

THE EFFECT OF CLATHRIN PROTEIN ADDITION ON INCREASING THE NUMBER OF ELECTRONS IN ORGANIC DYE-SENSITIZED SOLAR CELL (DSSC)

Prihanto Trihutomo✉

Department of Mechanical Engineering¹
prihanto.trihutomo.ft@um.ac.id

Marji

Department of Mechanical Engineering¹

Muchammad Harly

Department of Mechanical Engineering¹

Bambang Adi Wahyudi

Department of Mechanical Engineering¹

Muhammad Bustomi Radja

Department of Mechanical Engineering¹

*¹State University of Malang
Jl. Semarang No. 5, Malang, Indonesia, 65145*

✉ Corresponding author

Abstract

Dye-Sensitized Solar Cell (DSSC) is a solar cell that uses dyes to convert sunlight into electricity, which has a wide absorption spectrum, is inexpensive and environmentally friendly. Visible light sensitive dyes are used in Dye-Sensitized Solar Cell (DSSC) types to generate electricity. Natural sensitive dyes that are commonly used in DSSC are chlorophyll derived from plants. Chlorophyll is a source of electrons which will be excited when exposed to light, resulting in an electric current in the DSSC. The most basic problem in Dye-Sensitized Solar Cell (DSSC) is that the number of electrons produced is still lower than that of silicon solar cells. This is due to the high recombination process of free electrons due to limited diffusion of electrons trapped at the boundary between TiO₂ particles caused by less than optimal contact between particles. Clathrin is a protein that plays an important role in the formation of the vesicle layer which is responsible for the transport of molecules in cells. As a protein that plays an important role in the cell transport system, Clathrin can bind to ions in order to transport cells. This study has proven that the addition of Clathrin protein to the DSSC layer can increase the number of electrons generated in the DSSC. The method used in this study was to vary the addition of Clathrin content to TiO₂, namely the Clathrin concentration of 0 %, 25 %, 50 % and 75 %. The results showed that increasing the Clathrin content would increase the electric current and the number of electrons generated by the DSSC, namely the 75 % Clathrin content with an electric current of 5.247 mA and the number of electrons was 3.28×10^{16} .

Keyword: Clathrin protein, TiO₂, chlorophyll, number of electrons, Dye-Sensitized Solar Cell.

DOI: 10.21303/2461-4262.2022.001957

1. Introduction

Energy that comes from the sun is a renewable alternative energy that has the potential to continue to be developed. This is because every year the energy from the sun arriving at the earth's surface is predicted to be 10,000 times the overall basic energy requirement and is greater than the total energy supply on earth because each year the amount of solar energy radiating to the earth's surface is 3.9×10^{24} Joule = 1.08×10^{18} kWh [1]. Worldwide, the utilization of solar energy generates about 512 gigawatts of electricity from solar panels installed until 2018. The use of solar energy to generate electricity is still very small due to various obstacles [2].

The technical constraints for the development of solar cells are the need for single crystalline silicon to make solar cell panels in order to produce an efficiency of around 30 %, while producing single crystal silicon requires high costs. The low efficiency of solar cells causes the need

for large amounts of solar panels to produce large amounts of power [3]. The problem of pollution is the next obstacle to the use of solar cells, this is because solar panels are toxic. Although in use it does not cause pollution, in the process of making solar cells there is waste or pollution to the environment due to the use of toxic materials such as polysilicon in the process of making solar cells. The gas that creates the greenhouse effect, nitrogen tetrafluoride is also used in the manufacture of solar panels. This gas is 17,000 times stronger than carbon dioxide. This is what causes damage to the environment [4].

To overcome the problems found in silicon solar cells, a Dye-Sensitized Solar Cell (DSSC) was developed, namely a solar cell that uses dyes to convert sunlight into electricity [5]. DSSC is a solar panel device whose process resembles the principle Photosynthesis in plants is a photo-electrochemical system in which a wide-gap semiconductor is adsorbed by a dye which functions to absorb photons of sunlight to be converted to electrical energy by the process of transporting electrons in its structure [6].

The DSSC structure is composed of nano-sized semiconductors deposited in a dye that serves to capture photons of light (using synthetic dyes such as ruthenium complex or organic dyes), conductor glass, counterelectrodes and electrolytes. DSSC is also known as Gratzel cell or dye-sensitized solar cell (DSSC). DSSC is very inexpensive and easy to prepare, environmentally friendly, and the light thin film structure is compatible with automated manufacturing [7].

The nanoparticle coating that is often used is Titanium dioxide or TiO_2 [8]. The large band gap energy (E_g) value of 3.20 eV, good chemical stability, non-toxicity, environmental compatibility and low price are the advantages of the TiO_2 semiconductor material [9]. The anatase structure of TiO_2 can be used as an electrode in solar cells, lithium batteries and electrochromic devices [10].

The most basic problem in Dye-Sensitized Solar Cell (DSSC) is that its efficiency is still low compared to silicon solar cells. The low efficiency is caused by the low number of electrons produced by DSSC [11]. The current highest DSSC efficiency reaches 11 %, which is still lower than silicon solar cells which have an efficiency of around 20 % [12].

The low number of electrons produced of DSSC is due to the high recombination process of free electrons in the electron transfer process with oxidized dyes and electrolytes [13]. One of the reasons for the high rate of recombination is the limitation of electron diffusion in the TiO_2 layer. The low electron diffusion will result in electrons trapped at the boundary between TiO_2 particles [14]. Furthermore, the trapped electrons at the grain boundaries result in a higher chance of recombination. This low electron diffusion occurs due to less than optimal contact between particles [15].

Various attempts have been made to increase the efficiency of the DSSC. Increasing the efficiency of DSSC can be done by deposition or addition of nano-sized particles to the semiconductor layer structure by depositing Ag nanoparticles [16], doping Indium nanoparticles [17], adding bamboo charcoal powder particles to the TiO_2 layer [18] and addition of Li^+ particles [19]. Modifications to the semiconductor layer to increase efficiency have been carried out by making a ZnO/TiO_2 heterojunction photoanode layer [20] and making a SnO_2 - ZnO composite layer [21]. Dye engineering can also increase efficiency, use of a mercurochrome sensitizer [13], conjugation between ethylenedioxythiophene and dithienosilole in organic photosensitizers [22].

