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Performances characteristics of dye-sensitized solar cells based on counter electrodes with Pt films of different thickness

Xiaoming Fang [a,b], Tingli Ma [a,*], Guoqing Guan [a], Morito Akiyama [a], Eiichi Abe [a]

[a] *Institute for Structural and Engineering Materials (AIST Kyushu), National Institute of Advanced Industrial Science and Technology (AIST), Tosu, Saga 841-0052, Japan*

[b] *College of Chemical Engineering, South China University of Technology, Guangzhou 510640, PR China*

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Abstract

The effects of the thickness of Pt film on the property of platinized counter electrode and the performance of the dye-sensitized solar cell (DSC) were investigated. The Pt film sputtered on an FTO glass is constructed of Pt particles, and the grain size of the Pt particles gradually increased with the increase in the Pt film thickness. When the Pt film thickness exceeds 100 nm, further Pt deposition has no significant effect on the conductivity improvement. In the range between 10 and 415 nm, the Pt film thickness has no significant influence on the performance of the DSC. A high conversion efficiency of ca. 5% was obtained by the DSC composed of the counter electrode with Pt film of 10 nm thickness. These results are important for reducing the production cost by reducing the required amount of expensive platinum.

Keywords: Pt film; Counter electrode; Dye-sensitized solar cell; Sheet resistance; Performance

1. Introduction

The low cost and high conversion efficiencies (7–10% at AM 1.5) make dye-sensitized solar cells (DSCs) a promising alternative for the development of a new generation of solar cells [1–5]. The energy conversion working principle of a DSC is based upon the injection of electrons from the photoexcited state of a dye-sensitizer into the conduction band of a semiconductor. The oxidized dye accepts electrons from the iodide ions in the electrolyte, and the resulting tri-iodide is reduced back to iodide at the counter electrode [6–10]. The counter electrode is one of the important components in a DSC. It functions as transferring electrons to the redox electrolyte and catalyzing the reduction of redox couple, where Pt serves as a catalyst. In recent years, regenerative dye-sensitized solar cells have been under considerable investigations concerning the identification and synthesis of dye molecules, theoretical analysis on charge transport in mesoporous nanocrystilline TiO_2 films, substitution of solid-state heterjunctions for the liquid electrolyte, etc. However, less attention has been paid on the counter electrodes, except a few studies have been performed on the counter electrode in DSC [11–15]. Usually, the conducting glass sheets coated with Pt films are widely used as the counter electrodes for DSCs. Nonetheless, the Pt film thickness varies from author to author. Therefore, it is important to investigate the influence of Pt film thickness on the performance of the DSCs. Another aim is to clarify the quantity of platinum for reducing the cost of DSC. We have been performing systematic studies on counter electrodes. In this paper, we report the effects of the thickness of Pt film on the property of platinized counter electrode and the performance of the DSC.

2. Experimental

Platinized counter electrodes were fabricated by depositing Pt particles onto conducting glass sheets (Asahi Glass Co. Ltd, fluorine-doped SnO_2 over layer, FTO, sheet resistance: 10 Ω/□) using an rf, magnetron sputtering equipment (TOKUDA, MODEL CFS-4ES-231USC; power: 200 W; deposition rate, 2.8 Å/s). The Pt film's thickness was controlled by changing the deposition time. The relationship between the Pt film thickness and the deposition time is shown in Table 1. The sheet resistances (R_s) of the platinized counter electrodes were measured by a four-dot method (HL5500 PC Hall effect measurement system), and the results were also summarized in Table 1. The surface microstructures of

* Corresponding author. Tel.: +81-942-81-3640; fax: +81-942-81-3690.
E-mail address: tingli-ma@aist.go.jp (T. Ma).

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Table 1
The properties of platinized counter electrodes with Pt films of different thickness

Sputtering time (s)	Pt film thickness (nm)	Sheet resistance (Ω/□)
0	0	10
36	10	6.50
90	25	3.19
180	50	2.28
360	100	1.18
720	200	0.60
1080	300	0.39
1500	415	0.32

an FTO glass and the platinized FTO glass counter electrodes prepared were observed using a scanning electron microscope (SEM, Hitachi S–5200).

