

The Effect of Chlorophyll Concentration from Papaya Leaves on the Performance of Dye-Sensitized Solar Cell

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ABSTRACT

Dye-Sensitized Solar Cell (DSSC) is the third generation solar cell that has sandwich structure consisted of organic dye material and other components such as titanium dioxide (TiO₂) semiconductor, electrolyte, and substrates (counter electrode and working electrode). The dye in the device was made from green plant chlorophyll such as papaya. This research aimed to find the influence of dye concentration from papaya leaves chlorophyll on the performance of DSSC. The discussion covered the output power (P_{out}), Fill Factor (FF), and efficiency (η). The method in this research was explorative experimental with independent variables such as direct and indirect sunlight. The dependent variables were output power (P_{out}), Fill Factor (FF), and efficiency (η) from the DSSC. The procedures in this research consisted of substrates preparation, TiO₂ paste production, dye solution preparation, electrolyte preparation, counter electrode preparation, and DSSC assembly. The tests on chlorophyll concentration were conducted using spectrophotometry method while the DSSC performance test used 1,000 W/cm² halogen lamp. The results showed that 100% chlorophyll concentration resulted in 3.1295 mg/m³ chlorophyll content type a. The best DSSC performance was obtained by the DSSC sample that had 100% chlorophyll concentration and 1.1294 mg/m³ chlorophyll content. The direct light of DSSC achieved P_{out} of 0.9557 mW, FF of 0.07282, and efficiency of 1.499137%. The DSSC with indirect light obtained P_{out} of 0.00455 mW, FF of 0.01535, and efficiency of 0.049863%.

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I. Introduction

Electricity is the main factor in supporting national development. This situation caused the electricity requirement to increase around 3% per year, from 85 TWh (2014) to predictably 235 TWh (2050) [1]. Thus, the fuel availability in the world would gradually diminish; therefore, the efforts in developing alternative electrical energy, including renewable energy, are continuously performed.

The last two decades saw the Dye-sensitized Solar Cell (DSSC) that could replace silicon solar cell as the energy converter. DSSC is a solar cell that is sensitive to photo electrochemical dyes through the transfer of electric charges. The advantages of DSSC, among others, are low production cost, a wide range of material, environmentally friendly, and has high efficiency [2]. Changing the anode photo using titanium dioxide (TiO₂) could improve the DSSC efficiency [3], other than using synthesis or organic dye.

The dye also affects efficiency; for example, the use of ruthenium reaches 13% efficiency [4]. Although ruthenium dye achieved high efficiency, it is hard to synthesis and



has a high cost that is casting doubt in applying the dye in large-scale DSSC. Dye that is made from plant parts such as leaves, seed, and fruit, can be used as the alternative sensitized in the DSSC because they are environmentally friendly and abundant in nature. The contents of chlorophyll, beta-carotene, anthocyanin, and others in a plant can be used for sensitizer [5]. The dye is an organic compound with double conjugated bonds that generates electron transfer. In the DSSC structure, dye acts as the sunlight absorber to incite electrons excitation [6].

Papaya leaves are a source of chlorophyll-producing plants. The chlorophyll content in papaya leaves is quite high [7]. Chlorophyll contains electrons that excite when absorbing sunlight. Electrons in the dye are excited when the chlorophyll dye absorbs the photon light. Then, the electrons will be transferred to the TiO_2 photoelectrode layer and passed on to the outer circuit of DSSC because the presence of a counter electrode carbon catalyst causes electrons to travel to electrolytes which convert photon energy into electricity [8].

An organic dye influenced DSSC performance. The different concentration of organic dye also affected DSSC performance [9]. Besides, the DSSC performance is also influenced by the given light intensity. Therefore, this research aimed to find the influence of various dye concentrations that were made from papaya leaves on the DSSC performance in various light intensity.