Clathrin is a protein that plays an important role in the formation of the vesicle layer which is responsible for transporting molecules within cells. This protein is found in every animal, human and plant body. This protein is shaped like a tripod: three leg spindles joined together on a single hub. This form of triskelion consists of three Clathrin heavy chains and three light chains. Clathrin molecules easily combine with each other to form a kind of honeycomb (honey/honeycomb) – like a lattice/web on the surface of cells. When triscelia interact, they form a polyhedral lattice surrounding the vesicle. The combination of Clathrin lattices is formed with sizes ranging from 30–100 nm from about 36 clathrin molecular units consisting of 108 heavy chain Clathrins and 108 light chain Clathrins. When the right molecule attaches to the Clathrin, the lattice structure of the Clathrin wraps around like a pocket. This Clathrin pocket will carry the molecule to its destination [23].

The use of Clathrin has been carried out on various materials as a biotech substrate. Materials that have been successful in adding Clathrin are graphene, polymers, glass, and metals [24]. It is also known that Clathrin can bond with Titanium Dioxide (TiO_2) [25]. Titanium Dioxide is a semiconductor material that is often used in DSSC.

As a protein that plays an important role in the cell transport system, Clathrin must be able to bind to ions in order to transport cells. Examples of ions that can bind to Clathrin are positive ions in iron [26]. As a type of protein, Clathrin is composed of various amino acids. According to the Lewis theory, amino acids can conduct electrons [27].

In Sadasivan's research, has demonstrated the use of the Clathrin protein, as a polyhedral framework for the preparation of inorganic Cadmium Sulfide nanoparticles – Clathrin protein. From this research it is known that Clathrin can be easily transformed without disassembly or significant structural changes in organic and inorganic nanostructures in solid form embedded in the skeleton (organoclay/organosilica) or CdS polyhedra. The specific feature of organoclay or CdS bonding with Clathrin is the electrostatic interaction between amino acid residues on organic surfaces and inorganic CdS materials. This study also shows that Clathrin can be used as a nanoscopic framework for the fabrication of a new type of composite nanoparticle in which the Clathrin skeleton is trapped in a matrix [28].

Increased efficiency can be done by increasing the number of electrons produced by DSSC by increasing the electron flow in the TiO_2 semiconductor, thereby reducing the chance of electron recombination with oxidized dyes.

In conventional DSSC there are gaps or empty spaces at the grain boundaries of the combined TiO_2 molecules. This gap or empty space causes the inhibition of the electron transport injected into the TiO_2 semiconductor. Due to the internal resistance of TiO_2 , the electron diffusion is inhibited, resulting in a higher chance of electron recombination to dyes and electrolytes [15].

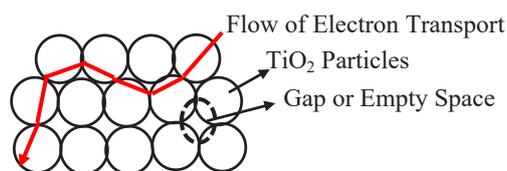


Fig. 1. Internal Resistance in DSSC [15]

In DSSC with added Clathrin, Clathrin molecules which have the ability to self-assemble and can wrap particles, and the size is 30 nm will wrap TiO_2 measuring 11–20 nm and fill gaps or empty spaces between TiO_2 grain boundaries so that it will reduce internal resistance and produce transport electrons are maximized.

In this study, an attempt to increase the number of electrons produced by DSSC was carried out by adding Clathrin protein to the TiO_2 layer so as to facilitate the flow of electrons in the TiO_2 semiconductor. The addition of Clathrin protein to the DSSC which will envelop the TiO_2 and dye layers resulting in maximum electron transfer because it can pass through all parts of the TiO_2 layer so that the number of electrons produced by DSSC will increase. Therefore, this study aims to determine the effect of adding Clathrin protein to the number of electrons produced in organic DSSC.

2. Materials and Methods

This study used an experimental method to determine the effect of adding Clathrin protein to the number of electrons produced in organic DSSC. The research procedure is carried out by preparing materials and equipment that will be used in the study, then DSSC assembly is carried out, and then testing of DSSC created. Preparation of materials needed are prepare protein from cow brain (Clathrin protein), TiO_2 paste, dye solution, electrolyte solution, carbon counter electrodes, and TCO glasses. Furthermore, the following are prepared equipment: Becker glass, measuring tube, pipette, magnetic stirrer, petri dish, Whatman filter paper, furnace, digital scale, mortar, scotch tape, multimeter, solar simulator, solar power meter, electrophoresis equipment, and centrifuges.

Clathrin protein was obtained from the isolation of protein in cow brain carried out in the lab. Biochemistry Brawijaya University. The steps for protein isolation and protein profiling using SDS-PAGE from cow brain tissue are as follows: homogenization of 300 mg of cow brain samples by grinding in a mortar and adding a solution of Phosphate Buffer Saline Tween pH 7.4 and

Phenyl Methyl Sulfonyl Fluoride 4 mM (5xvolume). Then sonicated for 10 minutes, the sonication method serves to shorten the contact of the sample and solvent by using ultrasonic waves at a frequency of 42 kHz. Then centrifuged at 6000 rpm for 15 minutes, to separate the cells molecularly by using gravity. After centrifugation, a supernatant layer was obtained which contained protein cells at the top and a precipitate at the bottom. After separating the supernatant from the sediment, the supernatant was added with ethanol in a volume ratio of 1:1. Ethanol was added to the topmost layer containing the plasmid, allowing it to form a precipitate at $-20\text{ }^{\circ}\text{C}$. The next step is centrifugation again at 10000 rpm, then Tris-HCl solvent is added with a volume ratio of 1:1 which serves to maintain the pH of the solution. The next step is to do a protein profile with Sodium Dodecyl Sulfate Electrophoresis – Polyacrylamide Gel (SDS-PAGE). The use of polyacrylamide to separate protein-containing materials by electrophoresis is called SDS-PAGE. Acrylamide gel was placed between two glass plates on SDS-PAGE. The Separating Gel solution was put in the electrophoresis plate and allowed to solidify. The gel with the most composition and placed on the bottom side is the separating gel. Then the Stacking Gel solution was added above the Separating Gel. Stacking Gel is a lower concentration polyacrylamide gel that is placed on top of the more concentrated separating gel (Separating Gel) on PAGE. The mixed gel was attached to a sample channel-forming comb and allowed to solidify and then the comb was removed. Then it was attached to the electrophoresis apparatus and the running buffer was poured. Then the gel is inserted into the plate. Furthermore, a complete electrophoresis apparatus was used. 1 L of sample was added and 14 L of Tris-HCL was added to a micro tube. Added with 15 L of Reducing Sample Buffer solution volume ratio 1:1. Then heated at a temperature of $100\text{ }^{\circ}\text{C}$ for 7 minutes in a water bath, and cooled at room temperature. Then injected into 10 wells with each well $30\text{ }\mu\text{L}$. Running with a voltage of 200 V until the blue color is $\pm 0.5\text{ cm}$ from the lower limit of the gel plate. Then the gel from the running process was soaked in a staining solution and then shaken using a shaker for 20 minutes. Then soaked in a de-colorizing solution (destaining) then shaken using a shaker until the band on the gel is clear. The bands in the electrophoresis gel were determined by the value of the Retention factor (Rf) and their respective relative molecular masses and then recorded in the form of data.

