Effect of Chlorophyll Concentration Variations from Extract of Papaya Leaves on Dye-Sensitized Solar Cell

Eka Maulana, Sholeh Hadi Pramono, Dody Fanditya, M. Julius

Abstract—In this paper, extract of papaya leaves are used as a natural dye and combined by variations of solvent concentration applied on DSSC (Dye-Sensitized Solar Cell). Indonesian geographic located on the equator line occasions the magnitude of the potential to develop organic solar cells made from extracts of chlorophyll as a substitute for inorganic materials or synthetic dye on DSSC material. Dye serves as absorbing photons which are then converted into electrical energy. A conductive coated glass layer called TCO (Transparent Conductive Oxide) is used as a substrate of electrode. 

II. METHOD

A. Structure Design

DSSC structure was designed by combining two layers of glass with different TCO opposite layer. The first glass (photo-electrode) is composed of layers of TiO₂ paste which has been soaked with a solution of chlorophyll and given electrolyte solution; while the other glass consists of layers of carbon as the counter electrode (counter-electrode). DSSC physical structure is shown in Figs. 1 and 2.

B. Material

A glass substrate was used in this research was conductive (Indium Tin Dioxide coated) transparent glass (Aldrich corp., TCO-ITO) cut with area of 2x2 cm with surface resistivity of 15-25Ω/sq. TCO (Transparent Conductive Oxide) is a transparent conductive glass that function as the body of the solar cell and it conductive layer. This solar cell body serves as a charge flows. Nano powder TiO₂ (Aldrich corp., titanium dioxide) 21 nm particles size were used as photoactive layer material. Nano-porous TiO₂ has a band gap energy of 3.2 eV is needed as transparent semiconductor in most solar light spectrum. In addition, the TiO₂ structure that the pore size in the nano-scale will increase the system performance due to nano-porous structure has the characteristics of high surface area so it will increase the amount of dye that absorb.

SOLAR energy is one of the alternative energy that can be used by humans today. Unlike fossil energy that is expected to be exhausted in 40 years for oil, 60 years for natural gas, and 200 years for coal [1]. Indonesia geographically located on the equator line leads this country can receive the sunlight more than other countries, approximately 4.8 kW/m²/day [2]. Based on this phenomenon, solar energy in Indonesia is the most potential energy to be used as a source of renewable alternative energy. One of the technologies that harvests sunlight and converts to electrical energy is solar cells.

DSSC (Dye-Sensitized Solar Cell) have been developed by Grätzel as alternative energy resource through the discovery of a new solar cell material with a mimic photosynthesis called photo-electrochemical reaction [4]. Photosynthesis process that converts light into chemical energy is the basic of the chemical approach to the process of changing light into electrical energy in the DSSC. Development has been offering cost-efficiency of production, flexible substrates, and low-cost materials.

Dye commonly used is Ruthenium (Ru) complex as this type of synthetic dye was almost close to pure resulting in an efficiency of 11% [5]. Due to the dye Ruthenium is high cost to obtain, so in this paper used chlorophyll dye substances obtained from papaya leaves. The dye role on DSSC acts as the photon absorption and then a process of excitation of electrons in the dye molecules to produce electrical energy [6]. The dye ability absorbs the photon is very important thing due to there is need for characterization. The characterization needed to determine ability of dye absorbs photons and will further affect the output power generated combined by TiO₂ layer [7]-[9]. Photon absorption level by chlorophyll dependent on the concentration of chlorophyll which is influenced by the amount of leaves used the solvent concentration and the duration of chlorophyll release process at stirring time. This paper investigates the effect of variations of this combination to obtain characteristic of the DSSC performances.
C. Substrate and Electrolyte Solution Preparation

TCO glass is placed in a clean container and soaked in ethanol for 10 minutes so sterile and eliminate impurities material so that no additional resistance values on TCO glass. After the cleaning is completed the substrate removed from the container and allowed to advance up to the glass ethanol evaporates. Making the electrolyte solution is done by the following procedure:

1. Mixing solution from 1 ml distilled water with 0.83 g (0.5 M) of KI (potassium iodide) and 9 ml of acetonitrile.
2. Add of 0.127 g (0.05 M) I₂ (Iodide) into the solution then stirred by magnetic stirrer.
3. Keep the solution in a dark bottle and wrapped by aluminum foil.