Porous TiO_2 films were prepared by coating the FTO glass sheet with a viscous paste of TiO_2 powder (P25, Nippon Aerosil) according to the procedure described in our previous paper [16]. In order to obtain homogeneous TiO_2 films, 25 pieces of them (area: 0.2 cm^2) were fabricated on one FTO glass sheet using a screen-printing technique (Screen: Mitani electronics, MEC3000) at one time. The thickness of TiO_2 film obtained was approximately 14 μm. After dried at 50–60 °C for 15 min on a hot plate, these TiO_2 films were sintered at 450 °C for 30 min. The films annealed were impregnated with a 0.05 M titanium tetrachloride solution in a hermetic glass bottle 70 °C for 30 min, followed by a firing at 500 °C for 30 min. The TiO_2 films obtained were immersed into an ethanol solution of *cis*-bis(isothiocyanato)-bis (2,2′-bipyridyl-4,4′-dicarboxylato)-Ruthenium(II)-bis-tetrabutylammonium (N719 dye, 5×10^{-4} M) for 12 h at 25 °C.

Current–voltage curves of the DSCs composed of the counter electrodes with Pt films of different thickness were obtained by scanning a bias voltage while measuring photocurrents under white light irradiation (1000 W/m^2) using a sandwich solar cell constructed of the dye-sensitized TiO_2 electrode and the platinized counter electrode. The electrolyte solution was composed of 0.1 M LiI, 0.1 M I_2, 0.6 M 1,2-dimethyl-3-propylimidazolium iodine, and 0.5 M *tert*-butylpridine in methoxypropionitrile.

3. Results and discussion

3.1. Surface microstructures of Pt films sputtered on FTO glass

Fig. 1 shows the SEM surface morphologies of a bare FTO glass and the platinized counter electrodes with Pt films of 100, 200, and 415 nm thickness. It can be seen from Fig. 1(a) that the bare FTO glass has a scalelike and rough surface structure owing to the fluorine-doped SnO_2 layer coated on the glass sheet. The 100-nm-thick Pt film sputtered on the FTO glass is constructed of Pt nanoparticles with grain size of ca. 14 nm, as shown in the inset of Fig. 1(b), and for the Pt films of 10, 25, and 50 nm thickness, the sizes of Pt particles are less than 10 nm (not shown here). When the Pt film thickness increased to 200 nm, the grain size of Pt particles grew to 40–60 nm (inset of Fig. 1(c)). As the Pt film thickness further increased to 415 nm, the granular surface microstructure disappeared, and an uneven Pt film was formed on the F-doped SnO_2 layer, as shown in the inset of Fig. 1(d). It was revealed that, the grain size of Pt particles gradually increased with the deposition time, due to the aggregation of the Pt nanoparticles during sputtering.

3.2. Effect of Pt film thickness on sheet resistances of counter electrodes

The variation of the sheet resistance of counter electrodes with the Pt film thickness is clearly depicted in Fig. 2. The R_s of counter electrodes decreased with the increase in the Pt film thickness, which decreased remarkably for the range between 2 and 25 nm, gradually in the range from 25 to 100 nm, and slowly for the range between 100 and 415 nm. These results indicate that the conductivity of the counter electrode can be improved by depositing a Pt film on a FTO glass; however, when the Pt film thickness exceeds 100 nm, further deposition has no significant effect on the conductivity improvement.

3.3. Effect of Pt film thickness on performances of DSCs

To investigate exactly the effect of the Pt film thickness of the counter electrode on the performance of DSC, all the dye-sensitized TiO_2 films used were prepared at one time by the screen-printing method, so that they can be considered to have the same microstructures. Table 2 shows the performance characteristics of the DSCs composed of counter electrodes with Pt film of different thickness, and the photocurrent density–voltage (J–V) curves of the DSCs are illustrated in Fig. 3.

As shown in Table 2, when a bare FTO glass was used as the counter electrode, the open-circuit photovoltage (V_{oc}) of the DSC was only 120 mV, the short-circuit photocurrent density (J_{sc}) was 1.9 mA/cm^2, and the overall energy conversion efficiency only achieved 0.38%. Whereas, when the counter electrode was constructed of an FTO glass covered with 10-nm-thick Pt film, the V_{oc} and J_{sc} of the DSC strikingly increased to 680 mV and 12.5 mA/cm^2, and the overall energy conversion efficiency achieved 4.92%. As the Pt film thickness further increased, no apparent difference in V_{oc}, J_{sc} and fill factors of the DSCs composed of the counter electrodes with Pt films from 10 to 415 nm thickness were observed, as shown in Table 2 and Fig. 3. The conversion efficiencies of the DSCs did not increase with the sputtered Pt film thickness.