The procedure for forming the TiO_2 paste is as follows: polyvinyl Alcohol (PVA) as much as 1.5 g was dissolved in 13.5 ml of distilled water, then a rotary motor was used to stir the solution at a temperature of $80\text{ }^{\circ}\text{C}$ for ± 30 minutes until it thickens. The suspension acts as a binder or binder for making pastes. Then 0.5 grams of TiO_2 powder was added to the suspension, about 7.5 ml, to form a paste. Good viscosity of TiO_2 paste is obtained by adjusting the binder and water content in the mixture.

Papaya leaf chlorophyll extraction is used to prepare the dye. Following are the steps for chlorophyll extraction: a total of 100 grams of papaya leaves with 500 ml (w/v) of acetone P. A as solvent. First, weigh the papaya leaves to be used, then clean the papaya leaves and drain. Cut the papaya leaves into small pieces and blend until smooth. The smooth papaya leaves were then mixed with 500 ml of acetone P. A in a Becker glass. Then stirred using a rotary motor for 30 minutes so that the chlorophyll is extracted from the leaves, until the acetone P. A solution turns green and the leaves turn white. Then gauze paper (Whatman) was used to filter the leaf dregs so that 500 ml of the solution was obtained. After that the dye is stored in a dark bottle tightly closed so that the dye does not get influenced by the external environment which can decompose and avoid light which can reduce the absorption of the dye.

The process of making iodide/triiodide electrolyte solution is as follows, a mixture of 0.8 grams of Potassium Iodide (KI) (0.5 M) and 10 ml of PEG 400 was used to make an electrolyte solution. Next, 0.127 gram (0.05 M) of iodine (I_2) was added and stirred until the three ingredients were completely dissolved. Then the electrolyte solution is stored in a closed dark bottle.

The counter-electrode is made by heating TCO glass with wax until soot appears on the surface of the conductive area of the glass evenly. This combustion process causes the substrate to be coated with carbon (carbon counter-electrode). This carbon acts as a catalyst which makes the triiodide reduction process faster.

After each DSSC component has been successfully made, then assembly is carried out to form solar cells with the following steps: on Transparent Conduction Oxide (TCO) with dimensions

of $1.5 \times 1.5 \text{ cm}^2$ in the conductive part using scotch tape an area of $1 \times 1 \text{ cm}^2$ is formed to deposit TiO_2 . The thickness of the TiO_2 paste is adjusted based on the thickness of the scotch tape.

The doctor blade technique was used to deposit TiO_2 on the prepared area on the conductive glass. The TiO_2 paste was flattened using a stirring rod. Furthermore, the layer is allowed to dry for 15 minutes and sintered/burned at a temperature of $450 \text{ }^\circ\text{C}$ for 30 minutes in the furnace. Conductive glass that has been deposited with TiO_2 paste and has been sintered within 24 hours is immersed in a dye solution containing chlorophyll until the TiO_2 layer on the conductive glass is green, indicating that the surface of TiO_2 has adsorbed chlorophyll.

Subsequently, Clathrin solution was applied to the TiO_2 layer and dye with varying concentrations of 0 %, 25 %, 50 % and 75 %. Variations in the percentage of Clathrin content were carried out to determine its effect on the number of electrons.

The electrolyte solution was then dripped onto the TiO_2 /dye/Clathrin layer. The counter-electrode that has been given a carbon catalyst is then placed on a layer of TiO_2 /dye/Clathrin/electrolyte resembling a sandwich structure with an area of 0.5 cm left on both ends of the electrode which functions as an electrical contact. So that the two conductor glass electrodes are connected tightly and firmly clamped using a clip. Furthermore, testing of Energy Dispersive X-ray Spectroscopy (EDS), Fourier Transform Infra Red (FTIR) and measurement of electric current in the prepared solar cells were carried out.

Measurement of DSSC current and voltage to determine the number of electrons produced is carried out in a research installation.

The electric current and voltage on the DSSC are generated by lighting using halogen lamps in the solar simulator, and then the resulting change in current and voltage is measured using a data logger to determine the performance of the DSSC. Schematically, the research installation is shown in Fig. 2.

The research installation consisting of a solar simulator which is a place to provide lighting to the DSSC so as to produce currents and voltages that will be measured to determine the performance of the DSSC. The solar simulator has a length of 300 mm, a width of 300 mm, and a height of 500 mm. The solar simulator equipment consists of 1000 W/m^2 intensity halogen lamps to provide lighting, Ultra Violet and Infra-Red filters to produce visible light, temperature sensors, intensity sensors, and fans that function to maintain a constant temperature. The current and voltage data generated in the DSSC were measured using the Arduino Uno ATmega 328 data logger microcontroller.

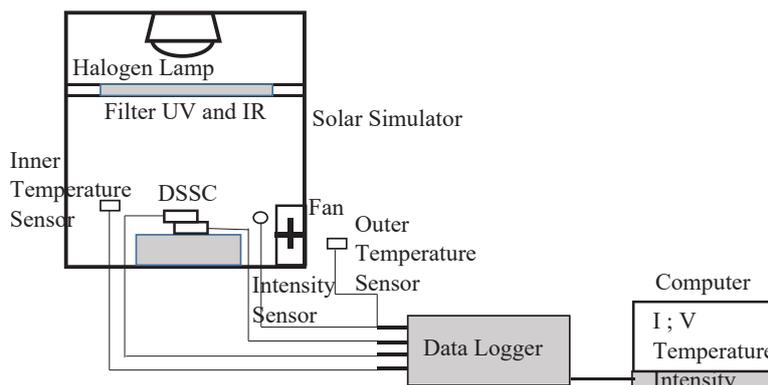


Fig. 2. Research Installation Scheme

The ASTM E948 standard specifies a set of general test conditions and methods for measuring the electrical performance parameters of photovoltaic cells [29]. The Standard Condition Tests are as follows:

1. The temperature of the device under test is $25 \pm 1 \text{ }^\circ\text{C}$.
2. $\text{AM1.5} \pm 25 \%$ light spectral distribution.
3. The measured irradiation on the solar cell plane is $1000 \text{ W/m}^2 \pm 2 \%$.

