A preliminary study of DSSC with PEDOT carrageenan as electrolyte system

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Abstract. This study aims to produce DSSC solar cells using PEDOT as a substitute for iodine. This experiment was carried out in the physics laboratory of the Tadulako University FKIP. TiO₂ was deposited on FTO glass measuring 2.5 x 2.8 cm using the doctor blade method. TiO₂ film was produced after heating in a furnace at 450 °C. Subsequently, the film was soaked in Routinized dye for 30 minutes. PEDOT Carrageenan Lambda 1:1 is then dripped on a TiO₂ / dye layer and covered with a platinum counter electrode. The results of measurements of current and voltage under direct sunlight with an intensity of 746 W/m² are 32.2 µA and 97.5 mV, respectively. These results indicate that the PEDOT Carrageenan solution has enough potential to be developed as a substitute for iodine electrolyte in the DSSC solar cell device.

1. Introduction
The world is experiencing a global crisis that is an energy crisis. Reliance on conventional energy cannot be tolerated due to its utilization which provides higher value. Most countries in the world still use conventional energy sources such as fossil fuels, natural gas and coal due to their high energy conversion efficiency value. However, with the depletion of energy sources requires humans to find alternative energy sources through New and Renewable Energy, one of which is through the use of solar power through solar cell tools. The use of energy through solar cells is a potential alternative because total amount of solar energy that reaches earth is huge, about 700 MWatt every minute [1]. Nevertheless, the utilization renewable energy including the category of utilization of solar power is still minimal in use among the community, especially domestic utilization (in Indonesia) due to the lack of industry support related to renewable energy generation components as well as the difficulty of obtaining low-interest funding, also being the cause of the stalled development of renewable energy [2].

Until now the development of solar cells has reached the 3rd generation and is dominated by polymer solar cells namely Dye Sensitized Solar Cell (DSSC). In 1991, DSSC introduced by Prof. Michael Gratzel which was the breakthrough in solar cell technology. The development of the principle of photoelectrochemistry that uses electrolytes as a medium transport payload that made of low purity materials through a low-cost process [3]. Through these new breakthroughs, various studies on DSSC continue to be conducted with the aim of increasing the efficiency rate of the DSSC.

Basicly the working principle that DSSC uses is to utilize electron transfer reactions. The DSSC work scheme is shown in Figure 1. When cell is exposed by sunlight, electron flow is created and can power an electrical device in external load. Inside the cell, the dye molecule was hits by photon from sunlight. Electron excitation occurs in the dye from ground state (D) to exited state (D*). Then with
enough energy the electrons can escape the molecule dye and move into the conduction band titania (TiO$_2$) so that the dye molecule is oxidized (D$^+$). When the electron move in to the titania, a hole is left behind. Electrolyte iodide (I$^-$) as a mediator fill the hole with one of its own, so the dye molecule returns to its ground state and prevents the re-capture of electrons by oxidized dye. After reaching the TCO electrode, the electron flows through the external circuit into the counter electrode. With the catalyst on the counter electrode, the electron is received by the electrolyte (I$^3$). With this cycle from the electrons travel there is a conversion of sunlight energy into electrical energy [1].

**Figure 1. Working Scheme of DSSC**

The series of chemical reactions that occur in the DSSC are [4]:

Anode: $D + hv \rightarrow D^+$ \hspace{1cm} **Absorption** \hspace{1cm} (1)

$D^+ \rightarrow D^{2+} + e^- (TiO_2)$ \hspace{1cm} **Electron injection** \hspace{1cm} (2)

$2D^+ + 3I^- \rightarrow 2D + I^3_3$ \hspace{1cm} **Regeneration** \hspace{1cm} (3)

Chatode: $I_3^- + 2e^- (Pt) \rightarrow 3I^-$ \hspace{1cm} (4)

Cell: $e^- (Pt) + hv \rightarrow e^- (TiO_2)$ \hspace{1cm} (5)

Research related to DSSC is still ongoing. Most research focuses more on improving the value of energy performance produced by DSSC as well as on the development of materials that can reduce production costs. Some related research is the utilization of natural dyes using the content of anthocyanin extract, the use of catalysts of the type of carbon pencil as well as the result of combustion, the use of iodine types and so on. The research on the use of electrolyte polymers in the form of poly polymer mixture (3,4-ethylenedioxythiophene) (PEDOT)-κ-carrageenan for DSSC obtained an efficiency value of 0.421% [5]. The value obtained indicates the potential for the development of PEDOT-carrageenan mixed-based electrolyte polymers.

