Influence of TiO$_2$ film thickness on photovoltaic properties of dye-sensitized solar cells

A. Drygała

Department of Engineering Materials and Biomaterials, Silesian University of Technology, Konarskiego 18a Str., 44-100 Gliwice, Poland

aleksandra.drygala@polsl.pl

Abstract. Generally, the dye-sensitized solar cells DSSCs are composed of a photoanode, a redox-coupled electrolyte, and a counter electrode. The nanocrystalline porous TiO$_2$ film is one of the most employed frequently photoanode materials in this type of solar cells due to its excellent optoelectronic properties. It significantly influences the photon-electron conversion efficiency of the solar cell, because of its good photo-excited electron transportation and dye adsorption. The surface morphology, crystalline phase, particle size, surface area, porosity, and dispersion of TiO$_2$ nanoparticles are the various influencing factors which determine the properties of DSSCs. In particular, the thickness of the photoanode is known to be one of the crucial factors determining the efficiency of solar cells. These properties strongly relate to the TiO$_2$ electrode method of fabrication and its parameters. Dye-sensitized solar cells based on TiO$_2$ films with different printing layers were fabricated by screen printing method. The prepared samples were characterized by scanning electron microscopy SEM and UV–Vis absorption spectroscopy. The effects of film thickness on the current-voltage characteristics of DSSCs were also investigated.

1. Introduction

Nowadays, the world is facing a major crisis with regards to the pollution of the earth and shortage of sustainable, safe and environmental friendly energy resources. To date, several forms of renewable energies have been harnessed by mankind such as wind power, hydropower, solar energy, biomass, biofuel and geothermal. Sunlight is one of the most promising forms of renewable energy due to its abundance and cleanliness. Solar cell is a device that converts the solar energy into electricity through the photovoltaic effect. Special materials called semiconductors are used for the construction of photovoltaic cells. The most commonly used material for solar cells is silicon (monocrystalline, multicrystalline, amorphous). Other materials used for the construction of photovoltaic cells are thin films such as gallium arsenide, cadmium telluride, and copper indium gallium selenide CIGS. However, this technology is restricted by resource scarcity of the required materials. Taking into account the new photovoltaic technologies, specifically like organic, perovskite and dye-sensitized solar cells, the current state of the art indicates a dynamic development in recent years. These new generation devices benefit from high throughput manufacturing, low-cost materials and low energy expenditure [1-7].

One type of solar cells is designed to imitate phenomena occurring in nature. To increase the competitiveness of solar energy, scientists have turned to the development of dye-sensitized solar cells DSSCs. This type of solar cells are regarded as prospective solar cells for the future generation of...
photovoltaic technologies. The working principle of DSSCs differs substantially from that of the standard silicon solar cells and is closely related to photosynthesis where light absorption and charge carrier transportation are carried out by different substances. The total efficiency of the DSSCs depends on the nature, optimization and compatibility of each one of the components of the solar cell. Generally, dye-sensitized solar cells consist of a photoanode, a counter electrode and a redox electrolyte (Figure 1) [8-10].

Figure 1. The structure and working principle of DSSCs [11].

Materials selection forms a key part of the product design process. The synergistic combination of materials and design is essential for development of efficient and desirable products [12-19]. The photoanode is a nanocrystalline film formed by a wide band gap semiconductor (usually TiO$_2$, ZnO) deposited on a glass substrate covered with the transparent conductive oxide TCO layer and then immersed in a dye. The photoanode serves as a scaffold for the dye sensitizer. The large internal surface area of the nanostructured semiconductor (about 1000 cm$^2$ per 1cm$^2$) insures the adsorption of sufficiently large number of dye molecules for efficient harvesting of radiant energy [20-22]. To be considered as an efficient for DSSCs application the dyes should: show wide and intense absorption of light in the range 400-700 nm, adsorb strongly on the surface of the semiconductor via anchoring groups such as –COOH, –H$_2$PO$_3$, –SO$_3$H, be stable in its oxidized form allowing it to be rereduced by an electrolyte [23,24].

The counter electrode is one of the key elements of the dye-sensitized solar cells, which acts as a catalyst for the reduction reaction and the redox couple and is used as the mediator to dye regenerate after electron injection. The counter electrode is usually prepared by depositing a thin layer of platinum catalyst on a transparent conductive oxide TCO coated glass, but it is also one of the factors that significantly increase productions costs [11,25]. The electrolyte placed between the photoanode and the counter electrode is of crucial importance for stable operation of a DSSC. The electrolyte undertakes the responsibility of dye regeneration and charge transport between the photoelectrode and the counter electrode. In the most cases it is organic liquid electrolyte with the iodide/triiodide couple. The triiodide (electron donor) in the electrolyte must reduce the oxidized dye to the ground state as rapidly as possible. The iodide (electron acceptor) goes to the counter electrode to compensate its missing electrons and the triiodide (electron donor) is regenerated. However, use of traditional organic liquid electrolytes have problems such as evaporation and leakage, corrosion of the counter electrode, hermetic sealing of the cells. These result in reduction long-term stability and performance of the
solar cells. Thus, many efforts have been made to substitute the liquid electrolytes with solid state or quasi-solid state electrolytes [26,27].

