Influence of Inorganic Binder Composition on the Structure-Property Relationship of Monolithic Dye-sensitized Solar Cells with Carbon-based Counter Electrode

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Abstract. In order to fabricate a low-cost dye-sensitized solar cell (DSSC), carbon has become a highly preferred catalytic material as counter-electrode, particularly for DSSC with monolithic structure. This paper presents novel synthesis method of carbon-based composite pastes using two types of carbon material, i.e. carbon nanopowder and activated carbon. The concentrations of the inorganic binder added to the composite pastes were varied to investigate their effect on the physical properties of the counter electrode and the electronic properties of the constructed monolithic DSSC. The inorganic binder used in this work was titanium dioxide nanoparticles, Evonik P25. After optimization, power conversion efficiency of 0.221% was achieved by the monolithic DSSC with counter electrode composite comprising activated carbon and titanium dioxide with weight concentration of 0.5 g and 0.25 g, respectively. Characterizations using gas sorption technique showed that the shape of the hysteresis curves obtained for all composites resembled the isotherm curve Type II and H3, indicating the presence of micropores. Furthermore, higher concentration of titanium dioxide nanoparticles as binder led to counter electrode with lower surface area. The solar cell efficiency, however, was found to be not only correlated to the surface area or the binder composition, but it was also determined by the type of the carbon material.

1. Introduction

Dye-sensitized solar cell (DSSC) has been considered as a promising alternative to replace solid-state silicon based solar cells due to its lower production cost. In addition to its cost, the attractive and colorful appearance, flexibility, transparency, as well as its short energy payback time have also became selling points that boost interest on the further development of DSSC. The performance of DSSC has progressed considerably since its breakthrough in 1991 [1-3]. However, much effort is still required especially for allowing DSSC to enter commercial market and industrialization as a future renewable power source.

One way to promote the use of DSSC could be carried out either by increasing the power conversion efficiency or by further lowering its production cost. At the moment, competing with the efficiency of silicon based solar cell that has already reached more than 20% appears to be rather difficult to achieve in a relatively short time frame. Thus, lowering the manufacturing cost of DSSC seems to be more reasonable solution. DSSC is generally fabricated on top of two glass substrates coated with a layer of...
transparent conducting oxide (TCO) that are sandwiched together [4, 5]. With regard to the production cost, the TCO glass holds a significant portion from the total material cost for fabricating DSSC, i.e. approximately 40-60% [6]. Not to mention, having two substrates often imposed on alignment issue particularly when it comes to the manufacturing of dye-sensitized solar modules in large sizes. DSSC with monolithic design offers an attractive solution for these challenges. The use of a single substrate in a monolithic structure could substantially reduce the cost for TCO substrates, thereby cutting back the material cost as well as simplifying the fabrication process [7, 8].

Further cost reduction could also be achieved by replacing the counter electrode material. It has been reported that the use of platinum as counter electrode could be replaced with inexpensive carbon based materials with comparable catalytic performances [8-11]. Furthermore, platinum iodide or PtI4 could also be formed in the triiodide-based electrolyte solution due to corrosion [12]. Not only serves as low-cost replacement for platinum due to its abundant availability, carbon also has several excellent properties, such as high conductivity and catalytic activity toward the redox couples existing in the electrolyte [13]. There are several requirements for obtaining carbon based composite material with suitable properties for DSSC counter electrodes. The carbon based composite materials with large surface area is typically preferred, since it could allow more contact with electrolyte. In addition, since a good bonding between carbon layer and glass substrate is required, a certain amount of binder is usually added to strengthen the mechanical properties of the film and prevent any cracking. Titanium dioxide nanoparticle is an inorganic binder that is commonly used for this purpose.

In this paper, the effect of the inorganic binder concentration on the physical properties of the counter electrode and the electronic properties of monolithic DSSC will be investigated by varying the concentrations of the inorganic binder added to the composite pastes. To date, the addition of titanium dioxide nanoparticles has been mostly aimed at improving the mechanical properties of the counter electrode films, however, further investigation on how it affect the electrical properties of the solar cells has not yet been reported. Herein, the effect of the binder concentration will also be correlated to type of carbon material, i.e. carbon nanopowder and activated carbon. The results of this work could be used as a future benchmark to formulate low-cost counter electrode materials for high performing monolithic DSSCs.

