

Development of Solid-state Photoelectrochemical Solar Cell Circuits Based on Chitosan-PEG Blend Electrolyte

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Abstract- Solid-state photoelectrochemical solar cells were fabricated using cadmium sulfide (CdS) films as photoanode and polymers blend based on chitosan and polyethylene glycol (PEG) as a solid electrolyte. CdS films were deposited onto the ITO glass substrates by chemical bath deposition method. The solid-state electrolyte was made by blending between chitosan and PEG as matrices for oxidation-reduction (redox) couple from potassium iodate/iodine (KI/I₂). The individual solar cells were formed into the sandwich structure ITO/CdS/Gel electrolyte/ITO. Influence of KI/I₂ in the polymer blend matrix to the ionic conductivity of electrolyte was studied. It found that addition of KI/I₂ into the polymers blend electrolyte significantly affected the performance of the solar cells. Irradiation source also significantly affected the performance of the solar cells, here was used solar light source and tungsten lamp source. To increase the electricity production, the four individual solid-state photoelectrochemical solar cells were connected together in the series, parallel and series-parallel combination circuits. Series circuit resulted in the open-circuit voltage (V_{oc}) is almost four times that of a single cell, on the other hand, the parallel circuit resulted in the short-circuit current (I_{sc}) is also almost four times that of a single cell. Meanwhile, the combination of series-parallel circuits produced a short-circuit current (I_{sc}) and an open-circuit voltage (V_{oc}) values that are between the value generated by the other series and parallel circuits alone.

Keywords- Cadmium sulphide, chitosan-PEG blend, photoelectrochemistry, polymer electrolyte, solar cell.

1. Introduction

Production of electricity for daily use can be realized by converting solar energy into electrical energy using solar cell devices that can be fabricated based on the junction of semiconductor materials [1-6]. Commercial solar cells that much gained in the market today is of the p-n junction of the silicon semiconductor [7-9]. Currently, it has been developed various variants of solar cell based on different materials and structures, either with a simple materials and structures up to a more complex structure, one of which is a photoelectrochemical solar cell [10].

Photoelectrochemical solar cell is a type of solar cell based on the junction between semiconductor electrode and electrolyte [10,11]. In the photoelectrochemical cell, both

semiconductor electrode as working electrode and counter electrode are immersed in electrolyte containing redox couples. The contact between the two materials with different phase causes the formation of the depletion region in the semiconductor side and Helmholtz layer at the side of the electrolyte [12]. When the semiconductor electrode is exposed by solar light photons with suitable energy, the negative (electrons) and positive (holes) charge carriers are generated in the semiconductor material, both the different charges move in opposite directions. The negative charge carriers (electrons) move through the bulk of the semiconductor to the current collector. This electrons movement is driven by the electrostatic forces in the depletion region of the semiconductor photoelectrode towards the outside circuit and generate electricity, then enter the cells to begin the next cycle. On the other hand, the positively charged holes that

generated in the valence band of semiconductor move into the electrolyte to initiate a reaction in the electrolyte. This cycle mechanism produces the process of converting solar energy into electricity directly [4].

In the early days, electrolytes used in photoelectrochemical solar cells is a liquid phase, but liquid electrolytes have the disadvantage that is easy to leak and not practical in use. To overcome these drawbacks, many researchers developed a solid electrolyte instead of liquid electrolyte with the advantage is easy to apply and does not leak [5]. Some of the options that can be used as a solid electrolyte are holes transport materials such as CuI [6] and CuSCN [7] or polymer gel loaded with redox couples to enhance ionic conductivity [8-10].

Currently has been developed several types of polymeric materials that can be used as a solid electrolyte, either synthetic polymers or natural-based polymers (biopolymers) can be taken from different bio-resources materials [11]. Synthetic polymers that widely used as a gel electrolyte include polyethylene oxide (PEO) [12, 13], polyethylene glycol (PEG) [14] and polyacrylonitrile (PAN) [15]. On the other hand, the natural-based polymer which has been developed as a solid electrolyte in photoelectrochemical system are chitosan [16], gelatin [17] and cellulose [18], each with the advantages and disadvantages. These polymers act as matrix that is loaded with redox couples, typically iodide/tri-iodide (I^-/I_3^-) from iodite salts such as KI and iodine (I_2) [19].

