Effect of Intermittent Spray Pyrolysis on the Characteristics of Fluorine-Doped Tin Oxide Conductive Glass for Dye Sensitized Solar Cell

Isdiriayani Nurdin[1], Pramujo Widiatmoko[1*], Hary Devianto[1], Anastasia Yuandy[1], and Rendy[1]

[1] Process Safety and Energetic Electrochemistry Laboratory, Department of Chemical Engineering,
Institut Teknologi Bandung
Jl. Ganesha No. 10 Bandung

*) Corresponding author: pramujo@che.itb.ac.id

Abstract

One of dye sensitized solar cell's (DSSC) component is conductive glass, a transparent glass substrate covered with semiconductor oxide, usually fluorine-doped tin oxide (FTO). An economic and scalable method used to deposit the FTO film is spray pyrolysis. A research conducted by Fukano et al. (2004) showed that introducing intermittence in spray pyrolysis using batch atomizer improves the glass' characteristics. This research aims to observe the effect of intermittence on spray pyrolysis method using nebulizer. A compressor nebulizer and hotplate were used, where the glass' surface temperature reached 300ºC. Transmittance, conductance, morphology and composition of the glasses produced were analyzed. Deposition time and intermittence were varied. Variation of time were 5; 7.5; 10; 16; and 39 minutes. Deposition time of 7.5 minutes showed the highest figure of merit (FOM) of 7.83×10^{-3} Ω^{-1}. Intermittence was performed by turning the nebulizer off during deposition, with varying period and amount of intermittence. Periods of intermittence were varied for 10, 20, and 30 seconds, and amounts of intermittence were varied 1, 2, and 3 times. Variation of 3 intermittences at 20 seconds each resulted in the highest FOM of 19.29×10^{-03} Ω^{-1}. DSSC's efficiency built using produced conductive glass are 1.9×10^{-4} % and 5.5×10^{-4} %.

Keywords: *fluorine-doped tin oxide; spray pyrolysis; intermittency in deposition; figure of merit; DSSC performance*

INTRODUCTION

The utilization of solar energy in Indonesia has a good prospect due to government's legislation support and geographical position that contributes to constant solar radiation throughout the year. Silicon-based solar cell is commonly used in Indonesia. However, cloudy conditions in Indonesia reduce the direct light intensity that reaches the cell and reduce its efficiency (Nann and Emery, 1991). Moreover, high mean temperature in Indonesia also reduces the performance of silicon-based solar cells (Dubey *et al.*, 2013). In hot and humid climate, as in Indonesia, the performance of solar cell with semiconductors with larger band gap is better (Peters *et al.*, 2018). This is

because a material with smaller band gap is more sensitive to increasing temperature.

A type of solar cell that utilizes large band-gap semiconductors is dye sensitized solar cell (DSSC). DSSC has many advantages, including its ability to convert diffused light into electric current, low energy consumption for its fabrication, environmentally friendly and a low operating temperature (Pujiarti, 2014). Along with the increasing usage of DSSC, the fabrication of its components, such as conductive glass, has also increased. The glass market for solar cell is projected to grow at an annual rate (CAGR) of 33.4% from 2017-2022 (Markets, 2017). Conductive glass is made of transparent conductive oxides (TCO), commonly tin-doped indium oxide (ITO) and fluorine-doped tin oxide (FTO). According to Sima et al. (2010), the use of FTO is more favorable for DSSC. To date, there is not any commercial conductive glass fabrication industry in Indonesia. Domestic demand of conductive glasses is still entirely met through imports. A scalable fabrication method, such as spray pyrolysis, needs to be developed for mass production.

A research conducted by Fukano *et al.* (2004) showed that characteristics of conductive glass produced by spray pyrolysis using a batch atomizer can be increased by introducing intermittence during deposition. Therefore, this study aims to produce FTO film and observe the effect of intermittence on spray pyrolysis method using nebulizer. In addition, the performance of the conductive glasses produced was tested to DSSC.