The structure and working principle of DSSC is shown in Figure 1. The working principle of dye-sensitized solar cells is not based on a p-n junction as in the conventional solar cells but on the photogeneration of an electron by a dye. Photoexcitation of the dye molecule under solar radiation results in the injection of an electron from ground state of the dye to the excited state, and the electrons subsequently injected into the conduction band of metal oxide generating the oxidized form of the dye. The electrons in the semiconductor are then transported to the fluorine-doped tin oxide (FTO) and flow to the counter electrode via an external circuit. The electrolyte, which is in contact with the dye, then donates electrons to the dye restoring it to the initial state. The counter electrode catalyzes the reduction of triiodide to iodide, thus regenerating the dye from its oxidized state to ground state. The oxidized dye molecule is again regenerated by electron donation from the iodide in the electrolyte [2,6-8,28].

One of the pivotal elements in the dye-sensitized solar cells is the photoanode, which is responsible for collection and transportation of photoexcited electrons. The photoanode are prepared by depositing a thin film of oxide semiconducting materials such as TiO$_2$, ZnO, Nb$_2$O$_5$, SnO$_2$ on a substrate (glass with a transparent conductive oxide coating on one side). These oxides have a wide energy band gap of 3÷3.2 eV. TiO$_2$ is the most commonly used semiconductor material for photoanode due to being non-toxic, less expensive and its easy availability. Among the various reported metal oxide photoanode materials, TiO$_2$ is found to exhibit the highest power conversion efficiency owing to its unique optoelectronic properties. TiO$_2$ is a material with wide energy bandgap that is existed in three crystalline phase; rutile (3.02 eV), anatase (3.2 eV) and brookite (2.96 eV). Anatase is usually used in DSSCs [29-31].

There are many methods for preparing TiO$_2$ films on the conductive side of fluorine-doped tin oxide (FTO) coated glasses: chemical vapor deposition (CVD) [32], physical vapor deposition (PVD) [33], sol–gel method [34], spin-coating [35], doctor blade method [36] and screen printing technology [37]. Among them, screen printing is a widespread method for industrial production of TiO$_2$ photoanodes due to its fast-coating technique, possibility of printing on large area and depositing facility with fine controlling of the position and thickness. Compared with other methods, the film thickness can be easily controlled in screen printing by the selection of paste composition, screen mesh size and squeegee pressure [37].

In this work the influence of TiO$_2$ film thickness on photovoltaic properties of dye-sensitized solar cells was studied. TiO$_2$ film was deposited using the screen printing method and the thicknesses of the TiO$_2$ films were controlled using numbers of printed layers.

2. Experimental

Prior to the fabrication of the TiO$_2$ photoanodes, fluorine doped tin oxide (FTO) glass substrates were cleaned with detergent, isopropyl and ethanol alcohol in an ultrasonic water bath. The commercial TiO$_2$ paste (18 NRT, Dyesol) was used to form the transparent active film. Titanium dioxide with five different film thicknesses from about 6.5 μm to 32.5 μm were screen-printed onto FTO coated glass. Next the TiO$_2$ film deposited on FTO glass was dried at 105°C for 5 min and then another layer was printed. To remove the organic compounds and to enhance electron transport the photoanodes were fired at 500°C for 30 minutes. Next the active film was immersed in N719 dye at room temperature for 24h. The platinum based counter electrodes were also prepared by screen printing method following by thermal treatment at 450°C for 30 min. In this study the iodide/tri-iodide redox couple (EL-HSE high stability electrolyte, Sigma Aldrich) was used. The dye-sensitized solar cells with an active area of 0.4 cm$^2$ defined by screen mesh during screen printing method were prepared.

Topography of the screen-printed TiO$_2$ film were analyzed using Zeiss Supra 25 scanning electron microscopy SEM. The absorbance of screen-printed TiO$_2$ films was measured by Thermo Scientific Evolution 220 spectrophotometer in the wavelength range of 280 nm÷850 nm. Electrical parameters of manufactured dye-sensitized solar cells were characterized by measurements of I-V illuminated
characteristics on PV Test Solutions Tadeusz Żdanowicz Solar Cell I-V Tracer System under standard AM 1.5 radiation and light intensity 1000 W/m².

3. Results and discussion

Figure 2 shows scanning electron microscopy (SEM) topography of TiO₂ film screen-printed on FTO coated glass after heating. It can be observed highly porous structure without cracks and gaps. The TiO₂ nanoparticles form agglomerates an average size 10-40 nm.