II. Material and Methods

Research Design

This research used explorative experimental design research. It is a method that identifies the base properties of the researched material before testing. The materials were papaya leaves, fluorine-doped tin oxide substrate, titanium dioxide, acetone, distilled water, polyvinyl alcohol (PVA), potassium iodide (KI), iodide (I_2), and polyethene glycol (PEG) 400.

The dependent variables of this research were output power (P_{out}), Fill Factor (FF), and the DSSC efficiency (η) whereas the independent variables were the DSSC performance test in two conditions, direct and indirect light.

Preparation of Transparent Conductive Glass

The transparent conductive glass that was used here was the FTO type in the size of $2.5 \times 2.5 \text{ cm}^2$. Two units of transparent conductive glass were needed to make one DSSC prototype. One of the glasses was used for the counter electrode, and the other was for TiO_2 paste, dye solution, and electrolyte. Since this research used four dye concentrations from papaya leaves, there needed eight transparent conductive glasses. Cutting the glasses was done using a glass cutter [7].

Preparation of TiO_2 Paste

The binder solution was created by mixing the polyvinyl alcohol (PVA) for 1.5 gr with 13.5 ml distilled water then stirred using a magnetic stirrer at 80°C for around 30 min. until it thickened. The PVA acted as the binding in TiO_2 paste. Gradually, added the TiO_2 powder until achieved a paste with desired viscosity. Binder solution adjustment aimed to get the optimised paste and was performed by controlling 7.5 ml binder solution and additional 0.5 gr TiO_2 powder [7].

Preparation of Dye

Dye preparation that was made from papaya leaves chlorophyll extraction was conducted by setting the concentrations for 25%, 50%, 75%, and 100%. The first step was to prepare all the materials such as 100 gr papaya leaves and 500 ml acetone P.A solution (b/v). Then, measure the papaya leaves, cleaned it, and drained. Cut the leaves into small pieces and blend until smooth. The smoother the leaves mean better extraction. The blended papaya leaves then mixed with 500 ml acetone solution in the beaker glass, stirred using a magnetic stirrer for around 30 min. After, the chlorophyll will be separated from the leaves that made the solution turned green, and the leaves turned white. Then, filter the solution using gauze paper (Whatman filter paper) to separate the solution from the pulp and obtained 500 ml dye. To get the 25% (v/v) concentrate, there needed to mix 25 ml of papaya leaves concentration with 75 ml acetone. The 50% (v/v) concentration required 50 ml of papaya extract and 50 ml acetone. The 75% (v/v) concentration required 75 ml papaya leaves extract and 25 ml acetone. Furthermore, lastly, to get 100% (v/v) concentration, there needed 100 ml pure papaya extract. Next, each concentration underwent chlorophyll level test using spectrophotometry method. Then, this research performed functional group in each concentration using the FTIR (Fourier Transform Infrared Spectroscopy). After the tests, each concentration was stored in a closed dark bottle until it was time to make the prototype.

Preparation of Electrolyte

Electrolyte was prepared by mix and stir 0.8 gr KI 0.5 M into 10 ml PEG 400 solution, then added 0.127 gr I₂ into the solution until all materials dissolve entirely. The electrolyte solution was stored in a closed vial bottle [7].

Preparation of Counter Electrode

Carbon counter-electrode was made by burning the substrate that would be used as the counter electrode using a candle flame that automatically formed carbon in the substrate area.

DSSC Assembly

The DSSC assembly was conducted after all components were done. First, cut the FTO substrate for 2.5 x 2.5 cm². Scotch tape was used to limit and shape the TiO₂ area for 2 x 2 cm² using doctor blade method and trim with stirring rod. Put it into the furnace at 450°C for around 30 min. The deposited TiO₂ then soaked for one day in the dye solution. After they merged, dropped the electrolyte solution evenly. The last step was to unite the active electrode substrate with a counter electrode using a binder clip with 0.5 cm offset at each end of the substrate. Repeat the steps for making another DSSC prototype according to variations in the concentration of the papaya leaf chlorophyll dye.

