Effect of The Addition of PEG and PVA Polymer for Gel Electrolytes in Dye-Sensitized Solar Cell (DSSC) with Chlorophyll as Dye Sensitizer

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Abstract. Dye-sensitized Solar Cell (DSSC) is a third-generation solar cell that consists of a working electrode, electrolyte and counter electrode. One of the most important parts of DSSC is an electrolyte that plays a medium and regenerates the electron transport of electrons in the dye. However, the liquid electrolyte has a lack of stability in long-term use and easily evaporate or leak in DSSC. Therefore, this study aims to investigate an effect of the addition of polymer material such as PEG 1000, 4000 and PVA 60000 for fabricating a gel electrolyte to solve the problems of liquid electrolyte. The synthesized TiO2 nanoparticles used in this study was prepared using co-precipitation (CPT) method which produces TiO2 anatase phase with a crystal size of 11.1 nm. DSSC has been successfully conducted and analyzed to evaluate its performance. The results showed that the efficiency of DSSC cells using gel electrolyte prepared with PVA 60000 was better than a liquid electrolyte, PEG 1000, 4000, with the efficiency could be obtained at 0.083, 0.018, 0.033, and 0.054%, respectively. The results demonstrated that the addition PEG and/or PVA could be enhanced the performance of DSSC due to gel electrolyte produced current and voltage more stable compared to the liquid electrolyte.

1. Introduction
The fabrication of conventional silicon solar cell has developed and used rapidly, but it still has several problems due to its expensive production and procurement of main materials costs. On the other side, Dye-sensitized solar cell (DSSC), known as Grätzel cells, has become a promising photovoltaic device to generate energy [1-3]. The previous study has reported that DSSC was considered as a prominent alternative to cover up the problems of the conventional silicon solar cells due to its simple fabrication process, relatively high energy-conversion efficiency, low cost, and flexibility [1-9].

To achieve a higher energy conversion efficiency, various studies have been conducted by modifying the material of photoanode, dye sensitizer and electrolyte [10]. Study of [11] had used nanostructured TiO2 film combining commercial titania powder with a titanium alkoxide sol as semiconductor on photoanode which was achieved high efficiency of 1.9%. Some studies had used natural dye sensitizer which contains anthocyanins and chlorophyll, extracted from the plant sources include leaves, fruits, flowers, etc. [2]. [12] successfully extracted 20 natural dyes from the plant sources including leaves, flowers, fruits, traditional Chinese medicines, beverages and used them as
sensitizers to make DSSC. The photoelectrochemical performance of the DSSC based on these dyes showed that the open circuit voltages (Voc) varied from 0.337 to 0.689 V, and the short circuit photocurrent densities (Jsc) ranged from 0.14 to 2.69 mA cm⁻². Specifically, a high Voc of 0.689 V was obtained from the dye extracted from mangosteen pericarp sensitizer. The photo-to-electric conversion efficiency of the DSSC sensitized by the ethanol extract of mangosteen pericarp without purification reached 1.17%. [13] reported that DSSCs were assembled by using the bougainvillea flowers, red turnip and the purple wild Silician prickly pear fruit juice extract as natural sensitizers of TiO₂ films. The best overall solar energy conversion efficiency of 1.7% was obtained, under AM 1.5 irradiation, with the red turnip extract, that showed a remarkable Jsc of 9.5 mA/cm² and a high Incident Photon to Charge Carrier Efficiency (IPCE) value (65% at λ = 470 nm). Also the purple extract of the wild Silician prickly pear fruit showed interesting performances, with a Jsc of 9.4 mA/cm², corresponding to a solar to electrical power conversion of 1.26%. Rosella, the kind of flowers, was employed as photosensitizer in DSSC by [14] and energy conversion efficiency of 0.70% was reported when the aqueous dye was extracted at 50 °C instead of 100 °C and pH of the dye was adjusted from 3.2 to 1.0. Moreover, DSSC stability was also improved by the changes in condition. [15] reported that DSSC made of Fe²⁺/Fe³⁺-based electrolyte and Reseda luteola extract as the natural dye has high efficiency of 2.17%. In the current study, a series of natural dyes extracted from the plant sources of Alfalfa’s leaf as a chlorophyll was used as sensitizer in manufacturing DSSC.

The conventional DSSC have limited long-term stability due to the unsatisfied liquid electrolytes performance. It is easy to evaporate and leak after long-term use [16]. It needs the improvement in electrolyte making by adding polymer material like a gel maker which has low volatility, high ionic conductivity at constant temperature and good stability for long-term use [17]. This has much-attracted attention recently to find out the best polymer materials. DSSC using electrolyte gel have been investigated by several researchers. [16] used polymer gel electrolytes (PGE) of PVDF-HFP/PVA blends and SiO₂ and TiO₂ nanoparticles as photoanode. The concentration of polymer blend was fixed at 10 wt% with ratios of 8:2. The TiO₂ and SiO₂ nanoparticles varied at 0.25 - 2.0 wt%. It was found that the best efficiencies of the DSSCs using PGE containing 0.25 wt% TiO₂ and 0.5 wt% SiO₂ were found to be 2.71±0.10% and 3.03±0.09%, respectively. The natural polymer solutions were used in other studies that prepared with electrospin fibers, such as poly(ethylene oxide) (PEO) in dimethylformamide and SiO₂ and aquadest. [18], polyurethane in N,N-dimethylformamide (DMF) [19], poly(ε-caprolactone) (PCL) in acetone [20], PVDF in acetone/ N,N-dimethylformamide (DMAC) (7:3 by weight) [21] and regenerated cellulose in 2:1(w/w) acetone/DMAc [22].