Lately, compared to the other natural polymers, chitosan is very often studied its properties including ionic conductivity [20]. Chitosan widely applied as electrolytes in electrochemical systems including for energy storage devices such as solid proton batteries [21], electrochemical double layer capacitors [22] and energy conversion devices such as solar cells [16,23,24]. Chitosan is cationic polyelectrolyte [25] that can be applied as solid electrolyte in the electrochemically energy conversion systems such as photoelectrochemical cell for solar energy conversion [26]. The availability of highly abundant chitosan derived from fishery processing wastes such as shrimp to be the reason for making functional materials such as polymer electrolytes.

In this work, the solid electrolyte was developed based on chitosan-based biopolymer blended with PEG as a plasticizer. The chitosan-PEG blend acts as a matrix for redox couples (commonly I_3^-/I^-) and to be a media for ionic species transport in the electrolyte. To this aim, into the polymer blend was added redox couple sources, such as KI/ I_2 , to increase the ionic conductivity of the electrolyte. The solid polymer blend loaded with redox couples will be applied as electrolyte in a photoelectrochemical solar cell. The chitosan-PEG blend serves to prevent the electrolyte leakage which will lead to a decrease in the performance of the solar cell. The solid-state photoelectrochemical solar cells were constructed in the sandwich structure using CdS films as photoanode and the chitosan-PEG blend loaded with KI and I_2 as a solid electrolyte. To increase the production of electricity then was connected several individual solid-state photoelectrochemical solar cells together, in the different configurations of series, parallel and combination of both.

2. Experimental work

2.1. Deposition and characterization of CdS films

Cadmium sulphide (CdS) films were grown by chemical bath deposition (CBD) method onto ITO-coated glass substrate that is transparent and conductive. At first, the precursor solution was prepared by mixing 20 mL of 0.1 M $CdCl_2$ (as a source of Cd) and 20 mL of 1 M thiourea (as a source of S) in the beaker while stirring with a magnetic stirrer. As the complexing agent was used NH_4OH 90% as much as 10 ml and as a stabilizer was added 5 ml TEA. ITO-coated glass substrates that have been cleaned were affixed to the inner wall of the small glass beaker by using a double tip with conductive side facing inwards, then precursor solution was poured into the beaker glass. The small beaker glass which has placed several ITO glass substrates on the inner wall was immersed in another beaker with larger size containing water. The beaker arrangement was placed on the surface of the hotplate stirrer, as shown at Fig. 1. The solution was heated at a temperature of 70 °C while was stirred with a magnetic stirrer at a speed of 300 rpm for 2 hours. After coated with CdS film, ITO glass substrates were removed from the glass beaker, then washed with hot water and dried. CdS films ready for characterization by XRD and UV-Vis spectrophotometer.

2.2 Preparation and characterization of polymer blend electrolyte

The polymer electrolyte was made by dissolving 0.15 g chitosan into 6 mL acetic acid (1%) and then added 0.15 g PEG. Into the mixed solution was added KI and I_2 solution with five variation of KI/ I_2 , that were 0.1M KI/0.01M I_2 ; 0.2M KI/0.02M I_2 ; 0.3M KI/0.03M I_2 ; 0.4M KI/0.04M I_2 ; and 0.5M KI/0.05M I_2 , respectively. Blending process was carried out on hotplate stirrer at 60 °C while stirred until homogeneous gel formed. The gel solution was poured onto a glass surface then allowed to dry at room temperature for a day and formed a gel film. In the same way, five other gel electrolyte films were made with different content of KI/ I_2 . After dried, the gel electrolyte films were measured their ionic conductivity by using an LCR meter (Hioki Hi-Tester 3522-50). The purpose of this measurement is to determine the optimal content of KI/ I_2 that produces the highest ionic conductivity, which will be applied to the solid-state photoelectrochemical solar cells.