The cross-section SEM images of photoanode are shown in Figure 3. It can be seen the TiO₂ film are uniformly deposited on the substrate. The film thickness of semiconductor with one printing layer is about 6.5 μm. The dimension of each printing layer is the same so the thickness of 2, 3, 4, 5 layers is about 13, 19.5, 26 and 32.5 μm respectively.

![Figure 2. Topography of TiO₂ film screen-printed on FTO coated glass.](image1)

![Figure 3. Cross-section of photoanode made from TiO₂ paste screen-printed on FTO coated glass after heating (one layer).](image2)

To determine the absorbance of the dye-loaded porous TiO₂ layers, UV-Vis spectra were measured. Figures 4 and 5 show UV-Vis spectra TiO₂ photoanodes of different thickness before and after dyeing. The TiO₂ film absorb only a small fraction of UV light. Due to the highly porous structure and the large surface area of the photoanode, a high number of dye molecules get attached on the TiO₂ surface so light absorption at the active film significantly increases.
Figure 4. Absorbance for TiO$_2$ photoanodes of different thickness.

Figure 5. Absorbance for TiO$_2$ photoanodes of different thicknesses after dyeing.
One of the most important indicators used to assess and compare PV technologies is the conversion efficiency, expressing the ratio between solar energy input and electrical energy output. Comparison of the I–V characteristics of the DSSCs based on TiO$_2$ photoanodes with different printing layers is shown in Figure 6. The electrical properties (conversion efficiencies ($E_{\text{ff}}$), fill factors ($FF$), short circuit current ($I_{\text{sc}}$), open-circuit voltages ($V_{\text{oc}}$), current and voltage for which the power ($P_{\text{m}}$) reaches its maximum value, (at $I_{\text{m}}$ and $V_{\text{m}}$)) of DSSCs are summarized in Table 1. The short circuit photocurrent $I_{\text{sc}}$ increases from 3.57 to 5.01 mA when the TiO$_2$ film thickness grows up from 6.5 to 13 μm and then starts to decrease. The smallest fill factor was obtained for dye-sensitized solar cells with 3 and 4 deposited layers. The highest efficiency of 5.13 % demonstrated DSSCs with TiO$_2$ film thickness of 13 μm (Table 1). These results indicate that the efficiency of DSSCs is mainly determined by the short circuit photocurrent density. On the one hand, increasing the active surface allows better dye loading and improving light absorption, on the other hand, it probably leads to increased resistance for the transportation of electronic charge cause the recombination of electrons with $I_{-3}$.

![Figure 6. Current-voltage characteristics of dye-sensitized solar cells manufactured with TiO$_2$ photoanodes of different thicknesses.](image)

| Table 1. The electrical properties of dye-sensitized solar cells with TiO$_2$ photoanodes of different thicknesses. |
|---|---|---|---|---|---|---|---|
|   | $I_{\text{sc}}$ [mA] | $V_{\text{oc}}$ [mV] | $I_{\text{m}}$ [mA] | $V_{\text{m}}$ [mV] | $P_{\text{m}}$ [mW] | $FF$ | $E_{\text{ff}}$ [%] |
| 1 layer | 3.57 | 697 | 3.07 | 500 | 1.54 | 0.62 | 3.81 |
| 2 layers | 5.01 | 674 | 4.33 | 476 | 2.06 | 0.61 | 5.13 |
| 3 layers | 4.92 | 668 | 4.22 | 431 | 1.82 | 0.55 | 4.48 |
| 4 layers | 4.01 | 691 | 3.40 | 446 | 1.52 | 0.55 | 3.72 |
| 5 layers | 1.27 | 696 | 1.04 | 534 | 0.55 | 0.63 | 1.35 |
4. Conclusions

Dye-sensitized solar cells are attractive as simple and low cost renewable energy source. This photovoltaic device is an alternative to standard solar cells operating thanks to the p-n junction, they consist of a photoanode, an electrolyte and a counter electrode. Photoanode is an important component in DSSC. It functions as a scaffold for dye molecule adsorption. The working electrode acts as medium for collection and transportation of photo-excited electrons from dye to external electric circuit. Usually the working electrode consists of nanoporous semiconducting metal oxide with wide band gap. In this work the TiO$_2$ films were formed by the screen printing method which is relatively easy, inexpensive and can be used for mass production.

These studies revealed that the photovoltaic properties of DSSCs significantly depend on the TiO$_2$ film thickness. The DSSCs with TiO$_2$ film thickness of 13 μm (this corresponds two printed layers) achieved the maximum efficiency value of 5.13 %. The efficiency in produced DSSCs is essentially determined by the short circuit photocurrent. Increasing metal oxide film thickness (in particular with adsorbed dye molecules) enhances the absorption of light. Due to higher dye absorption capacity, the efficiency of DSSCs initially improves with the increase in TiO$_2$ film thickness. The decrease in conversion efficiency at higher printing layers is probably due to the longer path length for electron transport, which increase the recombination of photo-excited electrons with I$_3^-$ ions at the surface of TiO$_2$ and the lower transmittance of TiO$_2$ thin film.

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