The stages of data collection are as follows: equipment arranged according to **Fig. 2**. Then, the DSSC is placed in the center with the distance to the exposure adjusted, so that the intensity is 1000 W/m^2 . Next, the lamp is turned on, thus, the current and voltage appear at DSSC. Then the DSSC was varied the percentage of Clathrin protein content on TiO₂, namely 0 %, 25 %, 50 %, and 75 %. Current data and voltage data obtained are then transferred to computer to calculate the number of electrons generated.

3. Results and discussion

The characterization of the DSSC layer with Energy Dispersive X-ray Spectroscopy (EDS) aims to analyze the elemental composition of the sample surface. **Table 1** shows the composition and variation of Clathrin content, namely 0 %, 25 %, 50 % and 75 % in DSSC.

Table 1
Composition and Content of Clathrin in each Percentage DSSC

Element	Weight %			
	0 %	25 %	50 %	75 %
Carbon	1.414	2.881	7.741	10.499
Oxygen	41.559	45.223	46.831	47.24
Sodium	0.429	0.616	1.777	0.962
Phosphor	–	0.16	1.648	2.345
Chlorine	0.325	0.565	1.128	1.547
Titanium	48.751	47.647	38.585	35.007
Tin	7.522	2.908	2.29	2.401

From the results of the EDS test, the elemental content and composition in the DSSC layer are shown in **Table 1** DSSC with 0 % Clathrin content contains elements of Titanium (Ti) and Oxygen (O) respectively 48.751 % and 41,559 %. The presence of Ti and O elements indicates the presence of TiO₂ molecules. While the presence of the element Carbon (C) of 1.414 % is an element in the chlorophyll dye. The presence of the elements Na, Cl and Sn are elements found in FTO glass.

In the TiO₂ nanoporous structure, the carbon element in the dye serves as a source of electrons which will be excited if it is subjected to external energy. These excited electrons will flow through the conduction region of TiO₂ causing an electric current to be generated by the DSSC. The high amount of carbon in the dye causes more electrons to be generated thereby increasing the electric current of the DSSC.

The high electrical conductivity of carbon is due to the fact that carbon is a source of electrons for the dye. The presence of unpaired valence electrons on carbon causes electrons on carbon to be easily released or excited when exposed to small energies. Dyes containing chlorophyll have the ability to absorb photon energy from light and utilize this light energy to release electrons contained in carbon.

Table 1 also shows data from Clathrin protein-deposited DSSC. From the table it appears the emergence of a new element, namely phosphorus. From the results of the EDS test, it is known that the addition of Clathrin to DSSC gives rise to a new element, namely phosphorus. Phosphorus is one of the elements that make up proteins, in addition to the elements carbon and oxygen [30]. From **Table 1** it can be seen that with increasing protein content added to DSSC, the elements carbon, oxygen and phosphorus also increased.

In the nanoporous structure of TiO₂, elements such as carbon, oxygen and phosphorus can function as electron transfer connectors. The hexagonal layer formed by the carbon molecule is three electrons used to make covalent bonds with the nearest neighboring C atom, so that there are free electrons that can move on the surface of the layer. The ability to conduct electric current by carbon is due to the presence of these free electrons [31].

Carbon is found in a number of very diverse forms because it can form many different types of bonds due to its unique electronic structure. Its six electrons are arranged around the nucleus

with two electrons in the innermost shell tightly bound and four electrons in the outer valence shell. The minimum energy ground state of carbon has two valence electrons in the 2 s subshell and two in the 2 p subshell. What makes carbon special is that it only takes a small excitation of an electron in the 2 s subshell to be promoted to the 2 p subshell. This is very advantageous because all four orbitals become exactly half full and can be used to form strong covalent bonds. The four orbitals on carbon that are half full provide the ability for electrons on carbon to move freely and make the carbon atom able to give rise to high electrical conductivity.

Phosphorus with five valence electrons is an *N*-type donor or doping agent. The conduction of electric current can be carried out by phosphorus because the fifth electron in the phosphorus is not bound anywhere [32]. Phosphorus is commonly used as an electron donor in semiconductors so that it becomes an *N*-type semiconductor. Phosphorus is a pentavalent element (there are 5 electrons as valence electrons). When there is an electric field on the phosphorus, the fifth electron is easily released and moved because the bond is weak. If a pure semiconductor gets the donation (donor) of these electrons, the resistivity of the *N*-type semiconductor will be low.

For example, a silicon semiconductor is doped by phosphorus causing the four valence electrons of the phosphorus to form covalent bonds with the nearby silicon atom, so that the fifth valence electron from the phosphorus will freely move to the original atom. Thermal energy will be generated from these electrons to break bonds even at room temperature, then along the crystal the electrons move so that in the semiconductor there is an increase in electron current. The transfer of electrons to the conduction band causes the formation of positively charged phosphorus ions. With the free movement of one of the phosphorus electrons along the crystal, the phosphorus atom is called an impurity donor. The positively charged phosphorus atom is due to the transfer of one of the electrons, has no freedom of movement in the crystal and does not produce a current. Therefore, if a semiconductor is given an impurity donor, free electrons will be produced without the formation of holes, so that the concentration of free electrons in the semiconductor can be adjusted. Semiconductors doped with impurity atoms (donors) are called *N*-type semiconductors because they have more electrons than holes [33].

While oxygen is an electron acceptor, which will capture the electrons produced by the dye [34]. The composition of 8 protons and 8 electrons in the oxygen atom gives oxygen the atomic number 8 ($Z=8$). The atomic number 8 means that oxygen has an electron configuration of 2,6 (requires 2 electrons). With the number of valence electrons 6, the stability (octet) of the electron configuration of the oxygen atom can be achieved if oxygen gains or accepts 2 electrons. So that the electrons from the dye will be captured by oxygen to create a stable electron configuration in oxygen.

In the presence of carbon, oxygen and phosphorus in TiO_2 , it can accelerate the flow of charge from the dye which is passed on by these elements to the next TiO_2 particle. This incident shortens the charge delivery distance in the TiO_2 layer, resulting in an increase in the number of electrons and electric current in the DSSC.

The functional groups in the DSSC layer due to the addition of Clathrin protein can be determined by testing the Fourier Transform Infra-Red (FTIR) spectrophotometer. Functional groups play a role in defining the characteristics of a carbon compound based on the atomic group or atoms of the carbon compound and are part of the molecule that is reactive to certain reagents.

