# *Application of Large Area $TiO_2$ Photoelectrode on Dye-Sensitized Solar Cells*

# Aplikasi Fotoelektroda $TiO_2$ Area Lebar pada Sel Surya *Dye-sensitized*

**Natalita M. Nursam [*], Lia Muliani, and Jojo Hidayat**

*Pusat Penelitian Elektronika dan Telekomunikasi, Lembaga Ilmu Pengetahuan Indonesia*
*Komplek LIPI Gedung 20 Lantai 4, Jl Sangkuriang, Bandung 40135, Indonesia*

***Abstract***

*The scale-up of dye-sensitized solar cell (DSSC) has been a big issue as the DSSC technology process progresses from laboratory scale to large area applications. Meanwhile, this type of solar cell has been of great interest among PV scientist and academics as it can be produced in lower-cost processes compared to the conventional solar cells which are mostly fabricated from silicon. The fabrication of DSSC prototypes with a relatively large active area of 9x9 $cm^2$ are demonstrated in this paper. Large area of $TiO_2$ surface has been shown to significantly increase the $I_{SC}$, as well as $V_{OC}$ and $P_{max}$. Nevertheless, deterioration of fill factor (FF) was observed as the result of the increase on series resistance with respect to the increase in the photoelectrode area.*

***Keywords:*** *DSSC, $TiO_2$, photo-electrode, efficiency.*

**Abstrak**

Peningkatan luas area pada pembuatan sel surya berbasis *dye-sensitized* (DSSC) merupakan salah satu kendala utama yang dihadapi pada saat ekspansi dari skala laboratorium menuju aplikasi dalam skala besar. Di lain sisi, pada saat ini jenis sel surya ini sedang menjadi tren penelitian di kalangan peneliti maupun akademisi dikarenakan rendahnya biaya proses fabrikasi yang dibutuhkan dibandingkan sel surya pendahulunya yang terbuat dari silikon. Tulisan ini membahas pembuatan prototipe sel surya DSSC dengan luas area aktif berukuran relatif besar yaitu 9x9 $cm^2$. Peningkatan luas area permukaan $TiO_2$ secara signifikan berakibat pada kenaikan nilai $I_{SC}$, $V_{OC}$, dan $P_{max}$. Sebaliknya, penurunan nilai *fill factor* dapat diamati sebagai hasil dari naiknya tahanan seri seiring dengan bertambahnya luas area fotoelektroda.

**Kata kunci*:*** *DSSC,* $TiO_2$, fotoelektroda, efisiensi.

## I. INTRODUCTION

Dye-sensitized solar cell (DSSC) is expected to be a promising candidate as the latest low-cost photovoltaic (PV) technology. The working principle of a DSSC employs the basic mechanism of photoelectron-chemistry, which is similar to that of the photosynthesis process within the plant's leaves. The DSSC technology has been developed very quickly since the work on this device was firstly reported by Gratzel and his co-workers in 1991 [1]. DSSC offers several benefits compared to the conventional silicon based solar cell such as: attractive colorful appearances, transparency, cheaper, and relatively easier to fabricate.

One of the DSSC applications that has recently been of great interest is to be incorporated as a green and sustainable yet attractive power source on the façade of building integrated photovoltaics (BIPV). BIPV system normally uses solar cells as outer walls or glass windows on the buildings, as recently studied by Yoon et.al. [2]. Figure 1 shows an example of DSSC implementation on BIPV system [3]. For such application, DSSC needs to be fabricated on a wide area of glass substrates, which therefore require further analysis upon the scale-up effect. The best efficiency of DSSC to date–that is around 11%–was reported by Graetzel [4] and Chiba et.al. [5]. However, both were fabricated on a lab-scale with a total active area less than 25 $cm^2$.

Figure 1. BIPV System Featuring 6 kV of DSSC Panels at the Atrium of CSIRO Energy Technology, Newcastle, NSW, Australia [3].

* Corresponding Author.
Email: nata002@lipi.go.id
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A wide area DSSC is generally fabricated in form of Z/W/Monolithic interconnected module [6] - [8]. However, such interconnection would reduce the active area by increasing the inactive parts. Therefore, we aim to fabricate a single large area of DSSC without the necessity to use additional interconnections. This paper will cover two main objectives. The first is to demonstrate the fabrication of a DSSC using screen printing technique on a 10x10 $cm^2$ glass substrate with a total active area of 9x9 $cm^2$ that was manufactured from nanocrytalline $TiO_2$ active layer. The second goal is to study the effect of such fabrication upon the electrical parameters of the cell which subsequently can be used to analyze the influencing factors in making large surface area of DSSC.