METHODOLOGY
Preparation

Fluorine-doped tin oxide (FTO) was made with a $SnCl_2$ solution containing 10%-wt NH_4F . High purity stannous chloride ($SnCl_2.2H_2O$– SmartLab, P.A.) was used as the source of tin atoms. The fluorine doping was achieved using ammonium fluoride (NH_4F– SmartLab P.A.). $SnCl_2.2H_2O$ (2 gr) was dissolved in 1 mL of concentrated hydrochloric acid (HCl – Merck P.A.). This mixture was heated for 10 minutes at 90^oC and then diluted by adding ethanol up to 5 mL. This served as the starting solution. For fluorine doping, 0.2 gram of NH_4F was dissolved in 5 mL demineralized water. This solution was added to the starting solution and magnetically stirred for 1 hour.

FTO Deposition

The fluorine-doped tin oxide thin films were prepared by spray pyrolysis using a compressor nebulizer (OMRON NE-C801). Prior to deposition, quartz glass slide (10 cm×10 cm×1 mm) was cleaned using demineralized water and ethanol. The glass surface's temperature was fixed at 300^oC. The apparatus set can be seen in Figure 1. Initial experiment was carried out by varying the deposition time until optimal. The optimal deposition time was then used as the basis for variations of intermittence. Variations of intermittence given were number of intermittence(s) (1, 2, and 3 times) and duration. Intermittence was given by stopping the compressor nebulizer during deposition.

FTO Characterization

Characteristics tested were transmittance, resistance, surface morphology, and elemental composition of the layer. Transmittance of the FTO was measured by using Ocean Optics Maya2000 Pro UV-VIS-NIR spectrometer. Resistance of the FTO was measured by four-point probe. Surface morphology was examined by using a scanning electron microscope (SEM) while the elemental composition of the layer was analysed using energy dispersive x-ray (EDX). The SEM and EDX device used was HITACHI SU-3500.

DSSC Preparation

Working electrode was made from anatase TiO_2 powder (5 gr) mixed with 5 mL solution made of 3 mL acetic acid and 12 mL demineralized water. Counter electrode was made from 8.4 g medical carbon black and 0.4 g PVDF mixed in 12 mL DMF. All electrodes were coated on FTO glass with an automatic doctor blade. Working electrode was sintered at 400^oC for 30 minutes, while the counter electrode at 100^oC for 5 minutes. Working electrode was immersed in Eosin Y dye for 24 hours. Electrolyte solution was prepared by adding an aqueous 0.5 M solution of potassium iodide into a 0.05 M solution of iodine (in acetonitrile). Both electrodes moistenedwith electrolyte were clamped together using paper clips. The DSSC series can be seen in Figure 2.
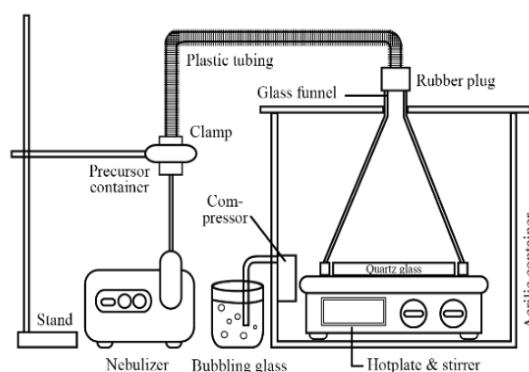

Figure 1. Set of apparatus used in producing conductive glass

Figure 2. DSSC built in this study

DSSC Characterization

Electrochemical impedance and I-V curve analysis of DSSC were carried out by using the potentiostat (Gamry Reference 3000). The light source used was a Phillips halogen lamp (150 watt). The halogen lamp was installed at a stand 20 cm above the DSSC.

RESULTS AND DISCUSSION

Effect of Deposition Time on Characteristics of Conductive Glass

Conductive glass on DSSC acts as a transmitter of the solar radiation, as well as a conductor of electric current produced by the cell. Therefore, main characteristics of conductive glass are transmittance and resistance. In this study, deposition time was varied at 5; 7.5; 10; 16; and 39 minutes.