The results of the FTIR test for each concentration of Clathrin protein addition to TiO_2 are shown in **Fig. 3**. From the results of the FTIR test, it can be seen that the functional groups formed in the DSSC layer. **Fig. 3** shows the appearance of a peak at the wave number $3300\text{--}3500\text{ cm}^{-1}$ which indicates the presence of an N-H group of amine/amide. Next, a peak appears at the wave number $2500\text{--}700\text{ cm}^{-1}$ which indicates the presence of an O-H group of hydrogen/phenol bonded alcohol. **Fig. 3** shows the appearance of a peak at the wave number $2850\text{--}2970\text{ cm}^{-1}$ which indicates the presence of a C-H group of Alkanes. From **Fig. 3** it is also known that a peak appears at the wave number $1610\text{--}1680\text{ cm}^{-1}$ indicating the presence of a C=C Alkene group. Furthermore, it is known that a peak appears at the wave number $1500\text{--}1600\text{ cm}^{-1}$ explaining the presence of the C=C group of the Aromatic Ring. **Fig. 3** also shows that peaks appear at wave numbers $1500\text{--}1570\text{ cm}^{-1}$ and $1300\text{--}1370\text{ cm}^{-1}$ which indicate the presence of NO_2 groups or nitro compounds. Then it is also known from **Fig. 3**, a peak appears at the wave number $1050\text{--}1300\text{ cm}^{-1}$ which indicates the

presence of the C-O group of alcohol. Next, a peak appears at the wave number 500–900 cm^{-1} which indicates the presence of a TiO_2 group [35]. The presence of N-H groups of amines, C-O, O-H, alkenes, aromatics and nitro compounds which are known from the FTIR test results indicate the presence of groups that make up amino acids. Amino acids are the building blocks of protein [36].

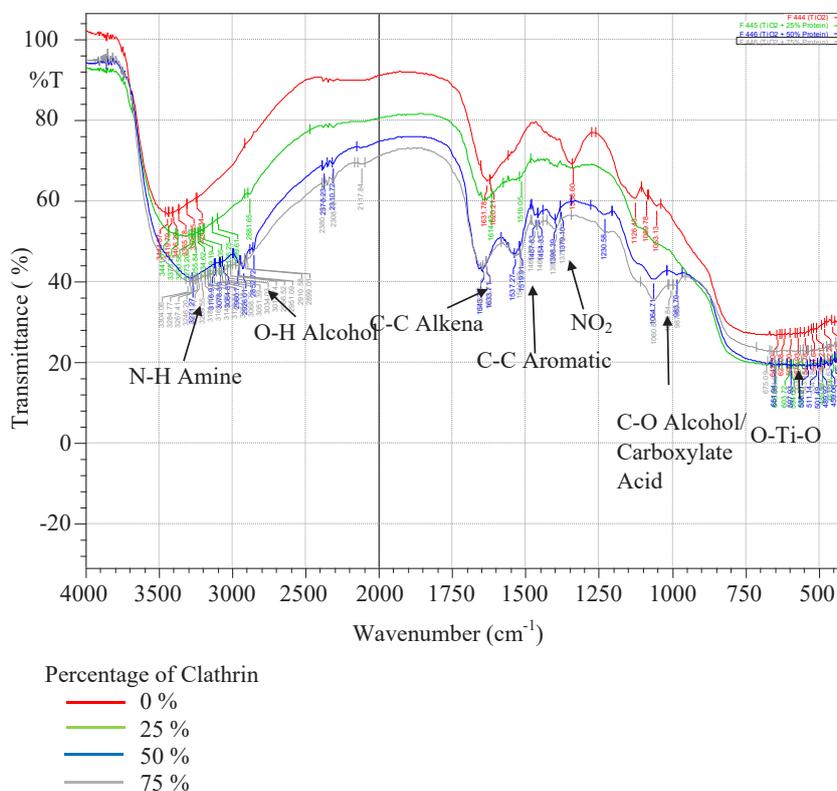


Fig. 3. Functional Groups in DSSC

Proteins are composed of chains of amino acids linked together by bonds called peptide bonds. Oxygen, hydrogen, carbon and nitrogen are the basic constituents of amino acids. In addition there are elements of iron, phosphorus, iodine and cobalt which make up certain amino acids. Peptide bond is a primary level bond resulting from the bonding of one amino group with the carboxyl group of another amino acid. A dipeptide bond is a shared bond between two amino acid molecules. If three amino acid molecules are bonded together, it is called a tripeptide and if there are more molecules bound together it is called a polypeptide. Proteins are polypeptide bonds because proteins consist of large amounts of peptide bonds of amino acids. Amino acids are formed by bonds between an amino group ($-\text{NH}_2$) and a carboxyl group ($-\text{COOH}$), one of which is located at the C atom right next to the carboxyl group (C alpha atom) [37].

Proteins contain large amounts of charge and have amphoteric properties that can react with acids or bases because at the end of the molecular chain there are amino groups and free carboxyl groups. Proteins will be positively charged in acidic solutions because the amino groups react with H^+ . If it is subjected to electrolysis, then there is a movement of protein molecules towards the cathode. While protein molecules are negatively charged in alkaline solutions because they will react as acids causing movement towards the anode by protein molecules [38].

The functional groups that make up amino acids can increase the electron transfer process in the DSSC layer because amino acids have amphoteric properties that can act as acids (donating protons to strong bases) and can act as bases (accepting protons from strong acids) [39]. Proteins are composed of amino acids that have one carboxyl group and one amino group. The structure of the amino acids can be seen in **Fig. 4**.

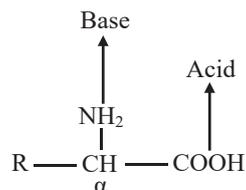


Fig. 4. Amino Acid Structure [39]

Amino acids in the form of zwitterions, namely the carboxyl group of amino acids can lose hydrogen ions to become negatively charged and amine groups can accept hydrogen ions to become positively charged [40]. The zwitterion form of the amino acid can be seen in Fig. 5.

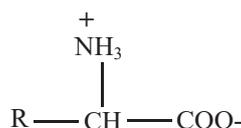


Fig. 5. Zwitterion Forms of Amino Acids [40]

From the results of the FTIR test, it appears that the higher the concentration of Clathrin in TiO_2 , the sharper absorption occurs in the wave number of the FTIR spectrum for the protein constituent groups. The sharper the absorption intensity indicates the higher the structure or functional group of amino acids formed and indicates the greater the energy absorbed by the functional groups formed from the increasing concentration of Clathrin protein in DSSC [41].

Current measurement aims to determine the electric current and the number of electrons generated from each DSSC. The results of the measurement of electric current and the number of electrons produced by DSSC with variations in the percentage of Clathrin content in TiO_2 are 0 %, 25 %, 50 % and 75 % as shown in Table 2.