2. Experimental Section

2.1. Materials
Fluorine-doped transparent tin oxide coated glass (FTO) with a conductivity of ~15 Ω/sq (TEC-15), TiO2 opaque paste (18NR-AO), Ru-based dye sensitizer (Z907), iodide-based electrolyte (EL-HPE), thermoplastic sealant (Surlyn®), and hermetic sealing compounds were purchased from Greatcell, Australia. Carbon nanopowder and ZrO2 were obtained from Aldrich and Solaronix, respectively. Isopropyl alcohol, ethanol, acetone, and ethyl-cellulose were obtained from Merck. The rest of the materials used were activated carbon, colloidal graphite (Polaron Instruments, Inc.), TiO2 powder (P25, Evonik, Germany), and α-terpineol (Aldrich). The resistivity of deionized (DI) water used throughout the experiments was higher than 15 MΩ.

2.2. Synthesis of Carbon Pastes
The carbon-based composites for the counter electrodes (CE) were prepared as follows: first, graphite paste was dried before the dried powder was collected. The carbon composite paste was made by grinding using mortar and pestle 2 g of graphite powder, 0.5 g of carbon nanopowder or activated carbon (alternately), 0.3 g of ethyl-cellulose, 4.25 g of terpineol, and various amount of P25. Herein, the amount of P25 was varied to 0.25 g and 2 g for CE with carbon nanopowder (namely CNP0.25 and CNP2, respectively) and activated carbon (AC0.25 and AC4, respectively). The obtained pastes were collected after being grounded constantly for at least 1 h and then stored at room temperature in closed containers.
2.3. Solar Cell Fabrication

FTO substrate glass were initially cut to a size of 20 mm × 15 mm and then sanded on certain areas to remove the FTO layer in order to isolate the anode and cathode sides. The FTO substrates were subsequently washed in acetone, soapy water, DI water, and isopropyl alcohol for 10 minutes each using ultrasonic cleaner bath (Branson 3200, Emerson Electric Co, USA). The layers on monolithic DSSC were deposited by screen printing method. TiO\textsubscript{2} paste was printed twice on the FTO substrate glass and dried at 120 °C for 10 min after each deposition before sintered at 500 °C in conveyor furnaces (Lindberg, USA) for 30 min. The sintered films were then immersed in 40 mM of TiCl\textsubscript{4} aqueous solution to 70 °C for 30 min as a post-treatment, followed by another annealing under the same conditions as the TiO\textsubscript{2} sintering. When the substrate was cool, Zr-Nanoxide paste (Solaronix, Switzerland) was then printed twice on top of TiO\textsubscript{2} layer and dried at 120 °C for 10 min after each deposition before sintered at 400 °C for 30 min in a conveyor furnace. Carbon composite paste was subsequently printed on top of the ZrO\textsubscript{2} layer and dried in conveyor oven at 120 °C for 30 min and sintered at 400 °C for 30 min (Radiant Technology Corp, USA). The photograph of the cells with complete layers is shown in Figure 1. The samples were then soaked in dye solution (Z907 Ru-dye, 0.25 mM in ethanol) for 20 h in dark. The dyed samples were then rinsed in ethanol, dried and then assembled using thermoplastic sealant and pressed for 120 °C for 30 s. Non-conductive cover slips were used to encapsulate the top part of the monolithic cells. Electrolyte (EL-HPE, Dyesol) was then dropped in the gap between the FTO and cover slip using syringe before the gap was sealed with hermetic sealing compound and then dried naturally.

2.4. Characterizations

The thickness of the counter electrodes was measured using thickness gauge (Mitutoyo), while the sheet resistance was measured using four-point probe with Hewlett-Packard 3468A multimeter and 6186C DC current source. The surface morphology of the carbon composite pastes was observed using field-emission scanning electron microscopy (FESEM, STEM JEOL JB-4610F). Meanwhile, the surface area and pore size analysis were conducted via nitrogen sorption technique (Quantachrome Nova Analyzer), wherein all samples were dried into powders and degassed while heated at 150 °C prior to the measurement. The electrical parameters of the monolithic DSSC were analyzed by measuring the current-voltage characteristics under sun simulator (Oriel 9112) with an intensity of 50 mW/cm\textsuperscript{2} equipped with AM1.5G filter using National Instrument I-V measurement system. The photoconversion efficiency of the cells was determined using the following equation:

\[
\eta = \frac{V_{oc}I_{sc}FF}{P_{in}} \times 100\%
\]

where \(V_{oc}\) and \(I_{sc}\) are the open circuit voltage and the short circuit current, respectively, \(FF\) is the fill factor, and \(P_{in}\) is the power input received during the illumination.