## II. OPERATIONAL PRINCIPLE OF DYE-SENSITIZED SOLAR CELL

The physical structure of a standard DSSC consists of two sandwiched glass layered with transparent conducting oxide (TCO). One electrode features a porous titanium dioxide ($TiO_2$) layer stained with dye molecules–named as photo-electrode, while the other is the counter-electrode in which platinum (or other catalysts) is deposited upon it. Electrolyte layer of redox species ($I^-$ and $I_3^-$) exists between the two electrodes after they are being sandwiched together. The general structure of a DSSC is illustrated in Figure 2.

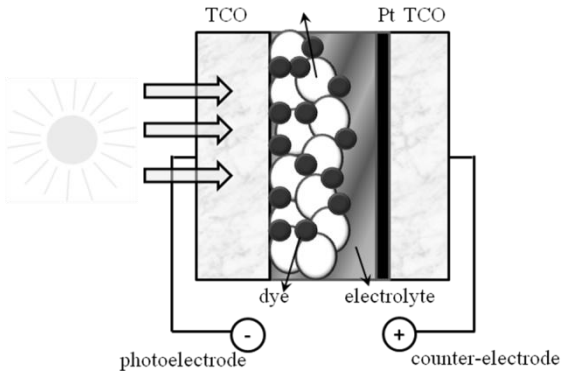


Figure 2. Basic Structure of Typical DSSC.

The working principle of a DSSC is based on the kinetics of the electron transfer reactions. The photoelectrochemistry mechanisms which occur during electron transfer within the DSSC are as follows: a dye molecule is excited upon photon ($h\upsilon$) absorption whereas electron is excited from highest occupied molecular orbital (HOMO – $D$) into lowest unoccupied molecular orbital (LUMO – $D^*$) as shown by Equation (1).

$$D + h\upsilon \rightarrow D^* \quad (1)$$

The free electron is subsequently injected into the conduction band of $TiO_2$ and transparent conducting oxide (TCO) towards the external circuit and left the oxidized dye molecul $D^+$ (Eq. (2)). Electron reach the catalyst layer (Pt or C) and then recombine with holes within the electrolyte, in form of tri iodide ($I_3^-$), to produce iodide ions ($I$) through redox reactions. This reaction was shown by Eq. (3). The negative charge of $I^-$ diffuses back into the dye and reacts with the oxidized molecule $D^+$ and a full electrical cycle is therefore completed (see Equation (4)). Further description with regard to the above mechanism can be found in Figure 3 (b). The overall reaction is actually similar to the photosynthesis process which occurs in plants as shown in Figure 3 (a).

$$D^* \rightarrow D^+ + e^- \quad (2)$$

$$I_3^- + 2e^- \rightarrow 3I^- \quad (3)$$

$$3I^- + 2D^+ \rightarrow I_3^- + 2D \quad (4)$$

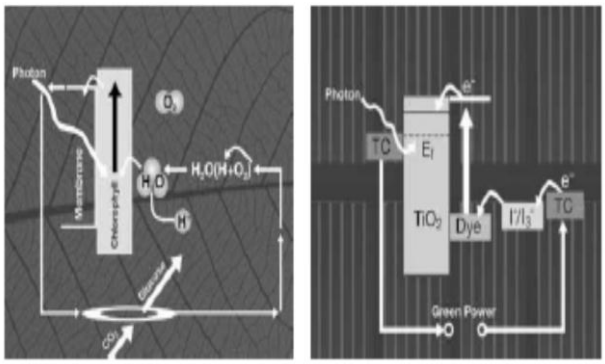


Figure 3.Mechanism Following Photon Absorption which Occurs on (a) Plants, (b) Dye-Sensitized Solar Cells [9].