Table 2

Test Results of Electric Current and Number of Electrons for various Clathrin Contents

Content of Clathrin	0 %	25 %	50 %	75 %
Electric Current (mA)	0.353	0.917	2.643	5.247
Number of Electron	2.21×10^{15}	5.73×10^{15}	1.65×10^{16}	3.28×10^{16}

From Table 2 it can be seen that with the increasing content of Clathrin in the DSSC, it results in an increase in the electric current and the number of electrons produced. The highest number of electrons is at 75 % Clathrin content and 5.247 mA electric current is 3.28×10^{16} electrons. The electrons generated are derived from the dye chlorophyll adsorbed on TiO_2 . These electrons are excited as a result of the absorption of photon energy by the dye and flow through the TiO_2 semiconductor. The increasing content of Clathrin in DSSC causes a decrease in the resistance to electron flow from the dye through the TiO_2 semiconductor and reduces the chance of electron recombination with the dye and electrolyte. The decrease in the electron flow resistance causes an increase in the number of electrons produced, thereby increasing the electric current generated by the DSSC.

The performance of the DSSC is strongly related to the electron transport resistance in the semiconductor photoanode. Modification of the interfacial and transport networks will significantly change the electron transport barrier. TiO_2 photoanode plays an important role in determining the performance of DSSC. A typical photoanode for DSSC applications generally consists of a porous TiO_2 layer coated on a conducting substrate (i.e., FTO) with a dye adsorbed on the TiO_2 surface. The porous TiO_2 layer basically functions for the collection and transport of photoelectrons injected by the photo-exciton dye through the TiO_2 conduction band to the conducting substrate and then to the external circuit.

The high porosity and suitable pore size of the porous TiO_2 layer increase the dye adsorption capacity and light scattering ability, which imparts high light harvesting yields and increased energy conversion efficiency. However, photoanodes constructed with nanoporous TiO_2 layers have several drawbacks. The porous nature of the TiO_2 layer may result in a portion of the FTO surface being uncovered. This state is, in essence, equivalent to the direct recombination of photoelectrons with dye, resulting in a decrease in energy conversion efficiency [42].

From the current and voltage test results on the DSSC, it appears that the addition of Clathrin protein will increase the number of electrons produced by the DSSC, this can be seen by increasing the current and voltage values of the DSSC. The increase in the number of electrons in DSSC is due to the compositing of TiO_2 with Clathrin, with the addition of Clathrin protein in DSSC it will fill the cavities or gaps between TiO_2 particles can increase connectivity between TiO_2 particles and produce closer contact of the semiconductor oxide thereby accelerating charge transfer in the photoanode. The increased connectivity between TiO_2 particles causes a reduction in the electron flow resistance in the DSSC layer by creating a short path of electron flow and thereby serves as an electron bridge between the porous TiO_2 molecules thereby reducing the possibility of recombination and resulting in an increase in the efficiency of the DSSC.

The addition of Clathrin to DSSC causes an increase in carbon, oxygen and phosphorus elements in DSSC, with the presence of these elements which are protein-forming elements in the DSSC layer, which is useful as an electron transfer bridge in TiO_2 which has a porous structure, thereby increasing the performance of DSSC. The increase in the number of electrons generated in the DSSC is due to the protein molecules added to the DSSC filling the gaps or empty spaces in TiO_2 because Clathrin protein is zwitterionic (acidic and basic) so that it can function as an electron bridge between the porous TiO_2 particles which produces reducing the resistance of the flow of electrons results in an increase in the electric current generated. Electron bridges can occur because of the ability of Clathrin proteins to carry out acid and base reactions at once or known as zwitterions [39].

Fig. 6 shows the Zwitterion phenomenon that occurs in the gap or empty space between TiO_2 molecules that have been filled with Clathrin protein, namely when electrons flow from chlorophyll will be captured by Clathrin protein molecules through an acid reaction, in acidic conditions the protein will donate protons to the base so that the protein tends to contain electrons and can be considered as a negative pole (anode), whereas in basic reactions, proteins will accept protons from acids so that proteins tend to contain protons and can be considered as positive poles (cathode). In this state, electrons will flow from acid to base. Through the alkaline reaction, these electrons will be released to TiO_2 so that electrons flow from chlorophyll to TiO_2 through the electron bridge of the protein Clathrin. So that the electrons can pass through all the pathways between the TiO_2 particles and increase the electric current in the DSSC.

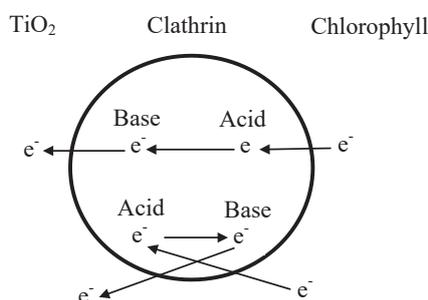


Fig. 6. Zwitterion phenomenon in the gap between TiO_2 particles [39]

From the number of electrons and currents generated in this study, the resulting efficiency can be found which is 1.465 %. When compared with other studies, namely the results of Chava's research which deposited indium on DSSC resulted in an efficiency of 1.8 % [17], Patle deposited copper resulted in an efficiency of 1.67 % [43] and Zainal who deposited Zn on DSSC resulted in an efficiency of 0.89 % [44], the difference is not very significant. This proves that organic

material, namely Clathrin protein can be used as a material that can increase the number of electrons generated in DSSC.

The limitation of this study is that research on the durability of DSSC has not been carried out because research on the durability of DSSC is a separate but interrelated topic. This causes the weakness of this study because the time period or life time of using DSSC is unknown. Therefore, in the future, researchers plan to conduct research on the effect of using Clathrin protein on the durability of DSSC.

4. Conclusions

Based on the results of research and discussion, it can be concluded that with increasing Clathrin content in DSSC, it will increase the number of electrons and electric current produced by DSSC. The increase in the number of electrons is due to the addition of Clathrin which reduces the electron flow resistance and decreases the chance of electron recombination so that it will result in an increase in the electric current in the DSSC. The highest number of electrons is in the 75 % Clathrin content and the current is 5.247 mA, which is 3.28×10^{16} electrons.

Acknowledgments

The authors would like to thank the Faculty of Engineering and LP2M State University of Malang (Indonesia), which has support the writing of this research article.