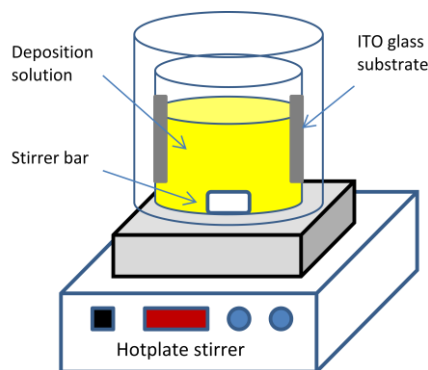


Fig. 1. Set-up for chemical bath deposition of CdS films.

2.3 Assembly and characterization of solar cells

To assembly the solid-state photoelectrochemical solar cells, by adopting that developed by Mohamad *et. al.* [26], CdS films on ITO glass substrates acts as photoanode,. The chitosan-PEG blend electrolyte containing KI/I₂ was dropped onto the surface of CdS films. Another ITO-coated glass substrate that acts as a counter electrode was placed onto the surface of the polymer blend gel to form a sandwich structure ITO/CdS/Gel/ITO, as shown at Fig. 2, the cells were allowed to dry for one day. Five cells were fabricated, one with the polymer blend electrolyte without KI/I₂ addition and other four cells with electrolyte containing KI/I₂ with ratio of 0.5M/0.05M that has highest ionic conductivity.

Solid-state photoelectrochemical solar cells were measured their I-V characteristics to investigate their performance. Measurements of I-V characteristics of individual solar cell were carried out for two different solar cells, one of the cells using chitosan-PEG blend electrolyte without the addition of KI/I₂ and the other with the addition of KI/I₂ at the optimal concentration, this measurements were done under the solar light source. Furthermore, to determine the response to the irradiation source was done measurements by using different light sources, namely with tungsten lamp and direct solar light sources. Cell tested was that used the polymers electrolyte with the addition of KI/I₂ (0.5M/0.05M) which has the highest ionic conductivity. From the current-voltage (I-V) curves can be determined the parameters of the solar cell.

To increase production of electrical power then was made different circuits configurations of individual solar cells by connecting four sandwich solid-state photoelectrochemical solar cells that have been fabricated. Three different configurations of solar cell circuits consisting of four individual solar cells were made, respectively the series, parallel and series-parallel combination circuits, as shown at Fig. 3. The solar cell circuits were measured their I-V characteristics to explore their performance with measurement set-up as was shown at Fig. 4.

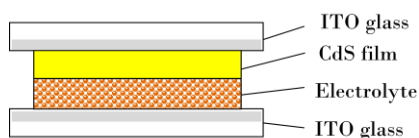


Fig. 2. Sandwich structure of individual solid-state photoelectrochemical solar cell

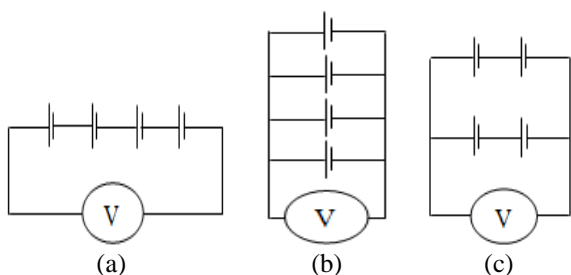


Fig. 3. Series, parallel and combination circuits of four individual solid-state photoelectrochemical solar cells

