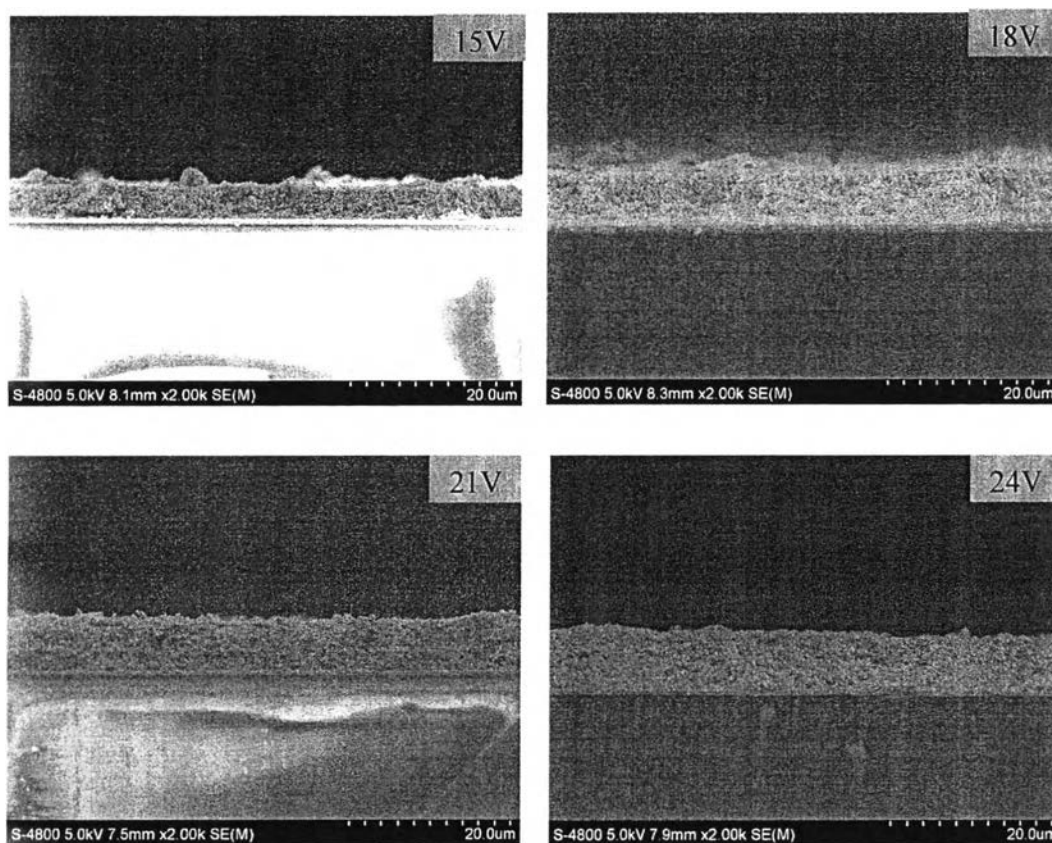


**Figure 5.5** Side view FE-SEM images of ZnO films fabricated by electrophoretic deposition at varied voltage for 5 min.
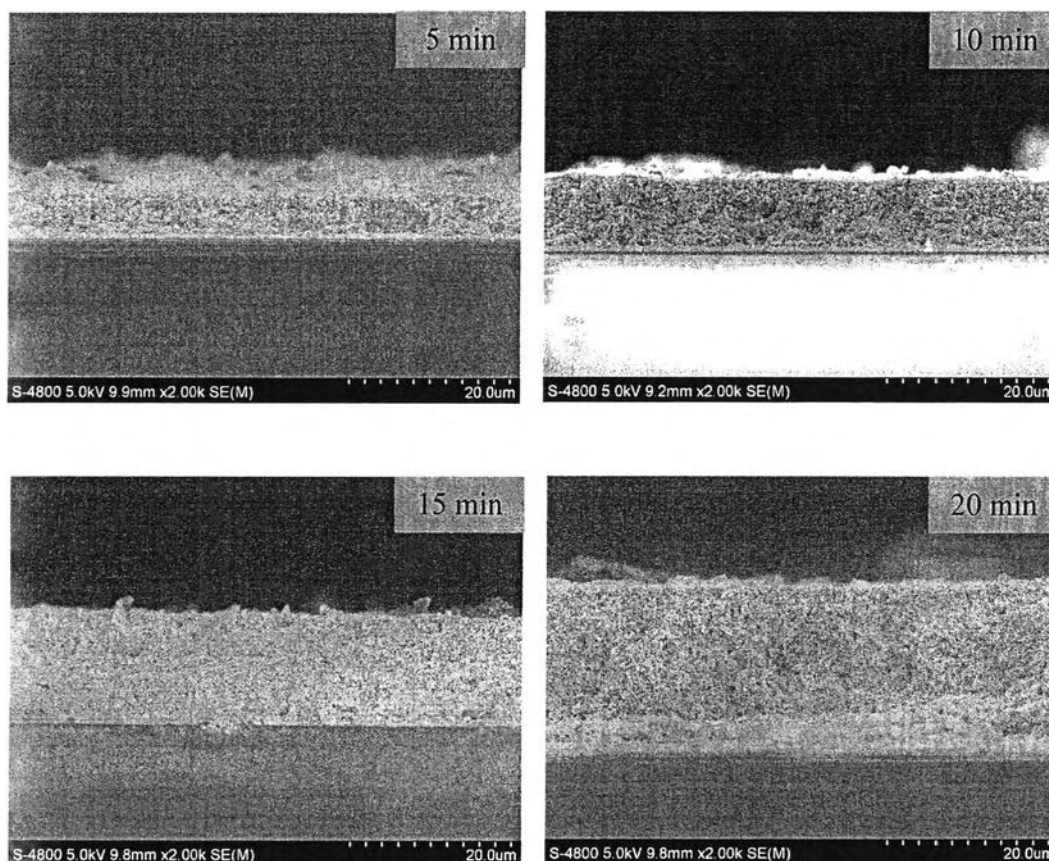
**Figure 5.6** Side view FE-SEM images of ZnO films fabricated by electrophoretic deposition at varied time and fixed voltage at 15 V.
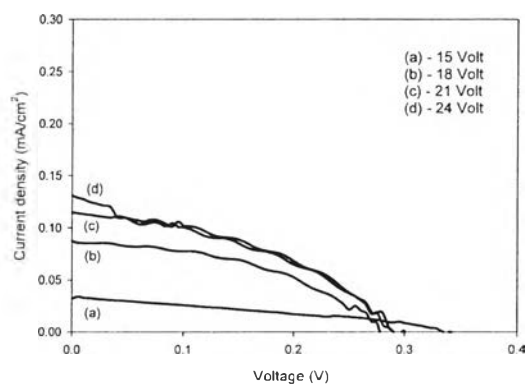


**Figure 5.7** The J-V characteristics of DSSC with fixed 5 min and varied voltage for deposition: 15 V (a), 18 V (b), 21 V (c) and 24 V (d).

**Table 5.2** The efficiencies of DSSC with fixed 5 min and varied voltage for deposition

| Voltage (V) | Thickness ($\mu$m) | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (V) | ff | $\eta$ ( %) |
|---|---|---|---|---|---|
| 15 | 4.1 | 0.03273 | 0.34 | 0.33 | 0.003704 |
| 18 | 5.8 | 0.08722 | 0.285 | 0.43 | 0.010791 |
| 21 | 7.1 | 0.13104 | 0.29 | 0.372 | 0.0141297 |
| 24 | 7.4 | 0.11503 | 0.29 | 0.411 | 0.0136884 |

Figure 5.7 and table 5.2 show the efficiency of ZnO film deposited at 18V is more than that of deposition at 15V. For deposition voltage at 15V, the electrophoretic mobility of the ZnO particles was probably too low; these films got loose and disordered structures (Pore size of film is 195.6 A°). For the films deposited at 18V had dense structures ((Pore size of film is 109.8 A°) and affected the efficiency of DSSC (Miao *et al.,* 2010). When the applied voltage increased, the thickness of ZnO films increased with the short-curcuit current ($J_{sc}$), and consequently, the efficiency of DSSC increased because the augmentation of ZnO contents and dye loading. For high deposition voltage (24V), the high electrophoretic mobility could occur in the suspension which could affect the uniform flow of particles arriving at the electrode. They cannot find enough time to sit in their best positions to form a close-packed structure and the low efficiency might occur (Besra *et al.,* 2007). Moreover, the fill factor increased from 0.33 to 0.41 as the applied voltage increased from 15V to 24V and affected to the increment of the efficiency of DSSC. This increase in fill factor is ascribed to the decrease in the pore size of the film and the improvement in ZnO interparticles connection, and consequently decreased in the resistance of the system (Yum et. al., 2005 and Yin et al., 2010). However, the open-curcuit voltage decreased with the increasing of ZnO film thickness. This is due to the additional charge recombination, recapture of electrons by the oxidized form ($I_3^-$) of redox couple in electrolyte and oxidized sensitized occur more