References

- [1] Duffie, A. J., Beckman, A. W. (2013). *Solar Engineering of Thermal Processes*. Wiley. doi: <https://doi.org/10.1002/9781118671603>
- [2] Trends 2018 in Photovoltaic Applications. Report IEA PVPS T1-34:2018. International Energy Agency. Available at: https://iea-pvps.org/wp-content/uploads/2020/01/2018_iea-pvps_report_2018.pdf
- [3] Bharam, V. (2012). Advantages and challenges of silicon in the photovoltaic cells. Available at: https://commons.trincoll.edu/wp-content/blogs.dir/438/files/2013/03/Final-Paper-Vishal-Bharam_-_Silicon-in-Photovoltaic-Cell.pdf
- [4] Fthenakis, V. M., Kim, H. C., Alsema, E. (2008). Emissions from Photovoltaic Life Cycles. *Environmental Science & Technology*, 42 (6), 2168–2174. doi: <https://doi.org/10.1021/es071763q>
- [5] O'Regan, B., Grätzel, M. (1991). A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films. *Nature*, 353 (6346), 737–740. doi: <https://doi.org/10.1038/353737a0>
- [6] Wongcharee, K., Meeyoo, V. (2008). Improvement of TiO₂ properties for Dye-Sensitized Solar Cell by hydrothermal and sol-gel processes. In *Technology and Innovation for Sustainable Development Conference*. Khon Kaen University, p. 485–488.
- [7] Gratzel (2003). Review Dye-Sensitized Solar Cells. *Journal of Photochemistry and Photobiology C: Photochemistry reviews*, 4, 145–153.
- [8] Tan, W., Chen, J., Zhou, X., Zhang, J., Lin, Y., Li, X., Xiao, X. (2008). Preparation of nanocrystalline TiO₂ thin film at low temperature and its application in dye-sensitized solar cell. *Journal of Solid State Electrochemistry*, 13 (5), 651–656. doi: <https://doi.org/10.1007/s10008-008-0605-4>
- [9] Morgan, D., Waclawik, E., Frost, R. (2006). Relationship of Titania Nanotube Binding Energies and Raman Spectra. 2006 International Conference on Nanoscience and Nanotechnology. doi: <https://doi.org/10.1109/iconn.2006.340550>
- [10] Maiyalagan (2006). Fabrication and characterization of uniform TiO₂ nanotube arrays by sol-gel template method. *Bulletin of Materials Science*, 29 (7), 705–708. Available at: <https://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.601.1311&rep=rep1&type=pdf>
- [11] Nazeeruddin, M. K., Baranoff, E., Grätzel, M. (2011). Dye-sensitized solar cells: A brief overview. *Solar Energy*, 85 (6), 1172–1178. doi: <https://doi.org/10.1016/j.solener.2011.01.018>
- [12] Halme, J. (2002). Dye-sensitized nanostructured and organic photovoltaic cells: technical review and preliminary tests. Espoo. Available at: <https://core.ac.uk/download/pdf/84757081.pdf>
- [13] Hara, K. (2000). Highly efficient photon-to-electron conversion with mercurochrome-sensitized nanoporous oxide semiconductor solar cells. *Solar Energy Materials and Solar Cells*, 64 (2), 115–134. doi: [https://doi.org/10.1016/s0927-0248\(00\)00065-9](https://doi.org/10.1016/s0927-0248(00)00065-9)
- [14] Li, X. D., Zhang, D. W., Sun, Z., Chen, Y. W., Huang, S. M. (2008). Open-circuit voltage improvement by using TiO₂ nanotubes as a working electrode of dye-sensitized solar cell. 2008 2nd IEEE International Nanoelectronics Conference. doi: <https://doi.org/10.1109/inec.2008.4585592>
- [15] Yu, J., Wang, D., Huang, Y., Fan, X., Tang, X., Gao, C. et al. (2011). A cylindrical core-shell-like TiO₂ nanotube array anode for flexible fiber-type dye-sensitized solar cells. *Nanoscale Research Letters*, 6 (1). doi: <https://doi.org/10.1186/1556-276x-6-94>

