Study on the effect of PVDF and TiO\(_2\) composition on quasi-solid state DSSC

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Abstract. Dye sensitized solar cell (DSSC) is a third generation solar cell that has become an interesting research topic on energy area due to its properties such as low cost, green technology and simple fabrication. DSSC is mainly constructed with three components consisting of semiconductor photoelectrode, counter electrode and an electrolyte, which usually contains \(I^-/I_3^-\) redox couple. Liquid electrolyte is commonly used in standard DSSC device, although it is vulnerable to leakage and susceptible to the environment. Furthermore, liquid electrolyte could react to some kind of sealing material that encapsulates the device as it affects the stability performance. Accordingly, this research attempted to develop quasi-solid-state DSSC (QS-DSSC) by replacing liquid to gel electrolyte in a sandwich structured DSSC with a size of 0.5 cm \(\times\) 0.5 cm per unit cell. The gel electrolyte prepared in this work was based on liquid electrolyte that was mixed with TiO\(_2\) and polymer material in the form of PVDF with various compositions for optimizing the gel electrolyte material. The performance of QS-DSSC samples was obtained using IPCE and \(I-V\) measurement, while the viscosity characteristic of the electrolyte was also assessed. The best performance of QS-DSSC sample achieved in this work had short-circuit current density, open-circuit voltage, fill factor, and photoconversion efficiency of 3.708 mA/cm\(^2\), 0.637 V, 0.64, and 2.98%, respectively.

1. Introduction

Dye sensitized solar cells (DSSC) have become interesting research topic in renewable energy area since Gratzel, \textit{et al.} reported their low cost and high efficiency solar cell based on dye-sensitized TiO\(_2\) film [1]. In regards to the experimental process, this photovoltaic device also offers simple fabrication, which could be easily produced by roll-to-roll printing technique and can be applied in various methods. DSSC typically has three main components consisting of semiconductor working electrode, an electrolyte and counter electrode, all of which are constructed in sandwich structure. In term of materials, DSSC commonly uses TiO\(_2\) as semiconductor materials, ruthenium-based dyes, and iodide-based electrolytes.

The development of DSSC is still in progress by optimizing its materials, design or fabrication method in order to produce device with high efficiency and stability. The durability is considered as
one of the major concerns since DSSC is susceptible to experience photochemical degradation caused by sealing problem or solvent endurance [2]. Related to this issue, the effort to produce more stable device has been done by replacing the liquid electrolyte with quasi-solid-state (QS) form that could minimize the leakage of electrolyte.

In the working principle of the DSSC, electrolyte takes the crucial part that handles the regeneration of the sensitizer [3] and obtains the electrons from the redox system, which converts iodide ($I^-$) into tri-iodide ($I_3^-$) [4]. Gel electrolyte is expected to be more effective to do the above role with its high ionic conductivity and thermal stability [5] instead of the liquid electrolyte. Some researchers have reported their progress on QS-DSSC study, applied on either glass or plastic substrate. For example, Elias et al. reported low temperature QS-DSSC with maximum energy conversion efficiency of 5.3% [6], Yasmina et al. obtained flexible QS-DSSC with efficiency of 6.4% [5].

In this study, gel electrolyte was prepared in three variations by combining poly-(vinylidenefluoride-co-hexafluoropropylene) (PVDF-HFP) and TiO$_2$ into liquid electrolyte for quasi-solid state DSSC. PVDF is considered as photochemically stable fluorine polymer, thus it is considered suitable for gel electrolytes. Furthermore, the mobility of the redox couple could be further enhanced by introducing TiO$_2$ as nanofillers. As reported by Katsaros et al. [7], TiO$_2$ addition into the polymer decreased the crystallinity of polymer and improved the $I^-/I_3^-$ migration. Several characterizations were applied to the prepared electrolyte and QS-DSSC, such as measuring the viscosity, incident-photon-current efficiency (IPCE) and current-voltage ($I-V$) characteristic to investigate the effect of PVDF and TiO$_2$ on the photovoltaic performance.

2. Experimental Methods

2.1. Photoelectrode and counter electrode preparation

This experiment used fluorine-doped tin oxide (FTO) glass as a conductive substrate with a conductivity of 15 ohm/sq and an area of 1.5 cm x 1.5 cm. First, the substrate was cleaned using ultrasonic cleaner for several times and immersed in ethanol for 15 min. After dried naturally, the substrate was coated with TiO$_2$ paste (Dyesol) using screen printing with an area of 0.5 cm x 0.5 cm. TiO$_2$ coating process was processed twice and the layer had a thickness of 8 μm. TiO$_2$ film then was sintered at 500℃ for 2 hours. After cooling to room temperature, TiO$_2$ film was immersed in dye solution (Z907 in ethanol). After 24 hours, dyed film was rinsed in ethanol and dried naturally. Meanwhile, counter electrode was prepared by coating the cleaned substrate with platinum by sputtering process.

