Effect of TiO₂ Coating Thickness on Photovoltaic Performance of Dye-sensitized Solar Cells Prepared by Screen-printing Using TiO₂ Powders

Deuk Yong Lee[†], Hun Cho, Daejun Kang, Jong-Ho Kang*, Myung-Hyun Lee*,
Bae-Yeon Kim**, and Nam-Ihn Cho***

Department of Biomedical/Materials Engineering, Daelim University, Anyang 431-715, Korea

**Energy and Environmental Division, KICET, Seoul 153-801, Korea*

***Department of Advanced Materials Engineering, Incheon National University, Incheon 406-772, Korea*

****Department of Electronic Engineering, Sun Moon University, Asan 336-708, Korea*

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ABSTRACT

Dye-sensitized solar cells (DSSCs) were synthesized using a 0.25 cm² area of a TiO₂ nanoparticle layer as the electrode and platinum (Pt) as the counter electrode. The TiO₂ nanoparticle layers (12 to 22 μm) were screen-printed on fluorine-doped tin oxide glass. Glancing angle X-ray diffraction results indicated that the TiO₂ layer is composed of pure anatase with no traces of rutile TiO₂. The Pt counter electrode and the ruthenium dye anchored TiO₂ electrode were then assembled. The best photovoltaic performance of DSSC, which consists of a 18 μm thick TiO₂ nanoparticle layer, was observed at a short circuit current density (J_{sc}) of 14.68 mA cm⁻², an open circuit voltage (V_{oc}) of 0.72V, a fill factor (FF) of 63.0%, and an energy conversion efficiency (η) of 6.65%. It can be concluded that the electrode thickness is attributed to the energy conversion efficiency of DSSCs.

Key words : Titanium dioxide, Films, Screen-printing, Nanomaterials

1. Introduction

Dye-sensitized solar cells (DSSCs) have been recognized as a promising alternative to conventional solar cells that rely on silicon-based photovoltaics. This is because the DSSCs have low cost and reasonably high efficiency.¹⁻⁷⁾ The DSSC consists of a dye-sensitized porous electrode made of TiO₂ nanomaterials, a platinum counter electrode, and an electrolyte solution between the electrodes. The dye-sensitized TiO₂ electrode should have a high surface area in order to enhance the efficient light-to-energy conversion of DSSCs. A number of methods have been studied to produce porous TiO₂ electrodes, such as spin-coating,⁷⁾ spray coating,^{2,8)} electrospinning^{1,3,9,10)} screen-printing,⁴⁾ sputtering,⁵⁾ and chemical vapor deposition.⁶⁾

Our previous studies revealed that DSSCs consisting of a TiO₂ nanorod layer as the electrode showed an energy conversion efficiency of 5.07%.⁸⁾ The TiO₂ nanorod layer prepared by spray coating has good adhesion on fluorine-doped tin oxide glass (FTO) substrates. No additives or conducting agents were used for electrode preparation.^{2,9)} Despite these advantages, the spray coating process can be somewhat troublesome and time consuming in achieving a uniform coating thickness. Among various synthesis methods, the screen-printing method is of much interest due to its simple

process of preparing nanostructured materials directly on a conductive FTO. The thickness of TiO₂ nanostructures can be controlled easily by the number of screen-printings. Although screen-printing is a suitable process to fabricate the DSSCs, the influence of TiO₂ nanoparticle thickness on the energy conversion efficiency of DSSCs has not been studied in detail. In this study, a DSSC was constructed using a 0.25 cm² area of a TiO₂ nanoparticle layer as the electrode and ruthenium dye as the sensitizer. The energy conversion efficiency of the DSSCs using TiO₂ paste on FTO glass is presented.

2. Experimental Procedure

The TiO₂ paste was prepared from TiO₂ nanopowder (P25, 25 nm, 80% anatase (d = 21 nm) and 20% rutile (d = 50 nm), Degussa, Germany), acetylacetone (99%, Junsei, Japan), hydroxylpropyl cellulose (HPC, Mw = 100,000, Aldrich, USA), and DI water. The solution consisting of acetylacetone (6.8 ml) and DI water (40 ml) was mixed at room temperature. HPC (4.5 g) was added to the solution and stirred at 80°C. Then, P25 (15 g) was added to the above solution to obtain a TiO₂ slurry. The TiO₂ pastes were finally obtained by mixing and deaeration using a planetary centrifugal mixer (ARE-310, Thinky, Japan).