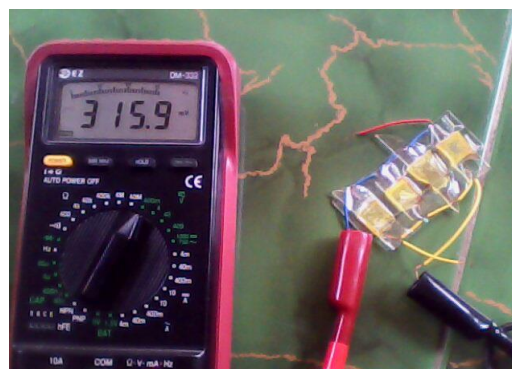


Fig. 4. Measurement set-up of solar cell circuits

3. Results and Discussion

3.1 Characteristics of CdS film

Figure 5 shows an X-ray diffraction pattern of CdS film grown on ITO-coated glass substrate by chemical bath deposition (CBD) method. Based on diffraction pattern it found that the CdS film on the ITO glass substrate still has low diffraction peaks compared to the peaks of indium-tin oxide (ITO) on glass substrate. It is because of the CdS film that grown on ITO surface has a very thin thickness so that the X-ray penetrating into the ITO layer, consequently peaks of ITO is more dominant than the peaks of CdS film. The peaks of CdS was identified at angle 2θ (hkl) = 26.5° (111); 28.6° (101); 30.4° (200); 44.4° (222); 52.3° (311) and 54.7° (222) that matched to the standard data of CdS crystal based on JCPDS Card Number 80-006 [27]. While the ITO peaks appear very strong at angle (2θ) of 21.5° (211), 30.5° (222), 35.4° (400); 45.6° (431) and 50.9° (440), respectively [28].

Figure 6 shows absorbance spectra of CdS film on ITO-coated glass substrate prepared by chemical bath deposition (CBD) method. CdS film absorbs a wide visible light spectrum below the green spectrum of electromagnetic waves so that makes it has a potential to be applied as a light energy absorbing material in photoelectrochemical solar cells as photoelectrode. In addition, the energy level of the conduction band edge of CdS is -3.9 eV [29] match with the redox potential of the redox couples I₃⁻/I⁻ (-4.9 eV) to lead a semiconductor-electrolyte junction as a necessary requirement in a photoelectrochemical cells [19].

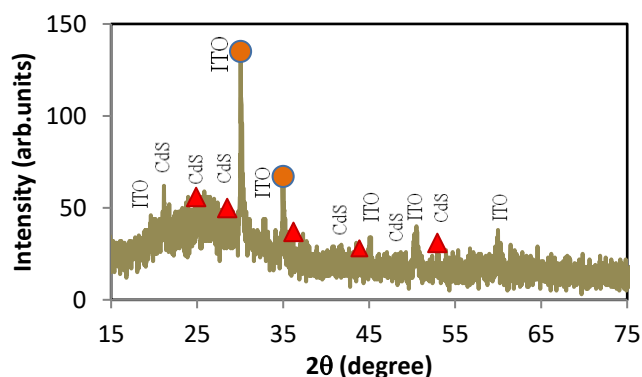


Fig. 5. XRD pattern of CdS film on ITO-coated glass substrate

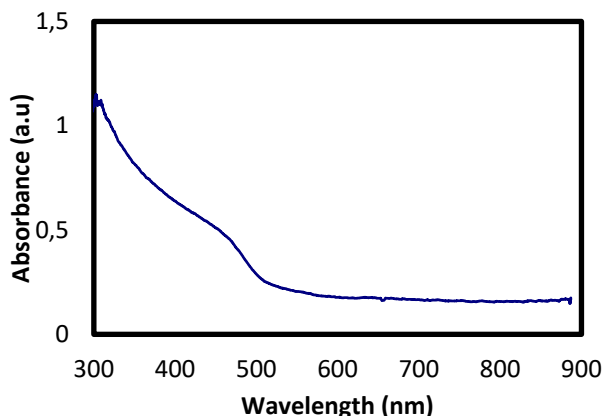


Fig. 6. Absorbance spectra of CdS film

3.2 Conductivity of chitosan-PEG blend film

Before applied as a solid-state electrolyte for photoelectrochemical solar cells, the chitosan-PEG blend gel film with variation content of KI/I₂, first measured their ionic conductivity. Figure 7 shows a curve of ionic conductivity of chitosan-PEG blend gel film loaded with variation of KI/I₂ content. The curve indicates that the ionic conductivity of chitosan-PEG blend gel films increases exponentially with the increase in the content of KI/I₂. Thus it can be concluded that the higher the content of KI/I₂ in the chitosan-PEG blend gel film resulted in increasing the ionic mobility so that the ionic conductivity increased, similar with resulted by other researcher [20]. The increase in the content of KI/I₂ will increase the ionic mobility thereby increasing the ionic conductivity of the polymer electrolyte. Increased ionic conductivity is due to the increasing number of charge carrier ion species of I₃⁻ resulting from the reduction of I₂, so that the increase of concentration I₂ contribute to increasing ionic mobility in electrolytes and so is the ionic conductivity of the electrolyte [30]. In this work, the highest conductivity was found for the highest content of KI/I₂ (0.5M/0.05M) is about 6.2 S/cm. This composition will be applied as a solid electrolyte in the solid-state photoelectrochemical cell cells.