Conductive glass used for DSSC is expected to have transmittance above 80% for visible light (Tsai and Tu, 2017). In this study, all transmittance measurement was done in comparison to air. Commercial quartz glass used has a measured transmittance of 94.27%. Effect of deposition time on transmittance can be seen in Figure 3. Lower transmittance was observed for longer deposition time due to an increase in the thickness of SnO_2 film produced. This phenomenon can be explained by Beer-Lambert law, which states that intensity of light passing through a solid will decrease exponentially with increasing thickness.

Resistance (R) describes the ability of an object to conduct electricity. Ideally, conductive glass has a very small value of resistance ($\sim 0\ \Omega$) (Supriyono *et al.*, 2015). Conductive glass produced at deposition time of 5 to 39 minutes is in the range of commercial conductive glass resistance (7 - 100 Ω / sq). The ability of an object to conduct electricity can also be expressed by conductance (R^{-1}). The relationship between resistance and conductance with deposition time is presented in Figure 4. Resistance decreases with increasing deposition time, which is also shown by an increase in conductance. Longer deposition time allows fewer voids between particles as the SnO_2 crystals enlarge and establishes good contacts between particles (Yuwono *et al.*, 2017). This phenomenon facilitates the
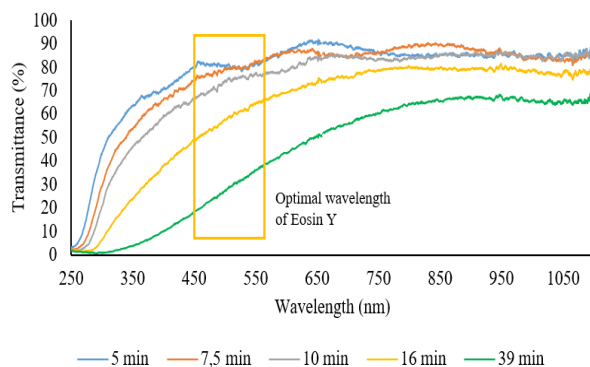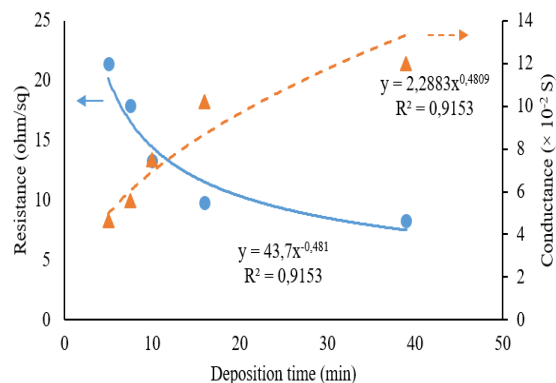

Figure 4. Resistance and conductance curve of the FTO film with variations of deposition time

transfer of electric current in the film layer and significantly reduces film resistance (Zhao *et al.*, 2008).

Figure of merit (FOM) is a parameter used to evaluate the efficiency of the FTO film on a conductive glass. This parameter takes into account both the electrical conductivity and optical properties possessed by the FTO film. FOM equation proposed by Haacke (1976) is defined by Equation 1.

$$\varphi = \frac{T^{10}}{R} \qquad (1)$$

R is sheet resistance (Ω/sq) and T is transmittance at the wavelength of 550 nm, which is the wavelength with highest intensity in the sunlight spectrum (Maurya *et al.*, 2017). The results of FOM calculations for each variation of deposition time can be seen in Figure 5. Therefore, it can be concluded that the 7.5 minutes deposition time gives the highest figure of merit. This deposition time was then used to determine the effect of intermittence on conductive glass' characteristics.

Effect of Intermittence on the Characteristics of Conductive Glass

In this experiment, the duration of intermittence does not significantly affect the characteristics of conductive glass produced. However, giving both

Figure 3. Transmittance curve of the FTO film with variations of deposition time
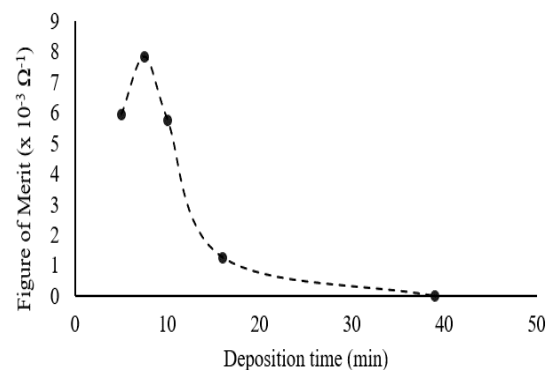