2.2. Electrolyte preparation

This experiment compared the use of liquid electrolyte and gel electrolyte in some variation. Liquid electrolyte typically contains $I^-/I_3^-$ redox couple and a commercial electrolyte HPE (in acetonitrile) from Dyesol was used for this experiment. Gel electrolyte was produced by mixing PVDF and TiO$_2$ with certain composition into the liquid electrolyte. The weight ratio of liquid electrolyte, PVDF-HFP and TiO$_2$ is listed in Table 1. For the gel electrolyte preparation, PVDF-HFP and TiO$_2$ was mixed and added to liquid electrolyte and ultrasonicated for 15 min. After that, the mixture was stirred at 100℃ for 180 min.

| Table 1. Composition of liquid electrolyte and gel electrolyte. |
|------------------------|---|---|---|---|
| Electrolyte          | O | A | B | C |
| HPE-Liquid Electrolyte (g) | 1.6 | 1.6 | 1.6 | 1.6 |
| PVDF-HFP (g)         | - | 0.1 | 0.2 | 0.4 |
| P25 TiO$_2$ (g)      | - | 0.2 | 0.2 | 0.2 |
2.3. Assembly and Measurement
The construction of photoelectrode and counter electrode was applied in a sandwich structure and can be seen in Figure 1. Both electrodes were sealed using thermoplastic Surlyn (Dyesol) and the liquid electrolyte was injected between the electrodes. When using gel electrolyte, the assembly process was preceded by smearing gel electrolyte onto the photoelectrode.

![Figure 1. Schematic configuration of DSSC and QS-DSSC with sandwich structure.](image)

In this experiment, $I - V$ characterization was observed by illuminating the cells under 500 watt/m$^2$ light intensity using sun simulator. The cells were also subjected to incident photon to current efficiency (IPCE) measurement using xenon lamp as the light source. The viscosity of the liquid and electrolyte gel were observed using Brookfield Digital Viscometer (type DV-I+).

3. Results and Discussion
This experiment optimized the performance of QS-DSSC by varying the PVDF-HFP and TiO$_2$ ratios as listed in Table 1. The photovoltaic performance of the QS-DSSC that correlated to the PVDF:TiO$_2$ ratio was also compared to that of the traditional DSSC that uses liquid electrolyte.

The viscosity characteristic of the electrolyte O, A, B, and C is shown by the curve of viscosity vs. shear rate in Figure 2. It can be seen that all electrolytes has a type of non-Newtonian flow behavior, as indicated by the change in their viscosity with the variation of shear rate. The curve shows that electrolyte C has the highest viscosity among the other electrolytes. Meanwhile, electrolyte O, A, and B has similar viscosity characteristic. This confirms that the viscosity of the electrolytes increases proportionally with the increase in the PVDF-HFP content.

![Figure 2. The viscosity characteristics of liquid electrolyte O and gel electrolytes A, B, and C.](image)

IPCE measurement was applied to the sample cells to analyze the effectiveness of the cells in converting the incident photon to photocurrent [8]. Figure 3 shows the graph of function of
wavelength to IPCE result. From the IPCE plot, it can be seen that the percentage of IPCE is higher as more PVDF-HFP is added into the liquid electrolyte within the cells. Gel Electrolyte A, B, and C has better result compared to the liquid electrolyte O, which confirm that the cells is succeeded to perform as the quasi-solid state device. Quantitatively, the highest value of 29.24% at the wavelength of 520 nm is achieved by the cell containing gel electrolyte C, while the cell with electrolyte O has the lowest value of 7.30% at the same wavelength. This result gives an indication that the cell containing electrolyte C has the most effective process in transferring electrons from iodide to sensitizer.

![IPCE spectra of QS-DSSC and DSSC samples.](image)

**Figure 3.** IPCE spectra of QS-DSSC and DSSC samples.

The photovoltaic performance of QS-DSSC was measured by $I-V$ characteristic. The $I-V$ graph exhibited in Figure 4 shows that the cells work properly as photovoltaic device. This measurement was done mainly to investigate the effect of PVDF-HFP and TiO$_2$ as material of gel electrolyte on QS-DSSC. The photovoltaic parameters received from the measurement are listed in Table 2.

![I-V curve of QS-DSSC and DSSC samples.](image)

**Figure 4.** I-V curve of QS-DSSC and DSSC samples.
As shown in Table 2, the trend appeared from the $I - V$ measurement is that the photovoltaic performance of the cells became better as the amount of PVDF-HFP increases. Quasi-solid state device containing electrolyte C shows the best result with the value of 0.637 V, 3.708 mA/cm$^2$, 0.64, and 2.94% for the open-circuit voltage, current density, fill factor, and photoconversion efficiency, respectively. Electrolyte C has the best cell performance as it works effectively to convert iodide into tri-iodide. Meanwhile, Electrolyte O that represents sample with liquid electrolyte is more likely to react with sealant and suffer from leakage that can lower the cells performance. According to these results, the addition of PVDF-HFP into electrolyte with certain composition clearly contributes positively to the DSSC performance.

**Table 2.** Photovoltaic parameters of DSSC with variation of electrolytes.

| Electrolyte | $V_{oc}$ (V) | $J_{sc}$ (mA/cm$^2$) | FF | $\eta$ (%) |
|-------------|--------------|----------------------|----|----------|
| O           | 0.611        | 2.828                | 0.61 | 2.09    |
| A           | 0.631        | 3.612                | 0.59 | 2.70    |
| B           | 0.631        | 3.400                | 0.65 | 2.78    |
| C           | 0.637        | 3.708                | 0.64 | 2.94    |

4. Conclusions

This experiment presents the preparation of quasi-solid state DSSC with gel electrolyte that contains PVDF-HFP and TiO$_2$. The effect of PVDF-HFP is particularly investigated by varying its composition during the gel electrolyte preparation. The result shows that DSSC containing gel electrolyte with the highest amount of PVDF-HFP had the greatest performance with photoconversion efficiency of 2.94%. The lowest performance was exhibited by DSSC using liquid electrolyte without PVDF-HFP and TiO$_2$ addition, with photoconversion efficiency of 2.09%. This result indicates that the combination of PVDF-HFP and TiO$_2$ significantly increases the effectiveness of electrolyte role in the photovoltaic device.

5. References

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