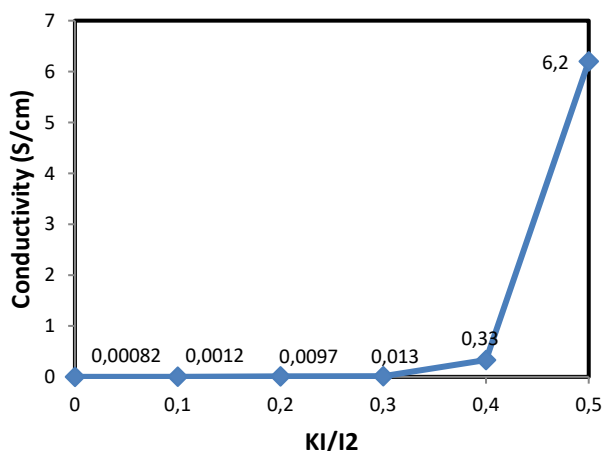


Fig. 7. Ionic conductivity of chitosan-PEG blend gel film with varied KI/I₂ content.

3.3 Characteristics of solar cells

Performance of solar cells were observed through the I-V characteristic curves of the cells, first to a single cell and then to three different circuits made from four individual solid-state photoelectrochemical solar cells. Figure 8 shows the I-V curves of two single cells using chitosan-PEG blend electrolyte, one without the addition of KI/I₂ and the other with the addition of KI/I₂ (0.5M/0.05M). On the I-V curve was found that cell using polymer blend electrolyte added with KI/I₂ produced open-circuit voltage (V_{OC}) is almost five times higher than the other cell without addition of KI/I₂. The increase of KI/I₂ content in the polymer blend electrolyte causes shift the redox potential of electrolyte away from the conduction level of the CdS photoelectrode thus widening the distance between the redox potential level of the electrolyte and the energy level of the conduction band edge of CdS photoelectrode, which this potential difference being the open-circuit voltage (V_{OC}) of the solar cell, consequently increasing the open-circuit voltage (V_{OC}) of the solar cell.

While the short-circuit current (I_{SC}) of the solar cell with polymer blend electrolyte loaded with KI/I₃ is six times higher than the other cell without addition of KI/I₂. Kenaikan arus ini dipengaruhi oleh kehadiran KI/I₂ di dalam sistem fotoelektrokimia. KI/I₂ redox couple plays a role in the electrons exchange process between the CdS photoelectrode and the electrolyte involving the redox reactions on the both electrodes initiated by photogenerated electrons from CdS photoelectrode. Oxidation of KI occurs in the n-type CdS photoanode vice versa the reduction of I₂ occurs at the counter electrode (cathode) [31]. Both the reactions contribute in the ion transfer and the exchange of electrons to increase the resulting current.

Thus the addition of KI/I₂ into the chitosan-PEG blend gel electrolyte significantly improved overall cell performance. In addition to the increased voltage and current, other parameters also increased significantly for the cells using polymer blend electrolyte added with KI/I₂ (0.5M/0.05M), includes values of maximum voltage (V_{max}), maximum current (I_{max}), and maximum power (P_{max}). The parameters of the fabricated solid-state solar cells were comparable with resulted by other researcher [26].