Figure 5. Figure of merit curve of the FTO film with variations of deposition time
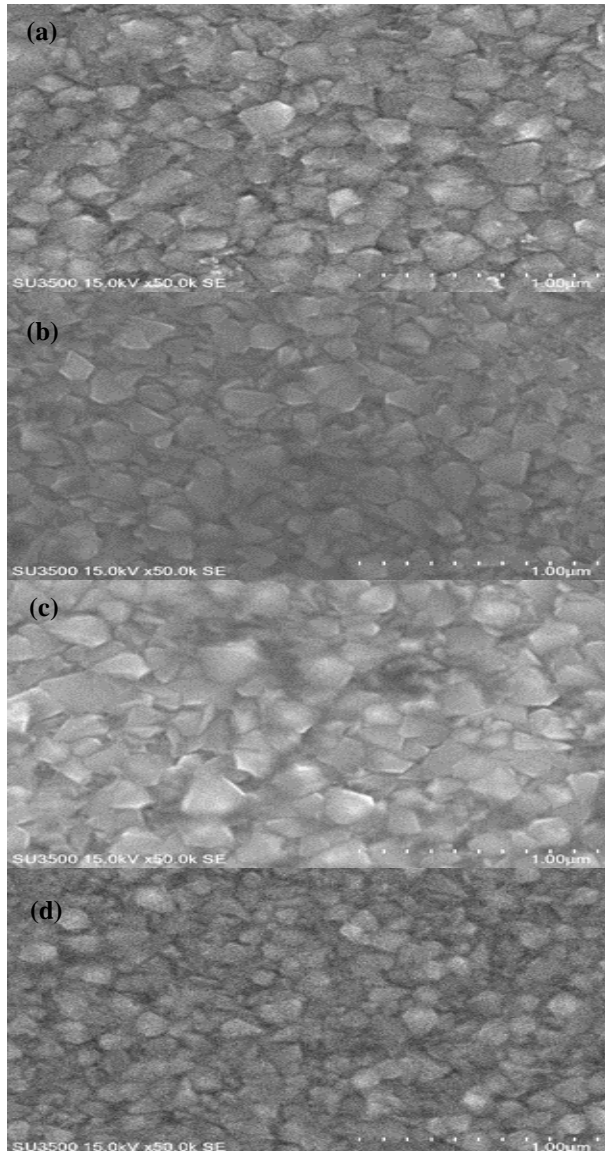
Figure 6. SEM images of FTO film prepared by spray pyrolysis: (a) without intermittence; (b) 1x20 seconds intermittence; (c) 2x20 seconds intermittence; (d) 3x20 seconds intermittence
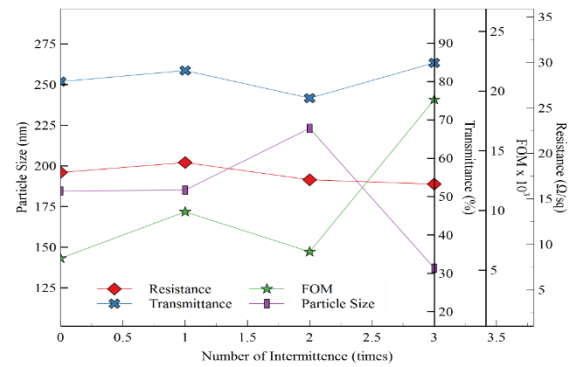

Figure 7. Effect of intermittence on the characteristics of conductive glass
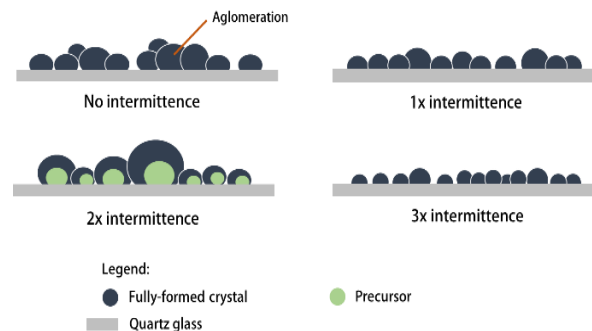