The carrageenan are natural products. There are three employed types of fractions that is, lambda (λ)-carrageenan, kappa (κ)-carrageenan, and iota (ι)-carrageenan [6] depending on the number and position of the sulfate groups per repeated disaccharide units [7]. The carrageenans is generally extracted from seaweed. The κ-carr is predominantly extracted from the seaweed *Kappaphycus alvarezii*. The ι-carr is mainly obtained from *Eucheuma denticulatum*. However, the λ-carr is extracted
from the species of the *Gigartina* and *Chondrus genera*. The sulphate ester functional groups which contain on those carrageenan have potential polyelectrolyte dopant for PEDOT [8].

The topic of research on the use of the PEDOT Lambda Carrageenan mixture is still not widely done, especially in its use as a substitute for iodine electrolytes in the DSSC layer. So that this research can add new reference regarding the utilization of PEDOT/Lambda carrageenan as electrolyte in DSSC. The PEDOT/Lambda carragenan dispersions is prepared in this study in 1:1 ratio by weight. In this study, researchers tested TiO$_2$ nanoparticle-based DSSC using solaronix-produced synthetic rhutenizer and modified the use of iodine electrolytes using PEDOT/Lambda carrageenan 1:1.

2. Materials and methods
The materials are Transparent Conductive Oxide/TCO glass, Titanium Oxide/TiO$_2$ [9], ethanol 96%, aquadest, ruthenizer, platisol, electrolyte [10], PEDOT/Lambda Caragenan 1:1 [14] and nitric acid. The dye was prepared by 10 mg Ruthenizer in to 25 ml of aquades [10]. PEDOT/Lambda Carageenan 1:1 is obtained from natural world of Indonesia. The carrageenan-doped PEDOT is synthesized with oxidative polymerization of 3,4-ethylenedioxythiophene monomer as Diah (2020) research [8]. The PEDOT/carrageenan Lambda (PEDOT/Carr Lambda) was in the form of powder. The sample was dissolved in aquades with a temperature of 70°C. After each component of DSSC has been ready then done DSSC assembly. Deposition TiO$_2$ paste onto the working electrode using the doctor blade technique. Next the working electrodes are soaked with dye for 30 minutes. Platinum is then deposited to the electrode counter via a heating technique in the furnace for 45 minutes with a temperature of 450°C [11]. Next both electrodes are clamped with a paperclip. The last step is to drip PEDOT Lambda Carrageenan 1:1 as an electrolyte approximately two drops into space between the working electrode and counter electrode. Next DSSC prototype ready to be tested. Figure 2 shows the whole processing step for preparation of DSSC.

![Figure 2. Processing step for preparation of DSSC](image-url)
The simple characterization sample used the circuit in Figure 3. The research was conducted under sunlight with a measurable intensity of 746 W/m². Current and voltage values are obtained through the remittance change of the potentiometer in a range from the minimum value to a maximum of 100 kΩ. The current value and voltage obtained are included in the table and converted in the I-V curve to interpret the efficiency of the solar cell.

![Figure 3. DSSC I-V characterization set](image)

3. Results and discussion
The DSSC prototype is assembled with the TCO-FTO (Anode)/TiO₂/Dye/Electrolyte/Carbon: Platinum/TCO-FTO (Cathode) sandwich arrangement. Working area size on TCO glass as working electrode of 2.5 cm x 2.8 cm. Dye used is dye synthetic production Solaronix also for the platinum, while the electrolyte used is PEDOT Carrageenan Lambda 1:1. The Assembly DSSC technique refers to the guidelines for making DSSC by Solaronix [10]. The results of the DSSC prototype that has been created is in Figure 4.

![Figure 4. DSSC prototypes that have been created](image)

The I-V testing of DSSC was conducted by using the circuit in Figure 3 resulting in a characteristic curve of I-V Figure 6. With the following parameters; Isc (short circuit) short circuit, Voc open circuit voltage, Vmax and Imax is the voltage and strong current at the maximum power value.