Chlorophyll Content Analysis

Chlorophyll content analysis from each concentration variation was conducted using spectrophotometry to find the level and type of chlorophyll in each variant.

DSSC Performance Test

After the DSSC prototype was made for each concentration, next was testing the performance under the direct sunlight and indirect sunlight (reflected light). The light from 1,000 Watt/m² halogen lamp was used because the glow from this lamp is more optimised compared to other types. When the glow of the halogen lamp was used, the input power on

the solar cell could be obtained by multiplication between light intensity and area of DSCC. The light intensity was achieved using the lux meter measurement device.

The DSSC performance was tested in the direct sunlight with 70,000 lux intensity while the second test used indirect light with 10,000 lux intensity.

Figure 1 shows the measurement by conducting a series of open-circuit voltage and short-circuit current and obtained the open-circuit voltage (V_{oc}), and short circuit current (I_{sc}).

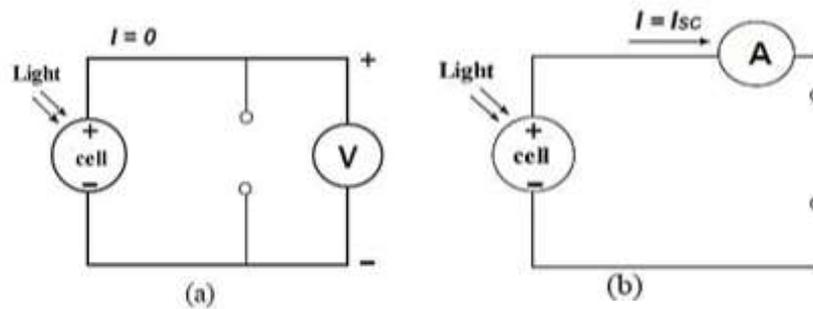


Fig. 1. Circuit (a) open-circuit voltage (V_{oc}) (b) short-circuit current (I_{sc})

Figure 2 show the measurement using maximum voltage and maximum current that produced V_m and I_m with loads from potentiometer so that it formed the current and voltage curves and in turn, obtained the maximum voltage (V_m) and maximum current (I_m).

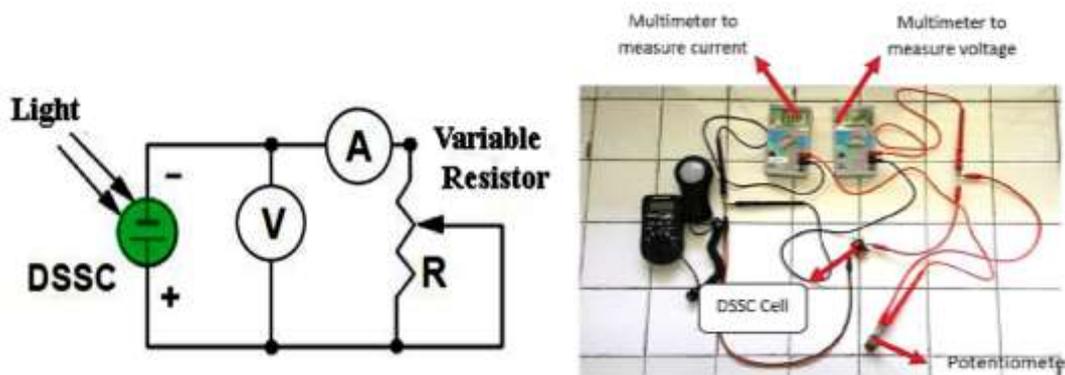


Fig. 2. Schematic measurement circuit of V_m and I_m

The output was noted then calculated the Fill Factor (FF), output power (P_{out}), and DSCC efficiency (η) using equation (1) to (6) using the following equation [9].