- [16] Hu, H., Shen, J., Cao, X., Wang, H., Lv, H., Zhang, Y. et. al. (2017). Photo-assisted deposition of Ag nanoparticles on branched TiO₂ nanorod arrays for dye-sensitized solar cells with enhanced efficiency. *Journal of Alloys and Compounds*, 694, 653–661. doi: <https://doi.org/10.1016/j.jallcom.2016.10.057>
- [17] Chava, R. K., Kang, M. (2017). Improving the photovoltaic conversion efficiency of ZnO based dye sensitized solar cells by indium doping. *Journal of Alloys and Compounds*, 692, 67–76. doi: <https://doi.org/10.1016/j.jallcom.2016.09.029>
- [18] Chou, C.-S., Chen, C.-Y., Lin, S.-H., Lu, W.-H., Wu, P. (2015). Preparation of TiO₂/bamboo-charcoal-powder composite particles and their applications in dye-sensitized solar cells. *Advanced Powder Technology*, 26 (3), 711–717. doi: <https://doi.org/10.1016/j.apt.2014.12.013>
- [19] Kuang, D., Klein, C., Snaith, H. J., Moser, J.-E., Humphry-Baker, R., Comte, P. et. al. (2006). Ion Coordinating Sensitizer for High Efficiency Mesoscopic Dye-Sensitized Solar Cells: Influence of Lithium Ions on the Photovoltaic Performance of Liquid and Solid-State Cells. *Nano Letters*, 6 (4), 769–773. doi: <https://doi.org/10.1021/nl060075m>
- [20] Javed, H. M. A., Que, W., Yin, X., Xing, Y., Shao, J., Kong, L. B. (2016). ZnO/TiO₂ nanohexagon arrays heterojunction photoanode for enhancing power conversion efficiency in dye-sensitized solar cells. *Journal of Alloys and Compounds*, 685, 610–618. doi: <https://doi.org/10.1016/j.jallcom.2016.05.325>
- [21] Sujinnapram, S., Moungsrijun, S. (2015). Additive SnO₂-ZnO Composite Photoanode for Improvement of Power Conversion Efficiency in Dye-sensitized Solar Cell. *Procedia Manufacturing*, 2, 108–112. doi: <https://doi.org/10.1016/j.promfg.2015.07.019>
- [22] Zeng, W., Cao, Y., Bai, Y., Wang, Y., Shi, Y., Zhang, M. et. al. (2010). Efficient Dye-Sensitized Solar Cells with an Organic Photosensitizer Featuring Orderly Conjugated Ethylenedioxythiophene and Dithienosilole Blocks. *Chemistry of Materials*, 22 (5), 1915–1925. doi: <https://doi.org/10.1021/cm9036988>
- [23] Pearse, B. M. (1976). Clathrin: a unique protein associated with intracellular transfer of membrane by coated vesicles. *Proceedings of the National Academy of Sciences*, 73 (4), 1255–1259. doi: <https://doi.org/10.1073/pnas.73.4.1255>
- [24] Dannhauser, P. N., Platen, M., Böning, H., Schaap, I. A. T. (2015). Durable protein lattices of clathrin that can be functionalized with nanoparticles and active biomolecules. *Nature Nanotechnology*, 10 (11), 954–957. doi: <https://doi.org/10.1038/nnano.2015.206>
- [25] Schoen, A. P., Schoen, D. T., Huggins, K. N. L., Arunagirinathan, M. A., Heilshorn, S. C. (2011). Template Engineering Through Epitope Recognition: A Modular, Biomimetic Strategy for Inorganic Nanomaterial Synthesis. *Journal of the American Chemical Society*, 133 (45), 18202–18207. doi: <https://doi.org/10.1021/ja204732n>
- [26] Templeton, D. (2002). *Molecular and cellular iron transport*. CRC Press, 848. doi: <https://doi.org/10.1201/9780367800536>
- [27] Miessler, G. L., Tarr, D. A. (1991). *Inorganic chemistry*. Pearson Prentice-Hall.
- [28] Sadasivan, S., Patil, A. J., Bromley, K. M., Hastie, P. G. R., Banting, G., Mann, S. (2008). Novel protein-inorganic nanoparticles prepared by inorganic replication of self-assembled clathrin cages and triskelia. *Soft Matter*, 4 (10), 2054. doi: <https://doi.org/10.1039/b803437k>
- [29] ASTM E948-09. Standard Test Method for Electrical Performance of Photovoltaic Cells Using Reference Cells Under Simulated Sunlight. doi: <https://doi.org/10.1520/e0948-09>
- [30] Fraga, F., Rios, A. F., Perez, F. F., Figueiras, F. G. (1998). Theoretical limits of oxygen:carbon and oxygen:nitrogen ratios during photosynthesis and mineralisation of organic matter in the sea. *Scientia Marina*, 62 (1-2), 161–168. Available at: https://pdfs.semanticscholar.org/bebc/e5e0462fea626fd4f413cea589cf390f8b64.pdf?_ga=2.127582797.1903911800.1628247763-1132255821.1618302288
- [31] Littlejohn, S. D. (2014). *Electrical Properties of Graphite Nanoparticles in Silicone: Flexible Oscillators and Electromechanical Sensing*. Springer, 166. doi: <https://doi.org/10.1007/978-3-319-00741-0>
- [32] Pierret, P. F. (2003). *Advanced Semiconductor Fundamentals: Volume VI*. Pearson. Available at: https://www.lti.kit.edu/rd_download/material_SS_2006/Advanced_Semiconductor_Fundamentals.pdf
- [33] Neamen, D. A. (2010). *Microelectronics: Circuit Analysis and Design*. McGraw-Hill. Available at: <http://powerunit-ju.com/wp-content/uploads/2018/01/Electronics-book.pdf>
- [34] Rich, P. R. (2003). The molecular machinery of Keilin's respiratory chain. *Biochemical Society Transactions*, 31 (6), 1095–1105. doi: <https://doi.org/10.1042/bst0311095>
- [35] Skoog, D. A., Holler, F. J., Crouch, S. R. (2007). *Principles of Instrumental Analysis*. Thomson Brooks/Cole. Available at: <https://drive.google.com/file/d/1sPpyXZCSd01zOSZ290j-wwfcnA6frg4n/view?usp=sharing>
- [36] Thatcher, R. W. (1921). *The chemistry of plant life*. McGraw-Hill. Available at: https://drive.google.com/file/d/1bR8_iLSrxM-NUiUNb1kLTqwONU6T7EEUw/view?usp=sharing
- [37] Cozzzone, J. A. (2002). *Proteins: Fundamental Chemical Properties*. Encyclopedia of Life Sciences. Available at: <http://www.sop.inria.fr/axis/cost282/kelsi04/Brito/Brito3.pdf>
- [38] Louda, D. W. (2012). *Overview of Biomolecules*. Florida Atlantic University. Available at: http://med.fau.edu/students/md_m1_orientation/Overview.pdf

- [39] Lin, S.-P. (2010). Amino Acids & Proteins. Institute of Biomedical Available at: <https://drive.google.com/file/d/1qY55WQDAFx8d2m8QTDxzjwHUnZDbsf3W/view?usp=sharing>
- [40] Dorothy, J.-L. (1934). The Proteins as Colloidal Electrolytes. Available at: <https://drive.google.com/file/d/1V83KfqvGAO49F-0naAPrdKWpONk8kU0SQ/view?usp=sharing>
- [41] Coates, J. (2006). Interpretation of Infrared Spectra, A Practical Approach. Encyclopedia of Analytical Chemistry. doi: <https://doi.org/10.1002/9780470027318.a5606>
- [42] Diamant, Y., Chappel, S., Chen, S. G., Melamed, O., Zaban, A. (2004). Core-shell nanoporous electrode for dye sensitized solar cells: the effect of shell characteristics on the electronic properties of the electrode. Coordination Chemistry Reviews, 248 (13-14), 1271–1276. doi: <https://doi.org/10.1016/j.ccr.2004.03.003>
- [43] Patle, L. B., Chaudhari, A. L. (2016). Performance of DSSC with Cu Doped TiO₂ Electrode Prepared by Dip Coating Technique. International Journal of Scientific & Engineering Research. 7 (8), 1004–1009. Available at: <https://drive.google.com/file/d/1vJu8D3WD3f4dfNxbJcpgsHR4oaLOwvsz/view?usp=sharing>
- [44] Arifin, Z., Soeparman, S., Widhiyanuriyawan, D., Purwanto, A., Dharmanto (2017). Synthesis, characterisation, and fabrication hollow fibres of Zn-doped TiO₂ for dye-sensitized solar cells. Journal of Engineering Science and Technology, XX (Y). Available at: <https://drive.google.com/file/d/1fKYijYKU3mz7J5tt0CAX-WbDzMJsvLBx/view>

Received date 27.07.2021

Accepted date 18.01.2022

Published date 31.03.2022

© The Author(s) 2022

This is an open access article
under the Creative Commons CC BY license

How to cite: Trihutomo, P., Marji, M., Harly, M., Wahyudi, B. A., Radja, M. B. (2022). The effect of Clathrin protein addition on increasing the number of electrons in organic Dye-Sensitized Solar Cell (DSSC). EUREKA: Physics and Engineering, 2, 15–27. doi: <https://doi.org/10.21303/2461-4262.2022.001957>