D. Dye Preparation

Manufacturing process of dye used the principle of extraction of chlorophyll from the leaves of papaya. Papaya leaves first weighed in accordance with the variation of the comparison that has been designed. Leaves washed using distilled water and then dried. Papaya leaves that have clean subsequently crushed with a porcelain cup until smooth and then put into 50 ml of ethanol solvent. Papaya leaf is shown in Fig. 3 (a).

The basic size was 100 grams of papaya leaves with variation ratio between the mass of chlorophyll (gram) and the volume of solvent (ml) of 1.5, 2.5, and 3.5. Solvent concentrations were varied include of 70%, 80% and 98%. The solutions were also stirrer for time variations consist of 30, 120 and 180 minutes. Observation was done by using the absorbance of chlorophyll by a Shimadzu UV-1601 Spectrophotometer at the wavelength of 300-800 nm. Based on the results obtained, amount of chlorophyll-a, chlorophyll-b and total chlorophyll contained in the dye is analyzed using the Wintemans and De Mots formula;

\[
\text{Chlorophyll a} = 13.7 \times 10^{-4} D_{665} - 5.76 \times 10^{-4} D_{6649} \tag{1}
\]

\[
\text{Chlorophyll a} = 25.8 \times 10^{-4} D_{6649} - 7.60 \times 10^{-4} D_{6665} \tag{2}
\]

\[
\text{Chlorophyll total} = 20.0 \times 10^{-4} D_{6665} + 6.10 \times 10^{-4} D_{6665} \tag{3}
\]

E. Preparation of TiO₂ Paste

In the manufacturing of TiO₂ paste, Polyvinyl Alcohol (PVA) of 1.5 g was added to 13.5 ml of distilled water, then the mixture is stirred with a magnetic stirrer at 80°C for approximately 30 minutes until the thickened and homogeneous solution. PVA serves as a binder in the manufacture of TiO₂ paste. Furthermore TiO₂ powder was weighed 0.5 grams, then the suspension which has been created is added to the TiO₂ powder with a ratio TiO₂ of 2 spatula spoons mixed with 15 drops or 0.75 ml of PVA.

F. Coating of TiO₂ Paste on TCO Glass

Formed area pasta deposited with the help of scotch tape on the conductive glass, forming an area of 2 x 2 cm. Scotch tape also functions as a regulator of the thickness of the TiO₂ paste. The Thickness of paste on the glass surface by the scotch tape can be stacked in layers according to need. Pasta TiO₂ deposited on top of the area that has been made by combination of the doctor blading and brush painting methods [10], [11] were applied to help the smooth paste. Areas which are formed of TiO₂ on the TCO glass were shown in Fig. 4 (b).

G. Firing Process of TiO₂ Paste

TiO₂ Paste has been flat on the surface of the TCO glass and then in-firing in an electric furnace for 30 minutes at a temperature of 450°C. it was made a better contact between the TiO₂ with TCO glass.

H. Immersion of TiO₂ in Chlorophyll Dye Solution

TiO₂-coating TCO layer was soaked in the dye solution for approximately 30 minutes, then a layer of TiO₂ will be green leaf. The TiO₂ layer immersion in the dye solution was shown in Fig. 3 (b).
I. Preparation of Counter-Electrode Carbon

Making counter-electrode is done by heating the conductive side of the TCO glass candle flame for about 30 seconds until the average carbon to cover the TCO conductive glass. Carbon TCO glass attached to the specified dimensions according to the dimensions of TCO coated glass TiO2 paste is 2x2 cm².

J. Provision of Electrolytes

Giving electrolyte by means of using a pipette dropped by 4 drops or as much as 0.25 ml. Electrolyte solution is used as the electron transport of carbon to the dye.

K. Assembling DSSC

After each component DSSC successfully created dah ready, then do the assembly process to form a solar cell. Assembly is done by gluing glass photo-electrode TCO and TCO glass counter-electrode sandwich structure and then clamped with a clip so that attachment is denser and does not shift. The results of the DSSC have shown in Fig. 4.

L. DSSC Investigating

The experimental setup of DSSC electrical characteristic was used to obtain the open circuit voltage and short circuit current. The light measured by lux meter trough the DSSC can be varied, then the output voltage and current varied too. The second method, the value of the load resistance is varied to get electricity performance of DSSC. Some parameters were observed are open circuit voltage (Voc) and short circuit current (Isc), maximum output voltage (Vmax), and maximum output current (Imax) to obtain the fill factor (FF) and efficiency (η). The FF is defined by the ratio of the maximum power output of DSSC device is its theoretical power output if both current and voltage were at their maxima, Isc and Voc, respectively [12].