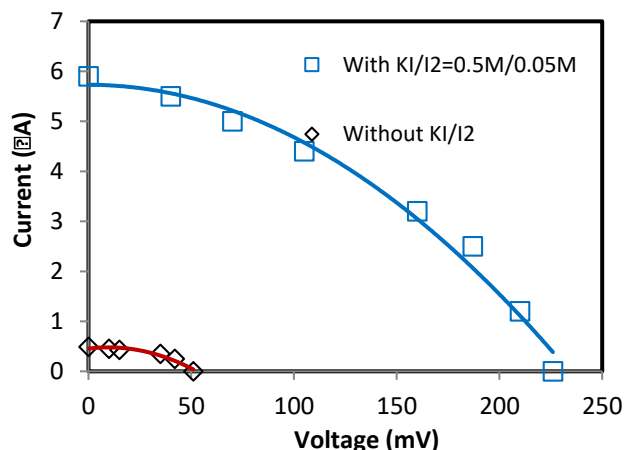


Fig. 8. The I-V characteristics for solar cell (with and without KI/I₂ addition)

To determine the influence of irradiation sources, the testing of solar cells was carried out on two irradiation conditions, namely irradiation with a tungsten lamp and direct sunlight sources. Cell tested was cell using polymer blend electrolyte added with KI/I₂ (0.5M/0.05) which has the highest ionic conductivity. Figure 9 shows the I-V curve of a solar cell that used a polymer blend electrolyte with the addition of KI/I₂ (0.5M/0.05M) in two different irradiation conditions. The I-V curves shows that exposure to direct solar light resulted in cell performance much better than the irradiation with a tungsten lamp. This is because of solar light has a very high intensity (145 W/m²) compared with the tungsten lamp with an intensity of 45 W/m² that measured using PMMA 2200 Photometer (SOLAR Light Co.). Interaction of solar light photons with a layer of CdS (as a photoactive layer) evoke negative charge (electrons) that much more compared with tungsten lamp, consequently generate currents higher, as shown in the short-circuit current (I_{sc}) value that is three times higher than the irradiation with a tungsten lamp.

Irradiation with direct solar light source also resulted in an open-circuit voltage (V_{oc}) of a much higher, three times higher than the irradiation with tungsten lamp source. Likewise, the output power of solar cells when was exposed to direct sunlight source has increased dramatically which is almost eight times higher than when irradiated with a tungsten lamp. Thus the performance of the solar cells will be better with direct solar light irradiation compared with tungsten lamp source irradiation, that is three times higher, it is because of the sunlight intensity is higher than the intensity of tungsten lamp source.

To increase the production of electricity, the solar cells were connected in different circuits configurations consisting of four individual cells that used polymer blend electrolyte with the addition of KI/I₂ (0.5M/0.05M). Four individual cells were arranged in three circuit configurations, each is series circuit (Fig. 3a), parallel circuit (Fig. 3b) and series-parallel combination circuit (Fig. 3c). I-V characteristic curves for three solar cell circuit configurations were shown in Fig. 10, measurements were taken at irradiation with direct solar light source.