Figure 8. Illustration of hypothesis from a macro viewpoint with the variation of 0, 1, 2, and 3 intermittence(s)

single (1) and three (3) intermittence(s) increases the FOM value, while giving two (2) intermittences decreases the FOM value. Surface morphology of the FTO films were characterized using SEM. Figure 6 shows SEM images of FTO film prepared by spray pyrolysis without and with intermittence. From the figure, the variation of 3 intermittences at 20 seconds gives the smallest particle size compared to other. Effect of intermittence on the characteristics of conductive glass can be seen in Figure 7. A macro viewpoint hypothesis was proposed to explain this result. Illustrations of the hypothesis can be seen in Figure 8. In this study, the best conductive glass is produced in the variation of 3 intermittences at 20 seconds each (3×20) with FOM of 19.29×10^{-3} Ω^{-1}. The lowest FOM value (4.52×10^{-3} Ω^{-1}) is produced in a variation of 2 intermittences at 30 seconds each (2×30).

The hypothesis from a macro viewpoint was based on a study by Mahajan and Takwale (2007) which concluded that intermittence given during deposition may cause particle size to decrease while improving the structure of particles. This structural improvement are a result of better crystallinity and lower defect density due to a more stable glass' surface temperature during deposition time (Elidrissi et al., 2000). Moreover, intermittence may also cause thinner film (Mahajan and Takwale, 2007). A single intermittence causes higher conductive glass' transmittance and resistance when compared to continuous deposition. It is assumed that the intermittence given diminishes agglomeration which results in a more compact particle structure and better light transmittance (Mahajan and Takwale, 2007). The increase in resistance is caused by thinner film produced.

On the other hand, two intermittences given result in lower transmittance and resistance when compared to continuous deposition. It is assumed that excess undecomposed precursor may still present, thereby causing larger crystal size due to agglomeration as the deposition was resumed. As a result, both transmittance and resistance decrease as the film thickens. When three intermittences are given, the conductive glasses produced were higher in transmittance but lower in resistance. No excess undecomposed precursor remained and resulted in smaller crystals formed.

Table 1. Elemental composition and EDX spectrum of produced conductive glass without intermittence
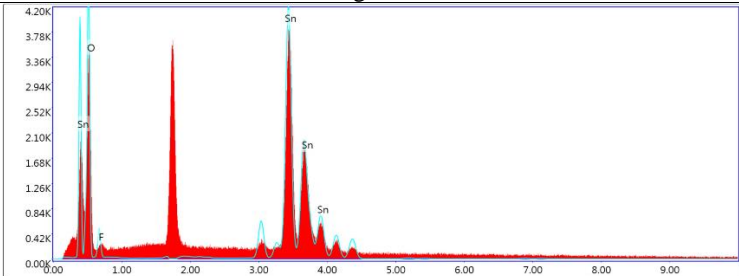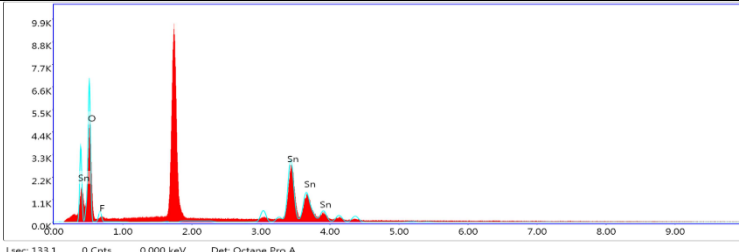
Figure	Element	%-atom
	O K	31
	F K	3
	Sn L	66
	F/Sn ratio	0.046

Table 2. Elemental composition and EDX spectrum of produced conductive glass with 3x20 intermittence

Figure	Element	%-atom
	O K	46
	F K	3
	Sn L	51
	F/Sn ratio	0.059

EDX mapping done on the glasses showed that fluorine has been successfully doped into the SnO_2 crystals. EDX spectrum and composition of FTO film produced is presented on Table 1 and Table 2. Ratios of F/Sn on the film produced, both with and without intermittence, are lower than the precursor. The same phenomenon also observed by Supriyono *et al.* (2015). Intermittence variation of 3 times @ 20 seconds (3×20) causes a higher F/Sn ratio than continuous deposition. This increase may result in increasing transmittance as it decreases internal defect, such as oxygen vacancy (Muruganantham *et al.*, 2011).