PEDOT is a derivative polymer discovered in 1980 by Bayer Lab. PEDOT is a type of polymer that has stable properties, small gap bands, and high electronic conductivity [12]. PEDOT is an organic polymer that is difficult to synthesize because it is not easily soluble in water or other organic solvents. Therefore, additional poly(styrenesulfonate) (PSS) doping is required in order to produce a system that can be easily salted and produce an effective coating for the film [13]. The κ-carrageenan doping was a natural anionic heteropolysaccharide that has a functional group of sulfate ester groups as contained in PSS. The addition of κ-carrageenan indicates a dispersion that is potential enough to produce high conductivity properties as well as visible light transparency [14].

Therefore, in this study used PEDOT Carrageenan lambda 1:1 to replace iodine electrolyte material. Iodine's role is as a redox reaction mediator, when PEDOT is used, the role is taken over through an existing polymer chain as in Figure 6. The study of the blend between PEDOT and λ-carr
has not been well studied. In addition to reducing production costs by using iodine materials produced by imported Solaronix, the carrageenan material contained in PEDOT Lamba Carrageenan 1:1 is a potential material sourced from the natural world of Indonesia. Table 1 shows the I-V measurement under sun radiation.

| No. | I (µA) | V (mV) | P (µWatt) |
|-----|--------|--------|-----------|
| 1   | 1.9    | 97.5   | 0.185     |
| 2   | 1.9    | 96.6   | 0.184     |
| 3   | 2.1    | 96.1   | 0.202     |
| 4   | 2.2    | 95.7   | 0.211     |
| 5   | 2.2    | 95.9   | 0.211     |
| 6   | 2.4    | 94.9   | 0.228     |
| 7   | 2.5    | 93     | 0.233     |
| 8   | 2.6    | 92.8   | 0.241     |
| 9   | 2.6    | 91.8   | 0.239     |
| 10  | 2.7    | 91.1   | 0.246     |
| 11  | 2.7    | 90.4   | 0.244     |
| 12  | 2.8    | 90.2   | 0.253     |
| 13  | 2.8    | 90.1   | 0.252     |
| 14  | 2.8    | 83.1   | 0.233     |
| 15  | 2.8    | 82.6   | 0.231     |
| 16  | 2.9    | 79.1   | 0.229     |
| 17  | 3.0    | 59.2   | 0.178     |
| 18  | 3.0    | 47.3   | 0.142     |
| 19  | 3.0    | 45.0   | 0.135     |
| 20  | 27.5   | 2.2    | 0.0605    |
| 21  | 28.0   | 1.9    | 0.0532    |
| 22  | 28.2   | 2.2    | 0.062     |
| 23  | 28.4   | 2.5    | 0.071     |
| 24  | 28.1   | 1.4    | 0.0393    |
| 25  | 28.1   | 1.3    | 0.0365    |
| 26  | 28.5   | 0.8    | 0.0228    |
| 27  | 29.8   | 0      | 0         |
| 28  | 32.2   | 0      | 0         |

Based on Table 1 data known the voltage of the DSSC open circuit reaches 97.5 mV. However, these results are still very low when compared to previous studies such as research by Camacho (2020) which produced a Voc value of 0.439 V in the use of PEDOT-carrageenan mixture as electrolytes [5]. The strong current value also produced in this study is still in the Ampere micro order. The short circuit current (Isc) obtained reaches 32.2 µA. The small output current produced by DSSC can be caused by the resistance of the TiO₂ semiconductor layer and a very large electrolyte solution [15]. As a result, the electron rate in the TiO₂ layer injected from the dye slows down. Other causes can be due to the uncontrolled thickness of the TiO₂ layer on the working electrode as well as the thickness of the platinum layer on the opponent's electrodes. In addition, based on this research showing that the efficiency obtained is very small below 1%, in the study before stated that the low efficiency value obtained is associated with a very rigid PEDOT configuration in PEDOT-carr solution as the electrolyte system [5]. Due to the rigidity of the PEDOT chain, electron transport is not as efficient as the iodine [10] as electrolyte system.

4. Conclusion
Based on this research can be drawn the conclusion that we have successfully make the DSSC by employing PEDOT Carrageenan for replacing iodine as electrolyte. The DSSC show the ability to
convert light energy into electrical energy even in a low value range. However, with indications of current value and measurable voltage indicates that the PEDOT Lambda Carrageenan 1:1 mixture can be an alternative organic electrolyte that can be applied to the DSSC.

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