## III. EXPERIMENTAL

### A. Materials Preparation

The glass substrates used for the counter-electrode were soda-lime glasses which is commercially available. Meanwhile, the FTO glass used for the photo-electrode was purchased from Dyesol, Australia with a conductivity of 15 Ω/□. Some of the other materials were also supplied by Dyesol, such as $TiO_2$ transparent paste (18NR-T), sensitizing dye B2(N719), electrolyte EL-HSE, Surlyn, and hermetic sealing compound. In addition to these materials, we also used Pt target and some chemical reagents which were also commercially available.

### B. Fabrication of Photo-electrode

$TiO_2$ deposition was performed using screen-printing technique which is relatively easy, low-cost, and industrially feasible. The screen used to deposit the $TiO_2$ layer was a Nylon #325 mesh and the printing was performed on an area of 9x9 $cm^2$ (see Figure 4). The $TiO_2$ pastes used in this experiment was Dyesol 18NR-T with a transparent sintered layer. The printing process was performed twice, whereas each step was ended with a drying on an oven at a temperature of 175 $^oC$ for 10 minutes. At the end of the process, all samples were sintered on a conveyor-belt furnace for 15 minutes. All samples were subsequently immersed on a solution consisting ruthenium dye Z907 and ethanol with a concentration of 20 mg/100 ml. The dyeing process lasted for 24 hours on a dark place and, in the end of the process; all samples were rinsed on ethanol to remove the dye residues or any existing water vapor.

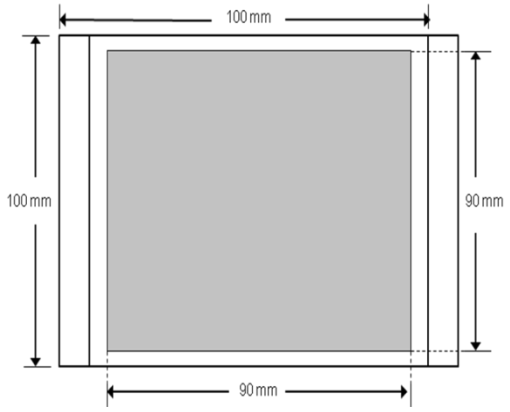


Figure 4. Schematic Diagram of the Fabricated DSSC.

### C. Fabrication of Counter-electrode

The catalyst material used as the counter-electrode for our samples is platinum (Pt). The reason for choosing sputtered-Pt as the catalyst has been explained in our previous work [10]. Deposition process for the counter-electrode, was performed using DC-sputtering process with an initial pressure of $6.6x10^{-3}$ Pa, argon gas pressure of $5.3x10^{-1}$ Pa, rotation speed 5 rpm and power 5 W, for 20 minutes. As comparison, we also fabricate another sample using transparent Pt which was deposited using Dyesol Pt paste (PT1). This printed electrode was subsequently sintered at 450 $^{o}$C for approximately 15 minutes.

### D. Cell Assembly

Both photo-electrode and counter-electrode were assembled into a sandwich structure using thermoplastic sealant (Surlyn) with a thickness of 50 µm as the spacer, being attached on the $TiO_2$'s surroundings. All samples were subsequently heated on a temperature of 120 $^{o}$C to strengthen the attachment process. Finally, Dyesol liquid electrolyte EL-HSE was injected into the assembled samples and the remaining air holes were subsequently sealed using hermetic sealing compounds.

### E. Current-Voltage Characterization

Solar cell characterization is generally performed based on current-voltage (I-V) measurements using one-diode model [11]. In our research, the I-V characterizations were done by measuring voltage when the DSSC was illuminated and connected to potentiometer with certain resistances. Other parameters that also essentials in characterizing solar cells are open-circuit voltage ($V_{oc}$), short-circuit voltage ($I_{sc}$), and efficiency. The latter can be calculated using following expression:

$$\%\eta = \frac{V_{OC} I_{SC} FF}{P_{in}} x100\% \quad (5)$$

Where $P_{in}$ is the amount of lower received by the cell (measured using pyranometer) and $FF$ is the fill factor which represents the quality of any solar cell's characteristics and is determined by following expression.

$$FF = \frac{P_{\max}}{V_{OC} I_{SC}} \quad (6)$$

The correlation between $P$, $V_{oc}$, and $I_{sc}$ is describedby the I-V curve of an ideal solar cell shown in Figure 5. Meanwhile, the electrical circuit configuration that was used to measure the I-V data is depicted in Figure 6.