$$FF = \frac{V_{mp} \times I_{mp}}{V_{oc} \times I_{sc}} \dots\dots\dots (1)$$

$$P_{out} = FF \times V_{oc} \times I_{sc} \dots\dots\dots (2)$$

$$P_{out} = \frac{V_{mp} \times I_{mp}}{V_{oc} \times I_{sc}} \times V_{oc} \times I_{sc} \dots\dots\dots (3)$$

$$P_{out} = V_m \times I_m \dots\dots\dots (4)$$

$$\eta = \frac{P_{out}}{P_{in}} \times 100\% \dots\dots\dots (5)$$

$$\eta = \frac{P_{out}}{I_r \times A} \times 100\% \dots\dots\dots (6)$$

Where:

- | | |
|--|--------------------------------------|
| V_m : Maximum Voltage (Volt) | I_m : Maximum current (A) |
| V_{oc} : Open-circuit voltage (Volt) | I_{sc} : Short-circuit current (A) |
| I_r : Light intensity (Watt/m ²) | A : DSSC area |
| P_{in} : Input power (Watt) | P_{out} : Output power (Watt) |
| FF : Fill Factor | η : Efficiency(%) |

III. Results and Discussions

Chlorophyll Extraction Analysis

Figure 3 presents the papaya leaves dye in each concentration.

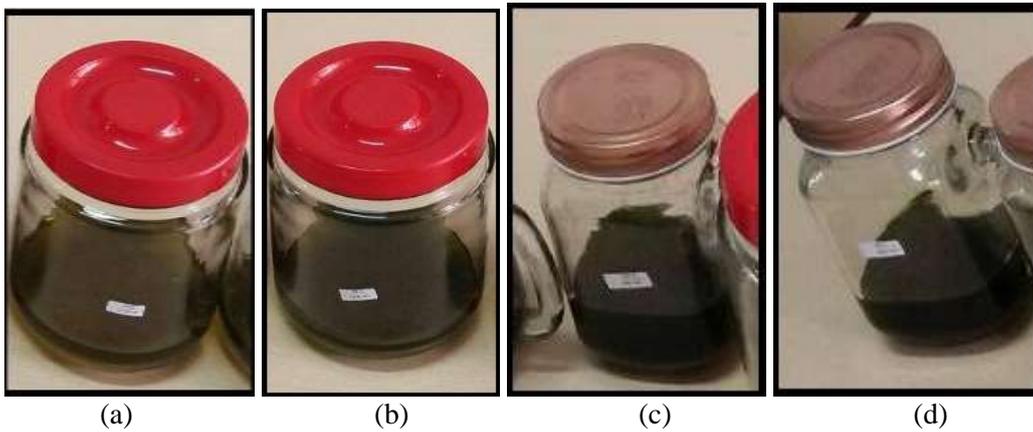


Fig. 3. Papaya leaf chlorophyll with concentration of (a) 25%, (b) 50%, (c) 75%, and (d) 100%

This research performed chlorophyll content level from each variant. The results are as shown in Figure 4 to Figure 8.

