

Characteristics of Nano-crystalline TiO₂ Dye-sensitized Solar Cells having Counter Electrodes with Different Preparing Process

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The Pt counter electrode of a dye-sensitized solar cell (DSSC) plays a role in helping redox reaction of iodine ions in electrolyte, also, transferring electrons into electrolyte. In this case, it is expected that characteristics of Pt electrodes strongly depend on fabrication process and its surface condition. In this study, Pt electrodes were prepared by a electro-deposition and a RF magnetron sputtering. Electrochemical behavior of Pt electrodes was compared using cyclic-voltammetry and impedance spectroscopy. Surface morphology of Pt electrodes was investigated by FE-SEM and AFM. I-V characteristics of DSSC were measured and discussed in association with the surface properties of counter electrode. As a result, electrochemical properties of electro-deposited Pt electrode were superior to that of sputtered Pt electrode. This is likely that enlarged area of surface in electro-deposited Pt electrode in comparison with the case of sputtered Pt electrode play a role in enhancing such electrochemical properties.

Keywords : Dye-sensitized solar cell, Pt counter electrode, Cyclic voltammetry, Impedance spectroscopy

1. INTRODUCTION

Nanocrystalline dye-sensitized solar cell (nc DSSC) is a sort of electrochemical device[1-3]. This consists of transparent conductive oxide on glass plate, nanoporous TiO₂ electrode, dye-sensitizer, electrolyte, and counter electrode. In DSSC, reaction of the iodide/triiodide redox couple occurs as the mediator that shuttles the charge between the photo-electrode and the counter electrode[4-6]. Transparent conductive oxide (TCO) coated glass substrates are presently used as cathodes in solar cells. However, it shows extremely poor catalytic property for iodine reduction[7,8]. In this reason, they have to be modified by the deposition of high catalytic materials on it. Material used for the count electrode of DSSC should satisfy the requirements of superior catalytic reactivity, high conductivity, and low potential of electrode reaction. Here, Pt is well known as a counter electrode material of DSSC[9]. Pt can be deposited on TCO by electro-deposition, thermal decomposition and sputtering processes.

In this paper, we report on the characteristics of Pt counter electrodes prepared by electro-deposition and sputtering method. To characterize Pt electrodes, cyclic

voltammetry and an ac impedance test were executed. Also, the effect of electrode preparation process on the solar cell efficiency was investigated.

2. EXPERIMENTAL PROCEDURE

2.1 Preparation of electrodes

The counter electrodes were coated on the F doped SnO₂ glass (FTO) by electro-deposition and sputtering methods, respectively. In the case of electro-deposition method, platinum plate (3×3 cm²) and FTO glass of substrate were used as an anode and a cathode, respectively. The electro-deposition was performed with the condition of constant current of 10 mA for 3 sec. in a 0.002M H₂PtCl₆ aqueous solution.

Sputtered Pt electrode was deposited on FTO glass by using a RF-magnetron reactive sputtering system under the condition of a base pressure of 1×10⁻⁵ torr, 5×10⁻³ torr working pressure, 150 Watts sputter power, and 50 sccm Ar gas flow.

2.2 Cell construction

A sandwich type cell was constructed for electro-

chemical measurements as shown in Fig. 1(a). In such cell, TiO₂ electrode was replaced to Pt counter electrode (C.E. in Fig. 1(a)) prepared by sputtering in order to investigate the redox reaction of iodide on the surface of counter electrode of DSSC. The Pt electrode of DSSC was used as a working electrode of electrochemical cell. The electrolyte containing I/I₃⁻ redox couple was introduced into the cell by capillary effect through thin gap, having approximately 50 μm thick between two electrodes. The gap was sealed with small amount of sealing materials, Amosil 4 (Solaronix SA).

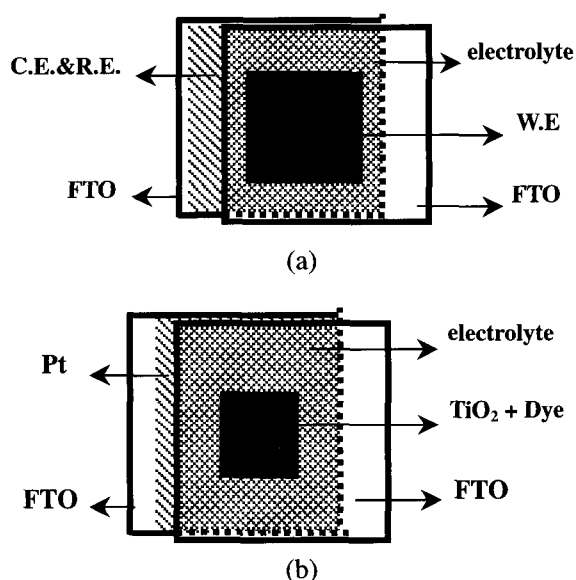


Fig. 1. Plane-view of (a) a cell for electrochemical measurement and (b) a dye-sensitized solar cell.