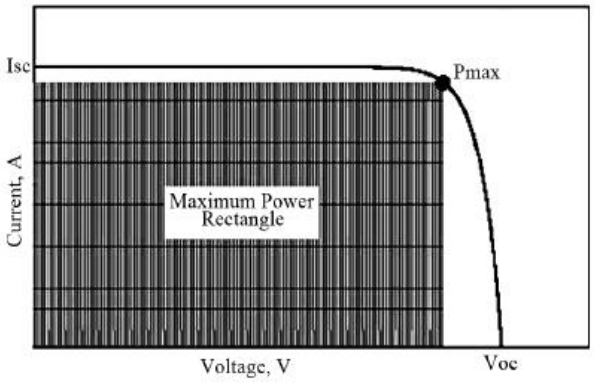


Figure 5. The I-V Characteristics of an Ideal Solar Cell [12].

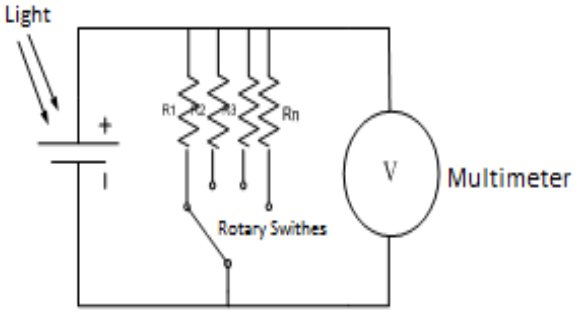


Figure 6. Electrical Circuit Diagram for I-V Characterization [13].

## IV. Results and Discussion

Figure 7 shows the photograph of our finished cell prototype featuring Pt from sputtering process, with a total size of 10x10 $cm^2$ and an active area of 81 $cm^2$.

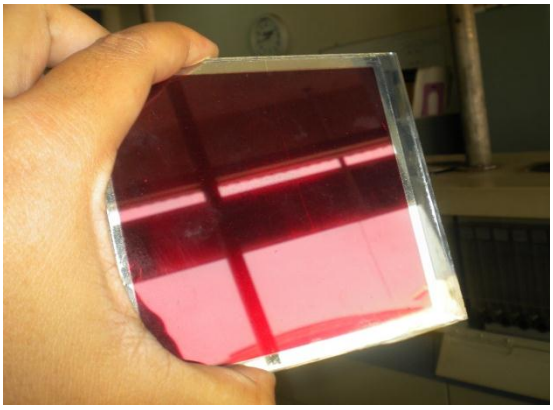

Figure 7. DSSC Prototype Having Total $TiO_2$ Active Area of 9x9 $cm^2$.

Figure 8 shows the I-V curve measured from two samples with different counter-electrodes, i.e. sputtered Pt and transparent-printed Pt, while the rest of the process conditions and parameters were maintained the same. These samples were measured under direct sun illumination with an insensity of 60mW/$cm^2$ (0.6 sun). It can be seen that the application of Pt sputtering was able to enhance both the efficiency and the maximum output power almost a factor of two higher compared to that of the sample featuring printed Pt. One of the possible causes of this phenomenon is suspected due to the

charge transfer resistance at Pt/electrolyte interface (RCT) [14]. The thickness of Pt layer which was deposited using sputtering technique is far less thick compared to that of the printing process, which therefore would reduce the RCT and improve the charge transfer activities. Nevertheless, this does not conclusively indicate that screen-printed Pt would always give less qualified catalyst compared to sputtering. Further optimization through printing technique and/or sintering conditions is therefore necessary.

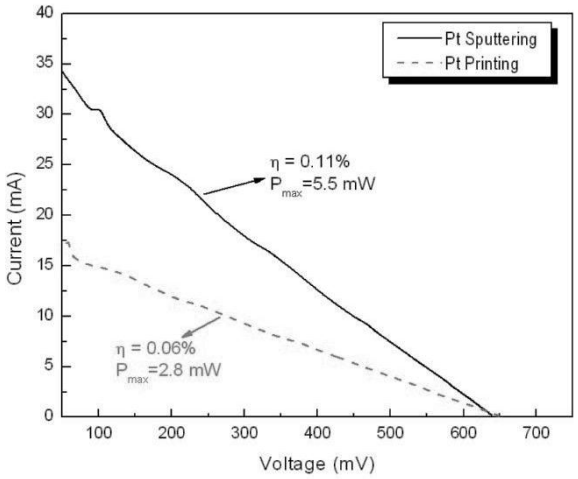


Figure 8. I-V Curve of 9x9 $cm^2$ DSSC Measured at 0.6 Sun With Different Catalyst Materials.