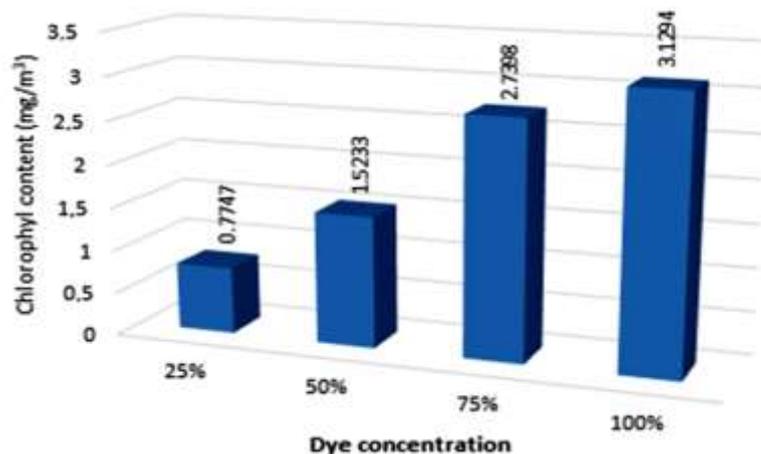


Fig. 4. The chlorophyll content in Papaya leaf dye

The results show that most variants contain chlorophyll type a (Figure 4). The plant usually has a dominant type a chlorophyll than type b. Extracting the chlorophyll could use alcohol, ether, and acetone solvents [10]. Chlorophyll a and b are the strongest in absorbing infrared with 600–700 wavelength and the least in absorbing green light with 500–600 wavelength [11].

The results also point that each concentration has different chlorophyll level; the higher concentration resulted in higher chlorophyll content. The sample with 25% concentration has 0.7787 mg/m^3 content and sample with 50% concentration had 1.5233 mg/m^3 . Meanwhile, 75% concentrate sample has 2.7398 mg/m^3 and 100% concentrate sample has 3.1294 mg/m^3 . The lowest chlorophyll dye content of papaya was obtained when the chlorophyll dye concentration was 25% while the highest chlorophyll dye content was obtained when the chlorophyll dye concentration was 100%. Thus, the more volume of dye from papaya leaves taken at the time of concentration, the greater the content of chlorophyll content.

DSSC Performance Analysis

Figure 5 shows the prototype of DSSC after each prototype from each variant was tested.

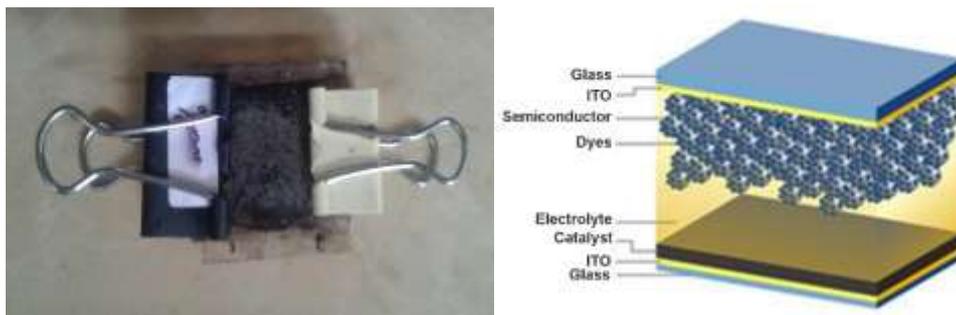


Fig. 6. DSSC prototype

The DSSC prototype shown in Figure 5 was tested that covered power output (P_{out}), Fill Factor (FF), and efficiency (η). In this research, the DSSC performance tests were conducted in two conditions: direct light and indirect light. The intensities between those two conditions were also different. Direct light had 70,000 lux, whereas indirect light had 10,000 lux.

Comparison of Output Power (P_{out}), Fill Factor (FF), and Efficiency (η) Direct Light DSSC prototype with Indirect Light DSSC

Figure 6 to Figure 8 present the comparison results of P_{out} , FF, and efficiency in the DSSC through direct and indirect light.