FTO glass was first surface cleaned by sonicating using distilled water, alcohol, and KOH (1 M), followed by rinsing and drying. The FTO glass (15 × 15 mm²) was used as a substrate. The thickness of the TiO₂ paste was controlled by

[†]Corresponding author : Deuk Yong Lee

E-mail : dylee@daelim.ac.kr

Tel : +82-31-467-4835 Fax : +82-31-467-4432

the number of screen-printings through a 325-mesh screen onto FTO glass. After screen-printing, the coatings were calcined for 1 h at 600°C.¹¹⁾ The sintered TiO₂ layer was further solution treated with TiCl₄ (40 mM) for 30 min at 75°C to provide improved connectivity between the nanoparticles, followed by calcination for 1 h at 500°C.^{1-3,8)} The TiO₂ electrodes were immersed in a mixture of ethanol and 0.5 mM of ruthenium dye (cis-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium (II) bis (tetrabutylammonium), N719, Solaronix, Switzerland) for 24 h at room temperature.⁸⁾ The soaked TiO₂ electrodes were washed with ethanol to remove non-anchored dye molecules and then dried in air. The film thickness was measured by a surface profilometer (SE3500, Kosaka Lab. Ltd., Japan).^{8,9)}

The DSSCs were synthesized using a 0.25 cm² area of a TiO₂ nanoparticle layer as the electrode and ruthenium dye as the sensitizer. A Pt counter electrode and a dye anchored electrode were assembled in a sealed sandwich type cell using a sealing tape (SX1170-60, Solaronix, Switzerland). The electrolyte solution (Iodolyte AN-50, Solaronix, Switzerland) was then injected into the cell through holes drilled on the counter electrode.⁸⁾ Photovoltaic measurement was conducted to evaluate the performance of the DSSCs. This was done by using a solar simulator (PEC-L11, Peccel Technologies, Japan) with a light intensity of 1000 W/m². The photocurrent-voltage curves were examined by a solar simulator with a 500 W Xenon lamp, where the sunlight intensity of AM 1.5 G was estimated. The microstructure of the coatings was evaluated using SEM (Hitachi S-3000H, Japan) and TEM (JEM-2000EX, Jeol, Japan). The crystalline phase of the films was analyzed by using a glancing angle X-ray diffraction (GAXRD, PW3040-60, PANalytical, Holland).

3 Results and Discussion

Commercially-available TiO₂ powder (P25, 80% anatase ($d = 21$ nm) and 20% rutile ($d = 50$ nm), Degussa, Germany) was used. The average particle size of P25 powder having a plate-like morphology was determined to be 25 nm, as depicted in Fig. 1. Screen-printing of the FTO glass with the TiO₂ paste was conducted at a maximum of six times because further screen-printing resulted in the peeling of the TiO₂ coating layer. SEM images of the surfaces of the TiO₂ coating layer with a thickness of 18 μ m are shown in Fig. 2. The sintered TiO₂ nanoparticles at 600°C were solution treated with TiCl₄ to provide improved connectivity between the nanoparticles and calcined for 1 h at 500°C (Fig. 2(b)). This was followed by anchoring with a Ru dye molecule (Fig. 2(c)). The porous structure of the TiO₂ nanoparticle layer (Fig. 2(a)) became smooth and dense after surface treatments, as displayed in Fig. 2(d).

The GAXRD result of the TiO₂ coating layer is shown in Fig. 3. The GAXRD pattern indicates that the layer consists of anatase (JCPDS-21-1272) with no traces of rutile TiO₂ (JCPDS-21-1276). The anatase TiO₂ peaks located at 25°, 38°, 48°, 54°, and 55°, which correspond to the (101), (004),

Fig. 1. TEM images of (a) P25 TiO₂ powders and (b) nano-rods.

Fig. 2. SEM images of the surfaces of (a) the TiO₂ paste layer, (b) the TiO₂ paste layer with TiCl₄ solution treatment, and (c) the TiO₂ paste layer surface treated with TiCl₄ and Ru dye, respectively. Note that (d) is the cross-section of the TiO₂ electrode surface treated with TiCl₄ and Ru dye.

Fig. 3. GAXRD pattern of TiO₂ nanoparticle/TiCl₄/Ru coatings.

(200), (105), and (211) planes, are clearly observed.⁷⁻¹⁰⁾ The crystallite size of anatase TiO₂ determined by the Scherrer formula is 17.3 nm.

The photovoltaic properties such as short circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF), and

efficiency (η) are summarized in Table 1. The J - V characteristics were measured under a simulated sunlight illumination provided by a 150 W Xenon lamp power supply (PECL11, Peccell Technologies, Inc.). The experimental parameters were obtained using the standard equation.¹⁾ The TiO_2 nanoparticle layer with a thickness of about 20 μm was found to have shown the best photovoltaic characteristics.^{2,8,12)} When the TiO_2 layer thickness was increased from 12 to 18 μm , the efficiency was dramatically improved due to the minimization of electron back transfer and the increased amount of adsorbed dyes.^{2,3,8,13)} The mechanisms limiting the efficiency are known to be resistive losses and the recombination of the electron-hole pair.¹⁴⁾ A thicker TiO_2 layer certainly reduces the direct electrolyte penetration through the TiO_2 nanoparticle network, thereby suppressing the electron back-transport reaction.^{2,14,15)} However, it has been reported that there is a critical thickness of the TiO_2 layer.⁸⁾ Above the critical thickness, the efficiency was deteriorated. It is well known that the electron back trans-