III. RESULT AND DISCUSSION

Absorbance chlorophyll dye solution of papaya leaves have been investigated and measured. Chlorophyll measurement using spectrophotometer by variation of the ratio papaya leaves with solvent, solvent concentration and time stirring were shown in Figs. 5-7. Data analysis of the absorbance to the wavelengths was used to calculate the number of chlorophyll a, chlorophyll b and total chlorophyll inside dye solution. The result of a, b, and total chlorophyll at ratio of 1:5 are 20.328 mg/l, 54.592 mg/l and 74.804 mg/l, respectively. The calculation analyses of the ratio of leaves mass and solvent volume is shown in Table I.

<table>
<thead>
<tr>
<th>Sample ratio</th>
<th>Chlorophyll a (mg/l)</th>
<th>Chlorophyll b (mg/l)</th>
<th>Total Chlorophyll (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:5</td>
<td>20.328</td>
<td>54.592</td>
<td>74.804</td>
</tr>
<tr>
<td>2:5</td>
<td>20.446</td>
<td>55.556</td>
<td>75.895</td>
</tr>
<tr>
<td>3:5</td>
<td>22.690</td>
<td>57.509</td>
<td>80.076</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample (ratio)</th>
<th>Total Chlorophyll (mg/l)</th>
<th>Voc (mV)</th>
<th>Isc (μA)</th>
<th>Pmax (watt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:5</td>
<td>74.804</td>
<td>160.7</td>
<td>2.8</td>
<td>112.64x10⁻⁹</td>
</tr>
<tr>
<td>2:5</td>
<td>75.895</td>
<td>203</td>
<td>4</td>
<td>203x10⁻⁹</td>
</tr>
<tr>
<td>3:5</td>
<td>80.076</td>
<td>235.5</td>
<td>14</td>
<td>824.64x10⁻⁹</td>
</tr>
</tbody>
</table>

Fig. 5 Absorbance of chlorophyll dye solution by the variation of ratio between leaves mass (m) and solvent volume (v)

Fig. 6 Absorbance of chlorophyll dye solution by the variation of ethanol solvent concentration

Fig. 7 Absorbance of chlorophyll dye solution by the variation of stirring time
The maximum number of a, b, and total chlorophyll was achieved from the variation of 3:5 mass and volume ratio correlated to the chlorophyll absorbance in Fig. 5. It is observed to the amount of chlorophyll released by solvent at 3:5 ratio catch more photons greater than 2.5:1 and 1:5 ratio. The electrical characteristic of DSSC was observed by variation ratio of leaves mass and solvent volume which is shown in Table II. The Voc and Isc were achieved maximize at ratio of 3:5 by 235.5mV and 14 μA, respectively. Fig. 6 shows that there are differences in the peak absorbance values generated by the three types of chlorophyll dye by variation of solvent concentration. The average maximum peak of 98% higher than the 80% and 70% of concentration of solvent, it was shown in Table III increasing linearly. This difference will have consequences on the rate of photon absorption and the subsequent effect on the voltage outputs produced by the DSSC. Increasing stirring time reduce the Voc, Isc, and chlorophyll number. Effect of variation stirring time is shown in Fig. 7 and Table IV. The maximum electrical characteristics were achieved at 30 minutes of stirring time. The result show the characterization of the output voltage against current is increasing linearly. The DSSC characteristic have already reached fill factors (FF) up to 25%.

### IV. Conclusion

According to the design of DSSC, chlorophyll absorbance investigation and electrical analysis it can be concluded that:

1) DSSC have been designed and characterized by following method: dye processing, TiO₂ paste, TiO₂-coated TCO glass, firing substrate, immersion TiO₂ TCO substrate into dye solution, counter electrode processing, and fabrication of DSSC by active area of 1.8 x 1.8 cm.

2) Refer to the variation of the ratio between leaves mass to solvent volume of 1:5, 2:5 and 3:5; it can be obtain the maximum chlorophyll number of 80.076 mg/l and fill factor of DSSC of 25% at ratio of 3:5.

3) Variation of solvent concentration was 70%, 80% and 98%. It can be achieved that the output power of DSSC was 824.64x10⁻⁹ watt at solvent concentration of 98%.

4) The variation of stirring time of chlorophyll extract was observed of 30, 120, and 180 minutes. The maximum chlorophyll number was achieved at 30 minutes by $V_{oc}$ and $I_{sc}$ of 235.5 mV and 14 μA, respectively.

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### REFERENCES


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