This research had used several types of polymers namely poly(ethylene glycol) (PEG) and poly(vinyl alcohol) (PVA). PEG is a synthetic polymer that has stable properties and can bind other materials such as pigments. PEG has an excellent solubility in water and having hydroxyl groups in its chemical structure. Then, PVA is a soluble polymer in water that is very attractive material for easy preparation of gel based electrolyte [23, 24]. PVA also has some good advantages such as high mechanical strength, biodegradable, bio-compatible, non-toxic, and excellent ionic conductivity [25, 26]. PVA has been used to fabricate lithium battery [27], electrochemical capacitor [28] and supercapacitor [29] that are environmental friendly electrochemical devices. Therefore, this paper had investigated the effect of the addition of PEG, and PVA polymer to the performance of DSSC.

2. Materials and Method

2.1. Materials
Chlorophyll dye used in this study was extracted from Medicago sativa (Alfalfa’s leaf) and was purchased from K-Link Norway AS (Norway). Hereinafter, the main materials for synthesizing and fabricating of TiO₂ in this study namely TiCl₄ solution (15%), NH₄OH (25%), and aquadest. Meanwhile, PEG (Mw approx. 1000 and 4000), PVA fully hydrolyzed (Mw approx. 60000), potassium iodide (99%), acetonitrile, iodine (>97%), ethanol (96%), Triton X-100 (purchased from Merck (Germany)), acetic acid, and chloroform were used for fabrication of electrolytes. Black Carbon (200 mesh) as the counter electrode, and Indium Tin Oxide (ITO) glass (42 Ω sq⁻¹ dimension of 2x2 cm²) as transparent conducting oxide substrates have been used in this study.
2.2. Synthesis of TiO₂ Nanoparticles

TiO₂ nanoparticles with anatase phase were synthesized by using co-precipitation (CPT) method. TiO₂ powder was made by mixing 20 mL of TiCl₄ in 100 mL of aquadest and then stirred for 1 hour. Subsequent, the NH₄OH solution was pipetted to that solution until pH 9. The solution was settled for 24 hours, and the sediment was calcined at 400°C for 3 hours to increase the crystallinity and to remove the carbonaceous materials present in TiO₂[30].

2.3. Preparation Liquid and Gel Electrolyte

Three vessels of liquid electrolytes were prepared by mixing 3 g of Potassium Iodide, 3 mL of Iodine and 10 mL of Acetonitrile [31]. Then, 7 g of each polymer materials namely PEG 1000, 4000 and PVA 60000 were added into each vessel, respectively. Next, 25 mL of Chloroform was added and homogeneously stirred for 20 minutes at 80°C.

2.4. Fabrication of the DSSC

DSSC cells consist of a working electrode, gel electrolyte, and counter electrode. The part of working electrode including 1×1 cm² active area of ITO glass coated with a TiO₂ nanoparticles paste that has been soaked in the dye sensitizer. The ITO glass had a positive potential (anode). The counter electrode consists of ITO glass coated black carbon (cathode). The distance of 2 cm was applied between two electrodes and an apparent area of the film was 1.5 × 1.5 cm². The gel electrolyte was spilled on the both of electrode layer. All components were assembled by sandwiching that illustrated in Figure 1.

2.5. Measurement and characterization

The current density-voltage (I-V) characterization of DSSC performed using Solar Simulator on input voltages up to 10 volts with a scale of 0.5 Volt. A xenon lamp as a source of light with the power density of 100 mW/cm² was used to evaluate the performance of DSSC. The performance of the DSSC cell was performed by analyzing the parameters of solar cells namely voltage open-circuit (V_{oc}), the current short-circuit (I_{sc}), Maximum Power Point (MPP), the voltage and current at MPP (V_{MPP} and I_{MPP}), fill factor (FF) and efficiency (η). Crystal phase and particle size of TiO₂ were analyzed using Match!® and MAUD (Material Analysis Using Diffraction), the software for crystal phase and size identification, respectively. The powder diffraction data from X-Ray Diffraction (XRD) can be used in that software package [32]. The absorbance spectrum of chlorophyll dye was characterized by Spectrophotometer UV-Vis with a wavelength range from 300 to 700 nm.

![Figure 1. Schematic of cell assembly with gel electrode.](image)

3. Results and Discussion

3.1 Analysis of Phase and Particle Size of TiO₂

The semiconductor of TiO₂ as photoanode has a very important role in improving the efficiency of DSSC. Characterization of TiO₂ was performed by X-Ray Diffraction (XRD) to determine the crystal
structure of TiO$_2$ which has three phases namely rutile, anatase, and brookite phase. The result of XRD test was shown in Figure 2.