Validity of the production method used in this study was tested by replicating four times the variation of 3×20. Resistance and transmittance of the four replications are presented chronologically on Table 3. The first data is inconsistent when compared to rest of the data obtained as the deposition apparatus was still fully occupied by air when starting the first replication. Therefore, it is suggested to allow the precursor to be nebulized first into the apparatus before initiating the first deposition.

Table 3. Resistance and transmittance of conductive glasses (four replications at 3×20 variation)

Run	Resistance (Ω/sq)	Transmittance (%)
1	21.61	83.68
2	15.68	75.99
3	16.63	81.41
4	16.63	81.33
Average	17.63	80.60
St. Dev.	2.69	3.26
CI (α = 5%)	13.35-21.91	75.41-85.79

DSSC Characterization

EIS analysis can be used to study interactions taking place inside a DSSC, such as charge transfer, internal resistance, capacitance, and ion diffusion. The plot obtained can then be fitted into an equivalent circuit to get quantitative parameters that describe the charge transfer, transport, and accumulation in a system (Sarker *et al.*, 2014). The Nyquist plot for two DSSCs built using the conductive glass of 3×20 variation (Cell A and Cell B) and a DSSC built using commercial conductive glass are presented on Figure 9.

Three semicircles should be identified on Nyquist plot of an active DSSC (Longo and De Paoli, 2003). The first semicircle occurs on higher frequency which represents the charge transfer on the interface of carbon counter electrode/electrolyte and FTO/electrolyte. Electron transfer resistance on the carbon counter electrode is linked to the redox reaction involving I^- and I_3^-. The second semicircle, on the mid frequency, represents the electron diffusion and the recombination of electron with oxidized species on the interface of TiO_2 working electrode/electrolyte (Sarker *et al.*, 2014). The third semicircle, on the lower frequency, is related to the diffusion of I_3^- ions in the electrolyte (Sarker *et al.*, 2014).

Table 4. Parameters of the equivalent circuit used

Cell	R_{TCO} (Ω)	$R_{TCO/TiO2}$ (Ω)	$R_{TCO/Electrolyte}$ (Ω)	$R_{TCO/Carbon}$ (Ω)
Replication 1 (Cell A)	20.88	28.88	66.17	1088.0
Replication 2 (Cell B)	28.45	56.74	983.00	208.90
Commercial	29.73	1627.00	568.00	134.00

Table 5. Parameters used in calculating DSSC's efficiency

	V_{oc} (mV)	I_{sc} (µA)	P_m (µW)	V_m (mV)	I_m (µA)	FF	η (10^{-4} %)
Replication 1 (Cell A)	31.6	20.1	0.163	15.843	10.3	0.256	1.9
Replication 2 (Cell B)	45.9	41	0.472	23.741	19.9	0.251	5.5
Commercial	38.6	160	1.848	16.200	82	0.27	84

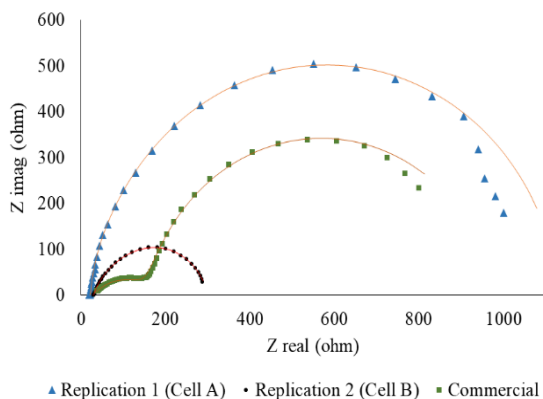Figure 9. Nyquist plot of DSSC using produced and commercial conductive glass