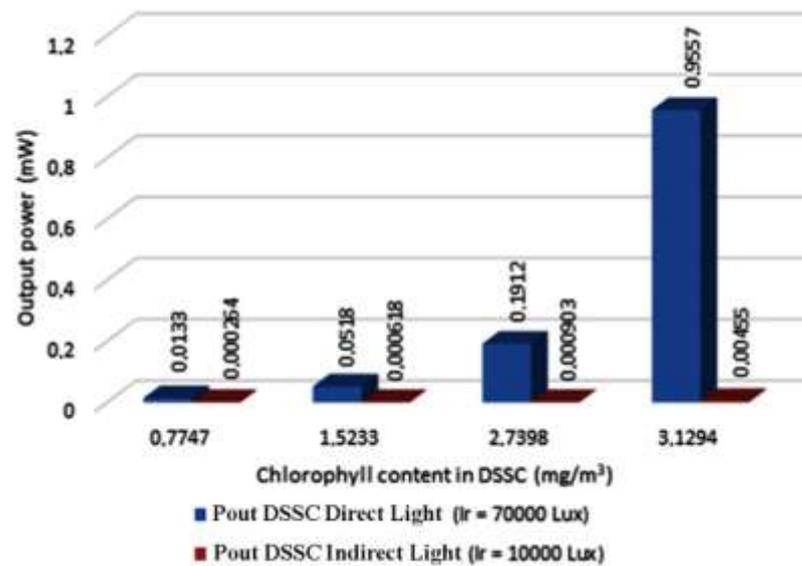


Fig. 6. Comparison of DSSC output (P_{out}) between direct light and indirect light

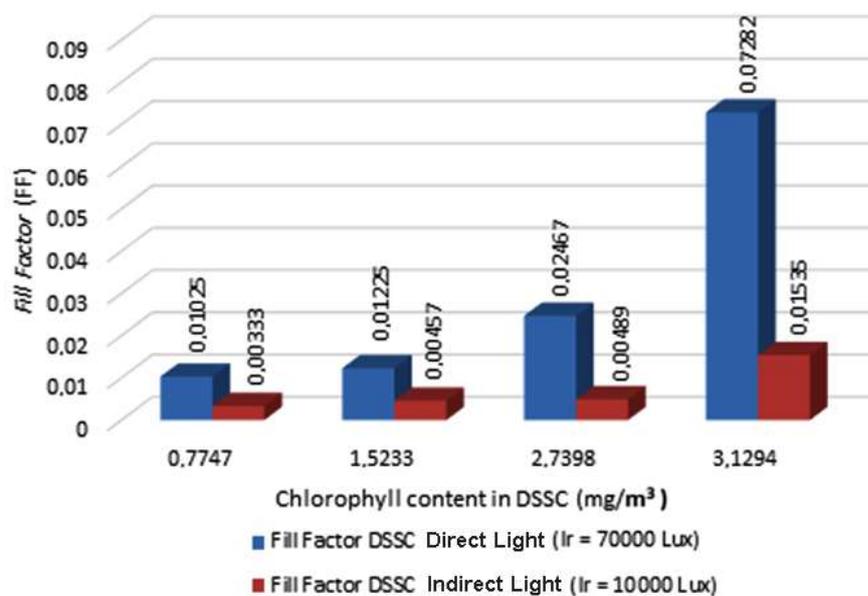


Fig. 7. Comparison of DSSC Fill Factor (FF) between direct light and indirect light

Although the comparison above shows increases according to the increased level of concentration, the energy conversion process was not optimized. For example, the sample with 100% concentration under direct light, in which the intensity was seven times than the indirect light, had FF value only four times higher than the FF under indirect light based on the division of 0.07282 direct light FF by 0.01535 indirect light FF value. This result did not correlate with the intensity ratio since there were three times the remaining efficiency residue. The P_{out} value from the direct light was 0.9557 mW divided with the value from indirect light of 0.00455 mW, resulted in 210 mW higher value of the sample with direct light. The amount should be considered enormous. However, the efficiency from the direct light was only 30% of the indirect one. The efficiency gap was the result of the 1.499137%

efficiency of direct light divided with 0.049863% efficiency from the indirect light. Achieving the 30% greater efficiency produced is not comparable to the P_{out} produced by 210 mW when it should not be far from the generated P_{out} .