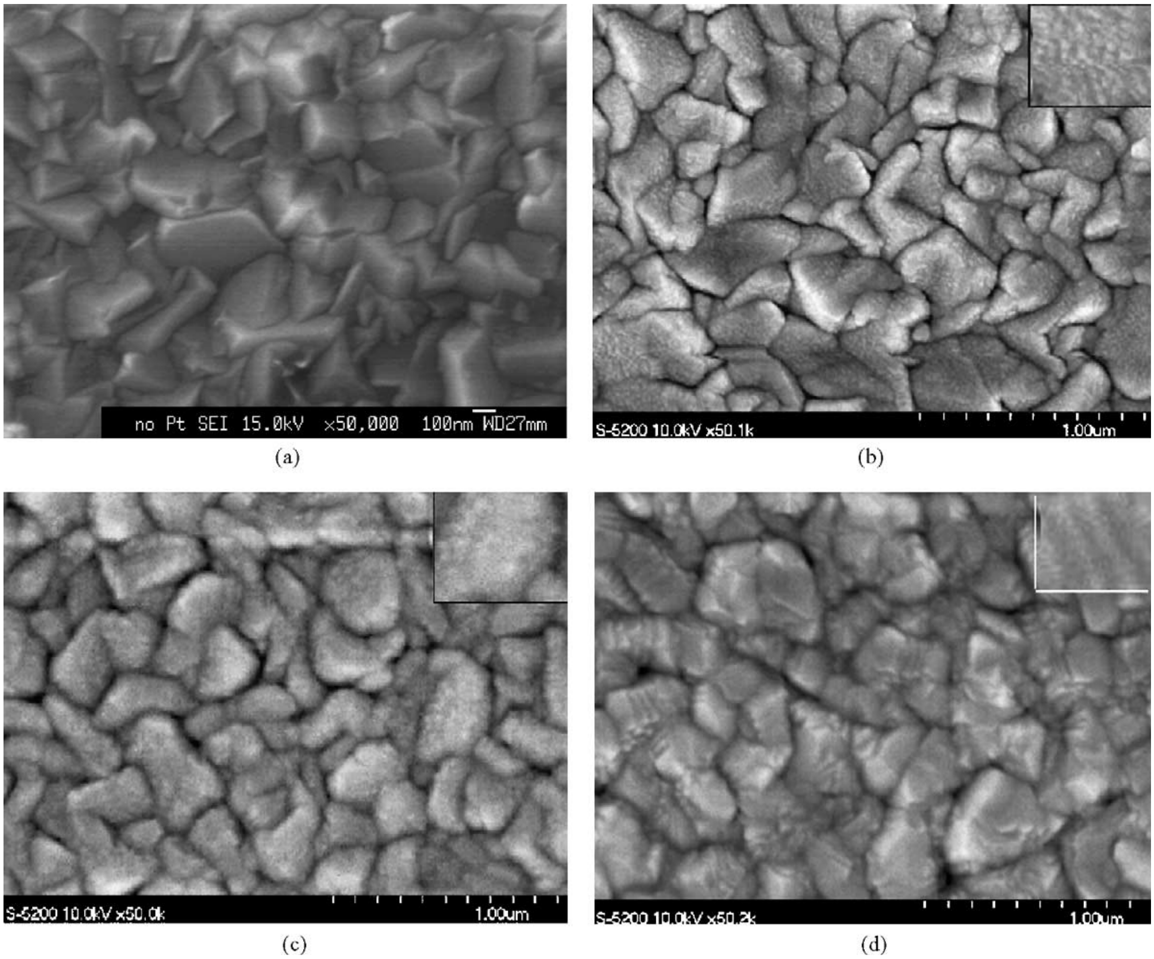

Fig. 1. SEM micrographs of FTO glass and platinized FTO glass counter electrodes (a) FTO glass substrate; (b–d) platinized counter electrode with Pt film of 100, 200, and 415 nm thickness, respectively.

It is known that the counter electrode for a well-operating dye-sensitized nanocrystalline solar cell should have the following characteristics: (1) good conductivity for transferring electrons, (2) excellent catalytic activity for tri-iodide reduction, and (3) well-reflecting characteristic to improve light harvesting efficiency [11,15]. It was observed that all the counter electrodes with Pt films from 10 to 415 nm thickness possessed obvious mirror surfaces. Therefore, it can be considered that the conductivity and the catalytic activity of the counter electrodes are the two factors that influence the performances of the DSCs composed of the counter electrodes with Pt films of different thickness.