Figure 10. I-V curve of DSSC using produced and commercial conductive glass

The frequencies used in the analysis were 0.1-35000 Hz to focus on the FTO performance, which is located at higher frequency. Thus only two semicircles can be identified in the Nyquist plot. Several factors affecting the efficiency of DSSC are recombination on the interface of FTO/electrolyte and internal cell resistance (Liberatore *et al.*, 2009). These factors are quantified by the value of R_{TCO} (TCO resistance), $R_{TCO/TiO2}$ (TCO/TiO$_2$ contact resistance), $R_{TCO/Electrolyte}$ (charge transfer resistance on the interface of TCO/electrolyte), and $R_{TCO/Carbon}$ (charge transfer resistance on the interface of TCO/carbon). These values are presented on Table 4.

High performance of conductive glass used in DSSC is shown by low internal resistance (R_{TCO}; $R_{TCO/TiO2}$; and $R_{TCO/Carbon}$) and high $R_{TCO/Electrolyte}$. High value of $R_{TCO/Electrolyte}$ shows lower recombination in the interface of TCO/electrolyte (Basu *et al.*, 2016). The internal resistance of TCO and contact resistance of TCO/TiO$_2$ are lower in the DSSC which use produced conductive glass in comparison to the commercial conductive glass. However, the recombination in the interface of FTO/electrolyte is higher on the DSSC using the produced conductive glass. This is due to cracks present on the working electrode which allow direct transfer of electrons from FTO to electrolyte.

Efficiency can be used to evaluate a DSSC's performance. DSSC's efficiency can be determined by comparing the output power to the light intensity (I_o) given to the DSSC. The I-V curve, as shown on the Figure 10, gives the parameters used in calculating efficiency. The parameters are shown on Table 5.

Efficiency of DSSC using the conductive glass produced (Cell A and Cell B) are lower than DSSC using commercial conductive glass. It is assumed that the lower efficiency is caused by significant amount of recombination taking place in Cell A and Cell B. This is in line with the findings from the EIS analysis.
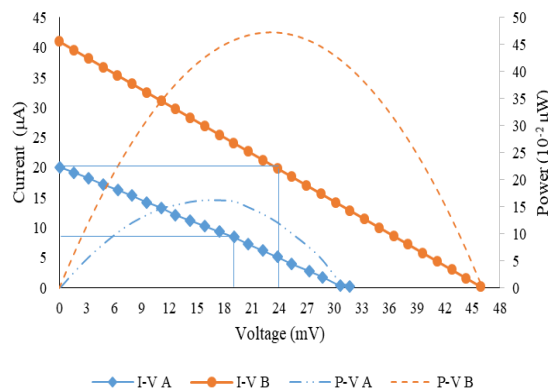
CONCLUSIONS

TCO produced through spray pyrolysis method with deposition time of 7.5 minutes continuously possesses a figure of merit of 7.85×10^{-3} Ω^{-1}. TCO produced with the same method with various intermittence(s) possess figure of merits within the range of $4.52–19.29 \times 10^{-3}$ Ω^{-1}. Introducing single and three intermittence(s) during deposition resulted in better conductive glass when compared to continuous deposition. In this study, it is concluded that varying duration of intermittence did not result in significant difference. DSSC's efficiency built with produced conductive glass are 1.9×10^{-4} % and 5.5×10^{-4} %.

ACKNOWLEDGEMENT

NOTATION

FF	: fill factor [-]
I	: current [A]
P	: power [W]
R	: resistance [Ω]
T	: transmittance [%]
V	: cell potential [V]
η	: cell efficiency [%]

Subscripts

oc	: open circuit
m	: maximum
sc	: short circuit

REFERENCES

Basu, K.; Benetti, D.; Zhao, H.; Jin, L.; Vetrone, F.; Vomiero, A.; Rosei, F., "Enhanced photovoltaic properties in dye sensitized solar cells by surface treatment of SnO2 photoanodes", Scientific Reports **6** (2016), 233

Dubey, S.; Sarvaiya, J. N.; Seshadri, B., "Temperature Dependent Photovoltaic (PV) Efficiency and Its Effect on PV Production in the World – A Review", Energy Procedia **33** (2013), 311-321.