fer ($\text{FTO}(2e^-) + I_3^- \rightarrow \text{FTO} + 3I$) between the FTO and electrolyte reduces the efficiency, as verified by the V_{oc} reduction.^{2,15)} The efficiency decreased when the coating thickness was above 20 μm . This was probably due to the recombination of electron-hole pairs and resistive losses.¹⁴⁾ As the coating thickness rose from 18 to 20 μm (Table 1), a slight reduction in V_{oc} from 0.72 to 0.69 V was likely to be attributed to the recombination of electron-hole pairs, as well as the high series resistance arising from the weak interconnection of TiO_2 nanoparticles.^{14,16)} The optimized thickness of the TiO_2 nanorod electrode (20 μm) was higher than that of the TiO_2 paste layer (18 μm). This was probably due to the higher porosity.⁸⁾ TiO_2 nanorods with a diameter of 130 nm and various lengths were agglomerated to reduce the surface energy. However, the TiO_2 nanorod layer usually contains many pores due to geometric effects, as shown in Fig. 1(b). A thicker nanorod layer (20 μm) may be necessary to suppress the direct electrolyte penetration through the TiO_2 nanorod network.

The photovoltaic-characteristics relationship with the TiO_2 nanoparticle layer thickness is shown in Fig. 4. V_{oc} decreased gradually with an increase in the thickness (Fig. 4(a)). J_{sc} and η had a peak value at the 18 μm thickness of the TiO_2 nanoparticle layer (Fig. 4(b) and (d)). A small reduction in FF was observed compared to that of V_{oc} (Fig. 4(c)). The harvesting efficiency of the DSSCs was increased with an increase in the amount of adsorbed dyes.³⁾ The best photovoltaic characteristics were a V_{oc} of 0.72 V, a J_{sc} of 14.68 mA cm^{-2} , a FF of 63.0%, and a η of 6.65%, as demonstrated in Table 1 and Fig. 5. The higher

Table 1. Photovoltaic Properties of DSSCs Having Different Thickness of TiO_2 Electrode

Thickness of TiO_2 electrode (μm)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	η (%)
12	0.75	11.23	60.9	4.54
14	0.73	12.26	57.3	4.89
16	0.72	12.88	59.3	5.88
18	0.71	14.68	63.0	6.65
20	0.69	14.64	62.8	6.49
22	0.68	11.61	61.3	5.06

Fig. 4. Photovoltaic-characteristics relationship with the TiO_2 nanoparticle layer thickness. (a) V_{oc} , (b) J_{sc} , (c) FF , and (d) η , respectively.

Fig. 5. Effect of TiO₂ nanoparticle electrode thickness on the photocurrent density versus the voltage characteristics of DSSCs.

values of η and FF as compared to the Fujihara's DSSCs ($\eta = 4.75\%$, $FF = 37.5\%$, thickness = $13 \sim 16 \mu\text{m}$) were observed due to the difficulty in electron back transfer as a result of a thicker TiO₂ nanoparticle network. In order to obtain a high conversion yield in solar cells, it is necessary to collect the ion carriers produced by photons as electrical current before their recombination. The collection of ion carriers must be carried out significantly faster than the recombination. A promising solution is to increase the electron emission length in a photo-anode electrode made of titanium dioxide nanoparticles and its one-dimensional nanostructures. The difference in cell performance may be due to the thickness of the TiO₂ nanoparticle layer. A further increase in the thickness of the TiO₂ layer reduces η from 6.65% to 6.49% due to the electron back-transport reaction, as verified by the reduction in V_{oc} .^{3,8,13-16} A porous and thicker nanoparticle layer was determined to be detrimental to the DSSC efficiency.

The Ru dye in the photovoltaic device acted as a photosensitizer, an electron transfer mediator, and an inhibitor of the electron-hole recombination. This was verified by the observation of an increase in J_{sc} and V_{oc} .¹⁶ Due to the porous structure of the TiO₂ nanoparticle layer, the Ru dye and the electrolyte loading increased gradually with an increase in the electrode thickness. However, the Ru dye had minimal contribution to J_{sc} and V_{oc} when the TiO₂ coating thickness was $20 \mu\text{m}$. This suggests that η was deteriorated due to the synergic effects of the electron back-transport reaction and the resistive losses. Some of the I_3^- ions in the electrolyte may have penetrated the porous TiO₂ network and came into direct contact with the FTO surface, thereby collecting the electrons from the FTO surface through a back-transport reaction.^{15,16} However, this warrants further studies.

4. Conclusions

The DSSCs consisting of a 0.25 cm^2 area of a TiO₂ nanoparticle layer as the electrode and Pt as the counter elec-

trode were synthesized. The TiO₂ coating layer with a thickness range of 12 to $22 \mu\text{m}$ was prepared by screen-printing the TiO₂ pastes on a FTO glass, followed by calcination for 1 h at 600°C . The sintered TiO₂ nanoparticle layer was solution-treated with TiCl₄ to provide improved connectivity between the nanoparticles. Then, the layer was calcined for 1 h at 500°C , followed by subsequent anchoring with a Ru dye molecule. The best performance of DSSC consisting of a $18 \mu\text{m}$ thick TiO₂ nanoparticle layer was observed at a J_{sc} of 11.54 mA cm^{-2} , a V_{oc} of 0.72V , a FF of 61.2% , and a η of 5.07% . Thus, the coating thickness is likely to have a significant influence on the efficiency of DSSC.

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