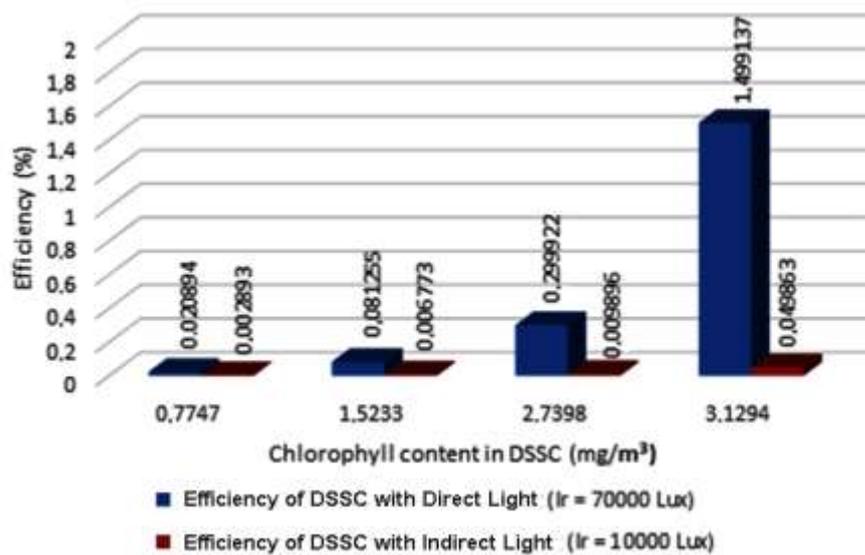


Fig. 8. Comparison of DSSC efficiency (η) between direct light DSSC and indirect light

Observed from the intensity comparison, the sample with 100% concentration had FF from direct light with the value of 0.9557 divided by 70,000 lux resulted in 1.04×10^{-6} value. Meanwhile, the indirect light FF was 1.535×10^{-6} , based on the division of 0.00455 by 10,000 lux. The largest FF occurred in the sample with indirect light, and the lowest was from direct light. The results were inversely proportional considered the largest intensity from direct light. However, the indirect light had a small efficiency of 0.049863% compared to 1.499137% from direct light. The first concern correlated to the high energy usage but low FF and high efficiency. The second was the small energy usage but large FF ratio and small efficiency. All the phenomena are described in Figure 9.

Figure 9 shows the energy conversion with voltage in the standard hydrogen electrode condition. The chlorophyll dye in the DSSC prototype had electrons inside that could absorb the light when excited [13]. The electron bounds in chlorophyll dye were high or HOMO (Highest Occupied Molecular Orbital) with the value of 1.0 V in normal condition. When the prototype obtained photon light from the halogen lamp, the light was absorbed by the chlorophyll dye so that the electrons were excited and the photon light overcame the energy bandgap (E_g). The DSSC prototype with larger intensity had more substantial chlorophyll content. Thus, the excited electrons were also the large amount and occurred in the prototype with 100% concentration of 3.1294 mg/m³ content and 70,000 lux intensities.

Meanwhile, the small light intensity would excite only some electrons, here, occurred in the prototype with 100% chlorophyll of 3.1294 mg/m³ content and 10,000 lux intensities. After the electrons were excited, the energy bounds were small or LUMO (Lowest Unoccupied Molecular) with the value 0.7 V that is also called free electron. The electrons then injected into the titanium dioxide (TiO₂) tape. Titanium dioxide acted as the electron acceptor/collector. The energy from this injection was -0.5 V. The electrons, then, were transferred through the outer circuit of DSSC to the counter electrode.