Elidrissi, B.; Addou, M.; Regragui, M.; Monty, C.; Bougrine, A.; Kachouane, A., "Structural and optical properties of CeO2 thin films prepared by spray pyrolysis", Thin Solid Films **379** (2000), 23-27.

Fukano, T., "Low-temperature growth of highly crystallized transparent conductive fluorine-doped tin oxide films by intermittent spray pyrolysis deposition", Solar Energy Materials and Solar Cells (2004).

Haacke, G., "New figure of merit for transparent conductors", Journal of Applied Physics **47** (1976), 4086.

Liberatore, M.; Decker, F.; Burtone, L.; Zardetto, V.; Brown, T.; Reale, A.; Di Carlo, A., "Using EIS for diagnosis of dye-sensitized solar cells performance", (2009).

Longo, C.; De Paoli, M.-A., "Dye-sensitized solar cells: a successful combination of materials", Journal of the Brazilian Chemical Society **14** (2003), 898-901.

Markets, M. Solar photovoltaic glass market by application (utility, residential, and non-residential), Type (AR coated, tempered, TCO, and others), end user (crystalline silicon PV modules and thin film PV modules), region - global forecast to 2022 (2017).

Maurya; Liu, Y.; Xu, X.; Woods-Robinson, R.; Das, C., "High figure-of-merit p-type transparent conductor, Cu alloyed ZnS via radio frequency magnetron sputtering", Journal of Physics D: Applied Physics **50** (2017).

Mahajan, C. M.; Takwale, M. G. "Effect of intermittent spray on optoelectronic properties of ZnO nanocrystallites synthesized by chemical spray pyrolysis", Institute of Electrical and Electronics Engineers, (2007).

Muruganantham, G.; Ravichandran, K.; Saravanakumar, K.; A.T, R.; Sakthivel, B., "Effect of solvent volume on the physical properties of undoped and fluorine doped tin oxide films deposited using a low-cost spray technique", (2011).

Nann, S.; Emery, K., "Spectral effects on PV-device rating", Solar Energy Materials and Solar Cells **27** (1991), 189-216.

Peters, I. M.; Liu, H.; Reindl, T.; Buonassisi, T., "Global Prediction of Photovoltaic Field Performance Differences Using Open-Source Satellite Data", Joule **2** (2018), 307-322.

Pujiarti, H., "Study of characteristic photovoltaic and impedance dye sensitized solar cell (DSSC) with gel electrolyte", Disertasi Doktor, Bandung Institute of Technology, (2014).

Sarker, S.; Ahammad, A. J. S.; Seo, H. W.; Kim, D. M., "Electrochemical impedance spectra of DSSC: Fundamentals and spreadsheet calculation", International Journal of Photoenergy (2014), 1-17.

Sima, C.; Grigoriu, C.; Antohe, S., "Comparison of the dye-sensitized solar cells performances based on transparent conductive ITO and FTO", Thin Solid Films **519** (2010), 595-597.

Supriyono; Surahman, H.; Krisnandi, Y. K.; Gunlazuardi, J., "Preparation and characterization of transparent conductive sno2-f thin film deposited by spray pyrolysis: Relationship between loading level and some physical properties", Procedia Environmental Sciences **28** (2015), 242-251.

Tsai, J.-K.; Tu, Y.-S., "Fabrication of Polymeric Antireflection Film Manufactured by Anodic Aluminum Oxide Template on Dye-Sensitized Solar Cells", Materials (Basel, Switzerland) **10** (2017), 296.

Yuwono, A. H.; Arini, T.; Lalasari, L. H.; Sofyan, N.; Ramahdita, G.; Nararya, A.; Firdiyono, F.; Andriyah, L.; Subhan, A., "The effect of various precursors and solvents on the characteristics of FTO conducting glass fabricated by ultrasonic spray pyrolysis", International Journal of Technology **7** (2017), 1336-1344.

Zhao, H.; Liu, Q.; Cai, Y.; Zhang, F., "Effects of water on the structure and properties of F-doped SnO 2 films", (2008)