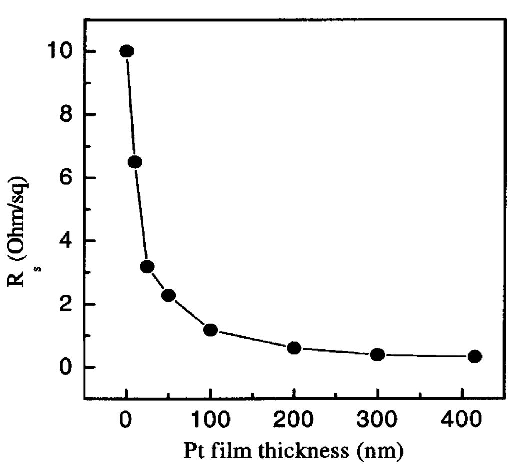

Fig. 2. The variation of sheet resistance of counter electrodes with the Pt film thickness.

Table 2
Performance characteristics of dye-sensitized solar cells composed of counter electrodes with Pt film of different thickness

Pt film thickness (nm)	V_{oc} (mV)	J_{sc} (mA/cm^2)	Fill factor (%)	η (%)
0	120	1.90	17	0.38
10	705	11.35	61	4.92
25	702	11.60	59	4.99
50	690	12.10	62	5.17
100	701	11.25	62	4.89
200	698	11.40	64	5.08
300	685	11.60	63	5.03
415	694	12.50	60	5.18

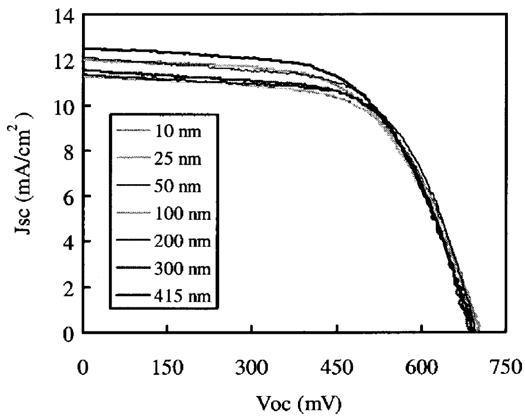

Fig. 3. Photocurrent–voltage curves of dye-sensitize solar cells composed of counter electrodes with Pt film of different thickness.

For the bare FTO glass counter electrode without Pt film, lack of the catalytic activity of the counter electrode was responsible for the very poor performance of the DSC. When the FTO glass covered with 10-nm-thick Pt film was used as the counter electrode, the considerable increase in the performance of the DSC was observed, indicating that the catalytic activity of the counter electrode play an important role in the performance of DSC. When the Pt film thickness ranged between 10 and 415 nm, as discussed in Section 3.1, the grain size of the Pt particles increased with the Pt film thickness. This may lead to the decline in catalytic activity of the counter electrode, because the catalytic activity generally depends on the surface area of the catalyst [17]. On the other hand, as discussed in Section 3.2, the R_s of the platinized counter electrodes decreased with the increased in the Pt film thickness, that is, the interconnection of Pt particles was improved, which contributes to the electron transfer at the counter electrodes. Therefore, when the Pt film thickness increased from 10 to 415 nm, the combined effects of catalytic activity and conductivity of the planitized counter electrodes resulted in no remarkable difference in the performances of the DSCs. The DSCs composed of counter electrodes with thin Pt films can obtain as high conversion efficiencies as those with thick Pt films. A high conversion efficiency of 4.92% was obtained even though the DSC was composed of the counter electrode with the sputtered Pt film of 10 nm thickness. These results mean that the purpose to lower the cost of DSC can be achieved by reducing the amount of expensive Pt used.

Considering the durability and stability of the DSC and the concern that a small amount of platinum might dissolve in the electrolyte by oxidation and complex formation with iodide/tri-iodide [12], accordingly, a too thin Pt film should be avoided in the fabrication of the DSCs. Studies on the charge-transfer resistances at the interfaces of the electrolyte and counter electrodes and the optimization of the Pt film thickness are in progress.

4. Conclusions

The Pt film sputtered on an FTO glass is constructed of Pt particles, and the grain size of the Pt particles gradually increased with the increase in the Pt film thickness. The conductivity of the counter electrode was gradually improved as the Pt film thickness increased from 10 to 415 nm, however when the Pt film thickness exceeds 100 nm, further Pt deposition has no significant effect on the conductivity improvement. It is revealed that the Pt film thickness has no significant influence on the performance of the DSC. A high conversion efficiency of ca. 5% can be obtained for the DSC composed of the counter electrode with Pt film of 10 nm thickness. The purpose of reducing the cost of DSC can be achieved by reducing the amount of expensive Pt used.

Acknowledgements

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