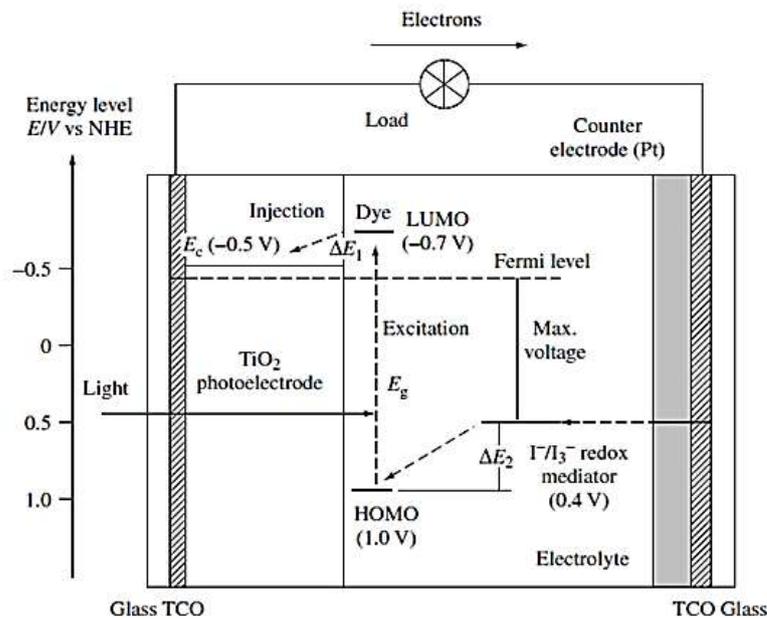


Fig. 9. Energy systematic diagram and DSSC operating principles [12]

Moreover, since the counter electrode used carbon catalyst, the electrons moved to the electrolyte. The electrolyte had energy bound of 0.4 V. Electrolyte redox usually made of iodide and triiodide (I^-/I_3^-) that act as mediators to create the cycle process inside the cell. The hole that was formed in the electrolyte (I_3^-), due to the electron donor from the previous process, combined with electron and formed iodide (I^-). The iodide was used to the donor the electron (0.4 V) in the oxidized dye (1 V) and formed an electron transport cycle. With this cycle, there was a direct conversion of light energy into electrical energy. In the process of converting photon energy into electrical energy, there is a Fermi level. The Fermi level is the level of energy that is filled by electrons.

The Fermi level during energy conversion caused the FF in the direct light DSSC in this research to the left three times inefficient energy. The residual energy than was used to generate energy from each electron bound until the conversion of the photon into electrical energy. A semiconductor material has sensitive property towards temperature and DSSC. The increasing temperature could reduce the DSSC bandgap and would influence its parameters such as open-circuit voltage (V_{oc}). The increasing temperature linearly affects the open-circuit voltage. The magnitude of this reduction is proportional to V_{oc} . The increasing V_{oc} resulted in a lower reduction when the temperature increases. The current generated by light was increased slightly along with the increasing temperature. It due to the carriers increase that was produced thermally in the cell. The high temperatures reduced the efficiency due to more significant changes due to the desorption of the sensitizer at higher temperature [14]. Therefore, in this study, the efficiency generated by direct light DSSC was only 30% times that of indirect light DSSC. These efficiency results were very much different from the P_{out} value from the direct light DSSC.

The Fermi level in the direct light DSSC prototype with 70,000 lux intensity created larger energy compared to indirect light prototype with 10,000 lux intensities. Since the Fermi level generated voltage maximum, the direct light DSSC obtained larger maximum voltage compared to indirect light. The maximum voltage influenced efficiency. The larger

maximum voltage created more substantial efficiency and vice versa. Therefore, direct light DSSC with 70,000 lux intensity had higher efficiency with the value of 1.499127%, whereas the indirect light had 0.049863% efficiency.

IV. Conclusion

The conclusion was that each concentration of chlorophyll from papaya leaves in the DSSC greatly influence the generated P_{out} . The higher chlorophyll content produced a higher P_{out} . Next, the concentration also affected the resulted FF. The higher chlorophyll content resulted in higher FF. The chlorophyll content of each variation of the concentration of papaya leaf colouring in DSSC dramatically affects the resulting efficiency. Increasing the papaya leaf chlorophyll content from 0.7747 mg/mm³ to 3.1294 mg/mm³ were able to increase the efficiency of DSSC from 0.022% to 1.499%.

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