In order to analyze the scaling up effect of the active area, we measured and compared the I-V curve of two samples with an active area of 9x9 $cm^2$ and 1x6 $cm^2$ which were prepared under similar conditions. The measurements were performed using monochromatic light with an intensity of 6 $mW/cm^2$. The measurement graphs can be found in Figure 9. It can be briefly concluded that the scaling up has caused significant increase on $I_{SC}$ but not much profound increase was observed on $V_{OC}$. Table 1 shows the detailed data from this measurement.

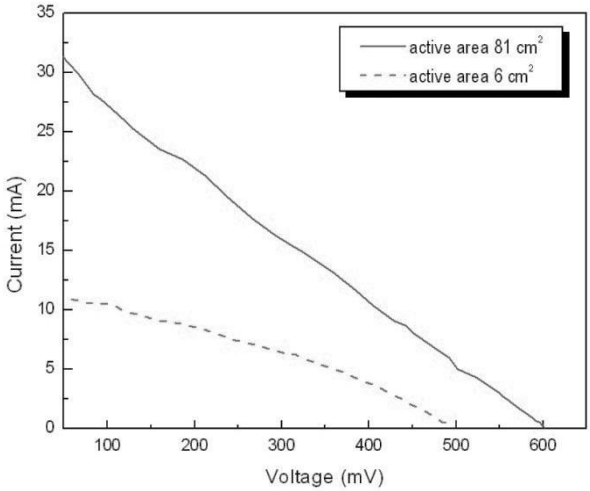


Figure 9. I-V Curve of DSSC With 9x9 $cm^2$ (solid) and 1x6 $cm^2$ (dash) Active Area Under 6 $mW/cm^2$Illumination.

It can be seen in Table 1 that the scaling up of active area around a factor of 13 has caused the overall photo-conversion efficiency to degrade by more than a factor of 4. Other than the efficiency, the main electrical parameters of the sample with 81 $cm^2$ active area is higher compared to those of the sample with narrower area, especially the current. This can be explained by the increase of dye molecule attachment; hence, the photon absorption area is increased as well. One of the most profound causes for the decreasing efficiency is due to the deterioration of fill factor (*FF*). We attribute the low *FF* to series resistance losses in TCO glass substrate ($R_{TCO}$) since the larger sample was made on larger substrate. Series resistance in DSSC is composed of three components, i.e. $R_{CT}$, $R_{TCO}$, and diffusion resistance of $I_3^-$ ions in electrolyte [15]. In this case, the second factor is suspected to dominate the cause of *FF* degradation. In order to prevent such occurrence, it is plausible to employ the $TiO_2$ active area in stripes design. However, the aperture ratio for designing stripe pattern would be the main challenge. From our results, we also conclude that our 81 $cm^2$ active area sample basically offers better effectiveness in the area utilization, as is shown in Table 1 by its higher aperture ratio. Aperture ratio is the ratio between active and inactive area.

TABEL I
I-V PARAMETERS OF DSSC UNDER 6 MW/CM$^2$ ILLUMINATION CONDITION

| Active Area ($cm^2$) | Aperture ratio | $V_{oc}$(mV) | $I_{sc}$ (mA) | $P_{max}$ (mW) | *FF* (%) | $\eta$ (%) |
|---|---|---|---|---|---|---|
| 81 | 8 : 2 | 619 | 28.6 | 4.83 | 27.29 | 1.19 |
| 6 | 6 : 8 | 520 | 10.6 | 1.97 | 35.75 | 5.47 |

## CONCLUSIONS

In this paper, we have demonstrated the use of screen printing method to fabricate a large size DSSC on a 100 $cm^2$ TCO substrate. The use of sputtering technique to deposit the Pt catalyst layer has shown a considerable increase in the photoconversion efficiency. The fabrication of large active area has shown improvements in some of the electrical parameters, however, the opposite effect was observed on the fill factor. The reason for this is suspected due to the increase of TCO resistance with respect to the increase in the $TiO_2$ surface area.

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