Figure 1. Photograph of the constructed cells with various counter electrodes: (a) CNP\textsubscript{0.25}, (b) CNP\textsubscript{2}, (c) AC\textsubscript{0.25}, and (d) AC\textsubscript{2}. 
3. Results and Discussion

3.1. Physical Properties of Carbon Composite Pastes
Nitrogen gas sorption measurements were performed to characterize the surface and microstructure of the carbon composite pastes. Prior to each measurements, all samples were degassed to achieve physical desorption from any residual liquid or moisture. Figure 2 shows that all samples exhibited gas sorption isotherms with similar shape, regardless of the carbon types and the binder concentrations. Herein, all of the isotherm profiles resemble Type II isotherm curve with H3 hysteresis loop, which are commonly associated with the characteristics of microporous materials having pore width below 2 nm according to the classifications from the International Union of Pure and Applied Chemistry (IUPAC) [14]. There was also a clear trend that the increase in the binder concentration produced higher gas uptake or more complete pore filling compared to the samples with lower binder concentration, particularly at high pressure ratio range ($P/P_0$~1.0). This phenomenon could be an indication that the carbon composites with higher P25 content had bigger cavities, possibly as the result of large aggregates, which will be further analysed via morphological analysis later in this work. Meanwhile, pore size determination using Barrett-Joyner-Halenda (BJH) [15] method also indicated that the increase in binder concentration also led to slightly larger pore diameter. For samples with carbon nanopowder the pore diameter for sample CNP$_{0.25}$ and CNP$_2$ was 2.43 and 14.58 nm, respectively, while the pore diameter for samples with activated carbon was 2.43 and 4.79 nm for AC$_{0.25}$ and AC$_2$, respectively. In terms of surface area, all of the carbon composites did not particularly show any profoundly high surface areas. The surface area in this work was determined using Brunauer-Emmett-Teller (BET) method [16], giving an approximate values of 49.4, 3.42, 54.22, and 50.52 m$^2$/g for sample CNP$_{0.25}$, CNP$_2$, AC$_{0.25}$, and AC$_2$, respectively.

![Figure 2](image.png)

Figure 2. Nitrogen gas sorption isotherms for carbon composite paste containing (a) carbon nanopowder and (b) activated carbon with P25 binder concentrations of 0.25 and 2 g, as indicated by the index.

Figure 3 shows the surface morphology of the carbon composite as counter electrode films. It can be clearly seen that P25 existed as smaller particles, which dispersed around carbon aggregates that have
significantly larger size, i.e. in the order of micrometre. The higher the P25 concentration added into the composite, the more dispersion of nanoparticles could be observed, regardless the type of carbon used (see Figure 2b and 2d). By comparing Figure 2a and 2c, there was an indication that the composites with activated carbon tends to form larger agglomeration with a size of tenths of micrometre compared to that of carbon nanopowder, wherein the basic form of the activated carbon itself was existed as thin flakes. Similarly, larger agglomeration in the activated carbon containing composites remained appear at higher P25 concentration (Figure 2d).

![Figure 3. SEM images of (a) CNP$_{0.25}$, (b) CNP$_2$, (c) AC$_{0.25}$, and (d) AC$_2$.](image)

3.2. Electrical Characteristics

Prior to characterizing the electrical parameters, the thickness and the sheer resistivity of the counter electrodes containing various carbon composites were initially measured and the results are summarized in Table 1. It is clear that the thickness of the counter electrode was consistently increased with the increase in the P25 concentration, regardless of the carbon type used in the composite. The thickest film was obtained on the counter electrode containing carbon nanopowder and P25 with a ratio of 1:2 (i.e. CNP$_2$). The sheet resistivity, however, did not suggest any particular trends with regard to the P25 concentration nor the carbon type. For the case of carbon nanopowder, the increase in the P25 concentration seems to slightly improve the film conductivity by lowering the sheet resistance. In contrast, the opposite effect occurred when it came to the composite with the activated carbon. This phenomenon might be related to the nature of the activated carbon that tend to form larger aggregates than carbon nanopowder, as previously discussed according to the SEM observation. Such behaviour may have led to the decrement in the conductivity, particularly at high P25 concentration, since the P25 nanoparticles could easily blend into the agglomeration of the activated carbon. Nevertheless, it was clear that the overall carbon-containing counter electrodes in this work has improved the conductivity of the counter electrodes, as indicated by their lower sheet resistance values compared to the blank uncoated FTO substrate.
Table 1. Thickness and sheet resistivity data of counter electrodes with various carbon composite films.