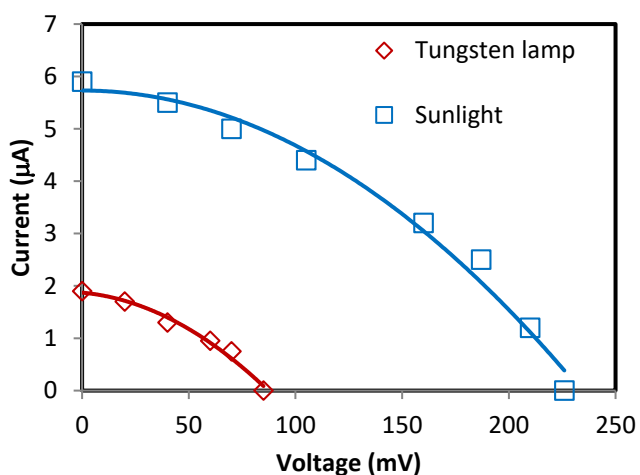


Fig. 9. The I-V characteristics under tungsten lamp and direct sunlight exposed

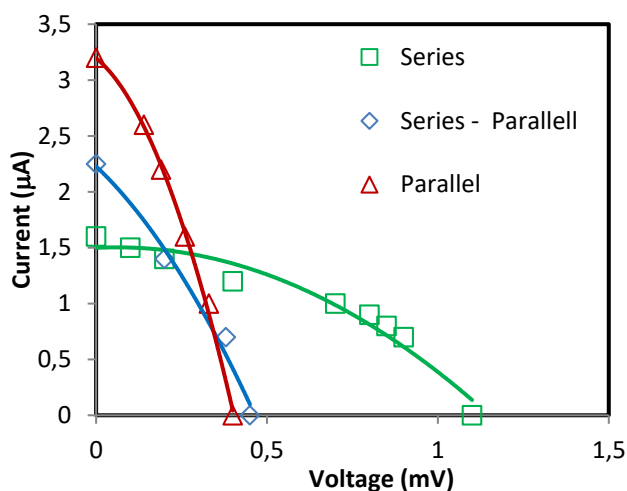


Fig. 10. The I-V characteristics for serial, parallel and their combination circuits

As seen in the I-V curves (Fig. 10) of three different solar cell circuits it found that the open-circuit voltage (V_{oc}) for the arranged in series is almost three times higher than for that are arranged in parallel, while the short-circuit current (I_{sc}) for parallel circuit is two times higher than the series circuit. On the other hand, the combination of series-parallel circuits resulted in short-circuit current (I_{sc}) and open-circuit voltage (V_{oc}) with values between the values generated by the other two circuits, series and parallel circuits. Maximum power output (P_{max}) is almost two times higher that arranged in a series than in parallel arrangement. Combination of series and parallel circuits (Fig. 3c) resulted in moderate performance compared with series and parallel circuits alone, as shown in parameters resulted (Table 1).

Table 1 shows the comparison of the values of the output parameters generated for three different circuit configurations. This results proven that solid-state photoelectrochemical solar cells can be assembled in different circuits to produce the desired output. For example, to produce maximal values of open circuit voltage (V_{oc}) and the maximum voltage (V_{max}) then the cells must be connected in series, in contrast, to generating maximal values of current short circuit (I_{sc}) and maximum current (I_{max}) then the cells must be connected in parallel. It has been further proved also that to produce the maximal value of maximum power (P_{max}) then all the cells connected in series. Results of this work proved that summation laws of the current and voltage in series and parallel circuits or a combination both applies to circuits of solid-state photoelectrochemical solar cells, same with the other electromotive force (emf) sources such as batteries.

Table 1. Parameters of solar cells for three different circuits

Type of circuits	V _{oc} (mV)	I _{sc} (µA)	V _{max} (mV)	I _{max} (µA)	P _{max} (µW)
Series	1089	1,58	782	1	0,782
Parallel	404	3,21	189	2,21	0,418
Combination	450	2,31	380	0,66	0,251

Based on the enhanced electricity production by making circuits of solar cell, it potentially and easily can be developed the photovoltaic module based on the solid-state photoelectrochemical solar cell. However, it takes a long time and a more vigorous effort to be implemented into commercial modules such as the current silicon module so it can not be utilized by the social environments in the near future as a counterpart of conventional electric energy sources.

4. Conclusion

Chitosan-PEG blend has been successfully utilized as polymer matrices for redox couple of KI/I₂ to develop solid-state photoelectrochemical solar cells. KI/I₂ content significantly affects the conductivity of polymer electrolyte further implicated to the performance of the solar cell. This study proved that the solid-state photoelectrochemical solar cells can be arranged in different circuits to increase performance output of the solar cells. Parameters of the solar cells drastically increased. A series circuit resulted in open-circuit voltage (V_{OC}) and the maximum voltage (V_{max}) values increasing with the values were sum of the single cell voltages. A series circuit also produced open-circuit voltage (V_{OC}) and the maximum voltage (V_{max}) values almost four times larger than that are arranged in parallel. In contrast to the series circuit, a parallel circuit resulted in short-circuit current (I_{SC}) and maximum current (I_{max}) values were two times higher than in series circuit. Highest maximum power (P_{max}) was resulted for series circuit, followed for combination circuit and parallel circuit, respectively. For further applications, solar cell module based on circuits of solid-state photoelectrochemical solar cells potentially can be developed.

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