easily before reaching the FTO glass, resulting in the decrease efficiency of DSSC. (Yin *et al.,* 2010 and Saito *et al.,* 2009)
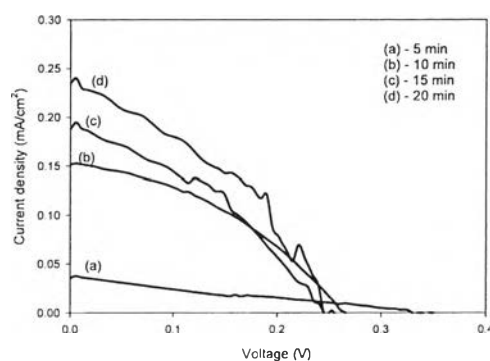


**Figure 5.8** The J-V characteristics of DSSC with fixed 15 voltage and varied time for deposition: 5 min (a), 10 min (b), 15 min (c) and 20 min (d).

**Table 5.3** The efficiencies of DSSC with fixed 15volatage and varied time for deposition

| Time (min) | Thickness (μm) | $J_{sc}$ (mA/cm²) | $V_{oc}$ (V) | ff | η ( %) |
|---|---|---|---|---|---|
| 5 | 4.1 | 0.03602 | 0.34 | 0.26 | 0.0031455 |
| 10 | 9.1 | 0.11406 | 0.265 | 0.389 | 0.0157029 |
| 15 | 13.1 | 0.18859 | 0.245 | 0.413 | 0.0190998 |
| 20 | 18.2 | 0.23552 | 0.245 | 0.390 | 0.0229393 |

Figure 5.8 and table 5.3 show the thickness of ZnO films increased with deposition time and $J_{sc}$. Consequently, Jsc results in the increased efficiency of DSSC due to the increment of amount of ZnO and dye loading. When the deposition time increased, the efficiency of DSSC increased because the ZnO particles had enough time to be deposited on electrode in the optimum position for forming a close-packed structure (Pore size of film decreased from 195.6 A° to 158.1 A°) (Besra *et al.,* 2007).

Furthermore, the increase in fill factor from 0.26 to 0.39 with the ZnO film thickness and deposition time increased. This result is attributed to the enhancement of interconnection between ZnO particles during electrophoretic deposition and subsequently, the decrease in resistance of the system. While the thickness of films increased, the $V_{oc}$ value decreased because the charge recombination easily occurred and the increase in distance of electron mobility (Saito *et al.*, 2008 and Yin *et al.*, 2010). In addition, the prolonged deposition time caused the agglomeration of ZnO in suspension (Jarernboon *et al.*, 2009 and Jun 2012) that indicated the pore size of the film increased (Pore size of film is 227.6 A°) and might result in the efficiency declined.

In next chapter, ZnO layer increases the electrode resistivity during electropolymerization of thiophene (Valaski *et al*, 2010). Hence, the optimum condition of EPD was set at 15V 5 min for polymerized thiophene because its thickness is thinner and less resistivity than other conditions.

## 5.5 Conclusions

ZnO nanoparticles could be deposited on conductive glass. The ZnO film thickness was controlled by changing applied voltage and deposition time. The efficiency of ZnO dye-sensitized solar cell prepared by the electrophoretic deposition method was investigated. It was observed that ZnO thickness increased with the voltage and deposition time. As a consequence, the short-circuit current and conversion efficiency of DSSC increased because of the increment of ZnO contents and dye loading. The increase in fill factor is attributed to the improvement of interconnection between ZnO particles during electrophoretic deposition and accordingly, the resistance of the system decreased. On the other hand, the open-circuit voltage declined due to the charge recombination possible occurred as the ZnO film thickness increased. Therefore, the conversion efficiency of ZnO-DSSC can be further improved by optimizing the ZnO film thickness on the photoanode.

## 5.6 Acknowledgements

## 5.7 References

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