XRD pattern in Figure 2 indicates that the nano-TiO$_2$ has mainly anatase phase. The diffraction peak at $2\theta$ = 25.3, 37.7, 48.04, 53.89, 55.09, 62.63, and 68.78$^\circ$ are identified in the spectrum of dense TiO$_2$ anatase and attributed to diffraction faces of (011), (004), (020), (015), (121), (024), and (116) respectively. In the present study, anatase phase was required because it has better photoactive and photocatalytic properties than other phases for achieving high energy efficiency [33]. In addition, the particle size characteristic was also needed in the DSSC applications. That had been analyzed using MAUD software. The synthesized TiO$_2$ was known as nanoparticle size of 11.15 nm of this research. In the previous study [34] was stated that the suitable particle size for applications DSSC was less than 30 nm.

![Figure 2](image-url)  

**Figure 2.** Crystal diffraction pattern of TiO$_2$ anatase phase.

3.2 *Absorbance Analysis of Chlorophyll Dye*

Dye plays a role as an absorber of photons energy that carried by light. Dye sensitizers can optimally absorb energy in a wide wavelength range, especially in a visible region which has the highest intensity of electromagnetic waves.

From Figure 3, it can be seen that chlorophyll of *Medicago sativa* leaves has wide absorption in the UV region (about 200-399 nm) of the light with optimum absorbance value at 290 nm (3.03 a.u). It can be also able to absorb visible light of solar radiation with optimum absorbance value at 400 nm (2.2 a.u) although in smaller absorbance region than UV light. Due to that ability, chlorophyll dye is expected to have higher photon-to-current energy conversion efficiency.

3.3 *The Effect of Gel Electrolytes on DSSC Performance*

DSSC electrolyte has a function as electron transport medium and regenerating the excited electrons. The liquid electrolyte has many disadvantages (like have been written before) that were caused by the type of solvent (organic solvent) that could evaporate during the irradiation process. If it occurs, the energy generation will be interrupted.

Therefore, this study used a gel electrolyte that has a capability to keep the DSSC performance for long periods without re-fabrication, beside to prevent the electrolyte leakage. The electrolyte gel was made by adding a polymer material namely PEG 1000, 4000 and PVA 60000 on the liquid electrolyte. The DSSC performance had tested and compared based on its current density-voltage and efficiency; liquid electrolyte was used as a control. The comparison DSSC performance using those electrolytes was summarized in Table 1.
Figure 3. Absorption spectra of chlorophyll dye using UV-Vis Spectrophotometer.

Table 1. Comparison of 1 cm² active area of DSSC performance

| Cell Names       | $V_{OC}$ (Volt) | $J_{SC}$ (mA/cm²) | $FF$ (%) | $\eta$ (%) |
|------------------|-----------------|-------------------|----------|------------|
| Liquid Electrolyte | 0.421           | 0.088             | 49.21    | 0.018      |
| PEG-1000         | 0.521           | 0.133             | 48.47    | 0.034      |
| PEG-4000         | 0.701           | 0.13              | 59.27    | 0.054      |
| PVA-60000        | 1.41            | 0.098             | 59.84    | 0.083      |

From Table 1, it can be concluded that the four DSSC cells have been giving good results. The highest efficiency value was at 0.083% for PVA 60000 gel electrolyte with a fill factor of 59.84%. Fill factor is a dimensionless quantity that states the maximum power ratio of the generated solar cells to the multiplication of the $V_{OC}$ and $J_{SC}$ [35]. Furthermore, the current density greatly affected on the DSSC efficiency than fill factor and voltage. The greater value of current density will generate the greater efficiency because it can increase the specific surface area that led to sufficient absorption of dye molecules [36]. The generated current and voltage value was plotted as shown in Figure 4.

Figure 4. Characteristic curve current density-voltage variations on DSSC with the addition of PEG and PVA polymer on the electrolyte.
Figure 4 shows the characteristic of current density-voltage of DSSC with under intensity light of 100 mW/cm². Based on Figure 4, DSSC using a liquid electrolyte has a lower current density than that of addition of PEG and PVA polymer. That addition of PEG or PVA could improve the performance and efficiency of DSSC because gel electrolyte could produce more stable current and voltage than the liquid electrolyte.

The average fill factor value of those DSSCs was about 50%. It was still too small because of its large series resistance that was affected by ITO glass resistance, electrolyte, and the counter electrode. ITO glass resistance and interface between the electrolyte and the black carbon (catalyst) influence the electrons transfer at short circuit conditions and facilitate the process of recombination. When the series resistance has greater value, the electron transfer process would be longer and the value of the fill factor became smaller [37].

4. Conclusion

The present work has investigated the performance of DSSC prepared with gel electrolytes formed from the addition of PEG 1000, 4000, or PVA 60000 into the liquid electrolyte. The results showed that the addition of PEG or PVA to liquid electrolyte could be enhancing the performance of DSSC. The best efficiency result of DSSC’s performance can be achieved from DSSC prepared with a mixture of liquid electrolyte and PVA 60000, with the value obtained of 0.083%.

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