| Sample  | Thickness (µm) | Sheet resistance (Ω/sq) |
|---------|----------------|-------------------------|
| CNP_{0.25} | 16.4 ± 4.0   | 11.1 ± 0.7              |
| CNP_{2}   | 17.8 ± 4.3   | 10.8 ± 0.3              |
| AC_{0.25} | 10.4 ± 1.3   | 10.7 ± 0.4              |
| AC_{2}    | 14.4 ± 3.5   | 11.5 ± 0.2              |
| Blank FTO | -             | 14.1 ± 1.2              |

The current-voltage ($I$-$V$) characteristics of the solar cells constructed in this work were measured under simulated solar irradiation with an intensity of 50 mW/cm$^2$ or equals to 0.5 Sun. The AM1.5G filter was also used during the irradiation, mimicking the standard solar spectrum at the earth’s surface. Additionally, it should be noted that all of the measured parameters during the $I$-$V$ measurements hereafter were normalized to the size of the cell active area that was fixed at 0.25 cm$^2$. Figure 4 shows the $I$-$V$ characteristics of DSSC with various carbon composites, while Table 2 summarizes the electrical parameters obtained from the $I$-$V$ measurements. The characteristic of the $I$-$V$ curves shown in Figure 4 describes an unideal $I$-$V$ curve, since the shape is rather straight with overall $FF$ values still less than 0.5. Such $I$-$V$ curve profile could be attributed to an incomplete filling of electrolyte [17], which is rather commonly observed in DSSC with monolithic structure due to the solid interfaces existed between the multiple layers of photoelectrode, spacer and counter electrode [8].

The best photovoltaic performance was achieved by sample AC_{0.25} with photoconversion efficiency of 0.221%. Despite still suffered from low $FF$, sample AC_{0.25} consistently produced the highest $J_{SC}$, $V_{OC}$ and $P_{max}$ among all samples, thus demonstrating the best photovoltaic performance. Interestingly, the electrical performance obtained was in good agreement with the previous trend observed on the sheet resistivity data (Table 1). In this case, the increase in the P25 binder concentration was advantageous for the samples containing carbon nanopowder, but vice versa for samples containing activated carbon. For instance, sample CNP_{0.25} and AC_{2} herein showed rather similar performance with almost comparable photoconversion efficiency, while their sheet resistance values were also rather proportional (see Table 1). However, although sample CNP_{2} and AC_{0.25} had comparably low resistances, their photovoltaic performance were significantly different. This phenomenon suggests that there is another factor that determine the electrical performance in addition to the sheet resistance or conductivity. According to the gas sorption data, it was suspected that the lower performance exhibited by CNP_{2} was caused by its significantly low BET surface area (i.e. 3.42 m$^2$/g). The relatively low BET surface area obtained on sample CNP_{2} could arise from the TiO$_2$ P25 nanoparticles blocking the large pores or voids between the particles of the carbon nanopowder composite. This phenomenon was plausible considering that the SEM results have suggested that the carbon nanopowder composite exhibited smaller particle size with better blending with the P25 binder compared to the activated carbon composite. Thus, the superior performance exhibited by sample AC_{0.25} was likely related to a combination between low sheet resistivity (i.e. 10.7 Ω/sq) and high BET surface area (i.e. 54.22 m$^2$/g).
4. Conclusions

Monolithic DSSCs with carbon composite based counter electrodes were developed. The type of carbon used as the main material in the composite and the concentration of TiO$_2$ P25 that was used as binder were varied in order to analyze their influence on the photovoltaic performance of the resulting DSSC. Herein, composites containing carbon nanopowder and activated carbon were compared. With regard to the presence of binder, it was imperative that a good blending between the carbon content and P25 binder needs to be fully achieved in order to gain an improved photovoltaic performance. Since the composites containing activated carbon existed as large aggregates and did not mix well with P25, increasing the concentration of P25 added into the composite reduced the conductivity and deteriorated the photovoltaic performance. The opposite effect was observed on the samples containing carbon nanopowder. The best performing DSSC was obtained when carbon composite containing activated carbon and TiO$_2$ P25 with weight concentration of 0.5 g and 0.25 g, respectively. The main contributor for its excellent performance was suspected due to the low resistivity and high BET surface area.
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