TiO₂ dye-sensitized solar cell for solar efficiency measurement was prepared as follows: mesoporous TiO₂ film was fabricated by screen printing method. TiO₂ paste for screen printing was prepared by mixing TiO₂ nano powder (Degusa P25) with α -terpineol. Nano-crystalline TiO₂ paste was coated on FTO glass substrate having the electric conductivity of 12 ohm/sq, optical transmittance of 80 % in the visible region. The film was sintered at 480 °C for 1hr in air. For sensitizing coated TiO₂ layer with dye, TiO₂ electrodes were immersed in a solution of 0.02 mg/cc red dye (RuL₂(NCS)₂[L=2,2'-bipyridine-4,4'-dicarboxylic acid] (N3) in absolute ethanol for 24 hr at room temperature, and rinsed in ethanol. Assembly of the Pt electrode and the dye-adsorbed TiO₂ electrode was executed with equal process to the case of the cell for electrochemical property measurement as shown in Fig. 1(b).

2.3 Measurements

Field emission scanning electron microscopy (FE-SEM), atomic force microscopy (AFM) and α -step (Tencor Alpha-step 200 profilo meter) were employed for the characterization of microstructure and thickness of the films coated by electro-deposition and sputtering methods. The sheet resistance was measured using 4-point probe method. To characterize Pt electrodes, both the cyclic voltammetry and the ac impedance test were executed. Measurement of cyclic voltammetry and impedance spectroscopy were performed with a Galvanostat/Potentiostat (EG&G 273A) and a Lock in amplifier (EG&G 5210). The ac impedance of a cell was measured in the frequency range from 100 kHz to 10 MHz.

For comparison of efficiency of DSSC having electro-deposited Pt counter electrode with the case of sputtered Pt counter electrode, a short-circuit photocurrent (J_{sc}) and an open-circuit voltage (V_{oc}) were measured using self-made program-attached fluorescent spectrophotometer and Keithley 2400 source meter.

3. RESULTS AND DISCUSSION

The FE-SEM image of Pt film coated by using an electro-deposition method is shown in Fig. 2(a). It was

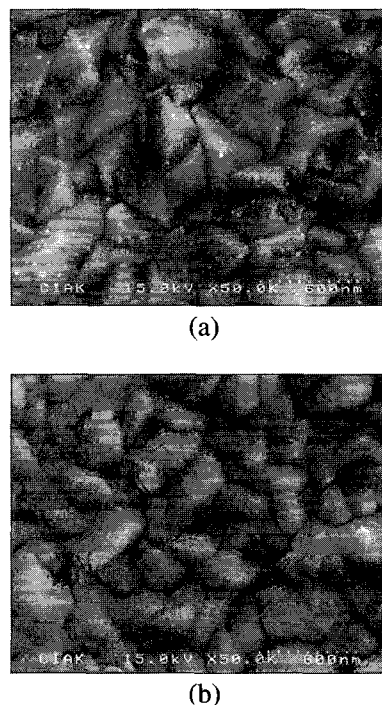


Fig. 2. The FE-SEM images of Pt films prepared by (a) electro-deposition and (b) sputtering.

found that the coated film is composed of an extremely small spherical particle of 2~3 nm size. The thickness of coated Pt was very thin as it will not be able to judge with the SEM image. The sheet resistance of electro-deposited Pt film is almost similar to that of FTO glass substrate.

Figure 2(b) shows the FE-SEM image of the sputtered Pt electrode surface. Pt was deposited as a thick film on rough FTO surface, and its thickness was approximately 0.5 μm . The sheet resistance of Pt sputtered film was measured as 4~5 ohm/sq. This is smaller than that in the case of an electro-deposited Pt counter electrode.

Figure 3(a) and (b) shows the surface morphologies of Pt electrode deposited by electro-deposition and sputtering, measured by AFM, respectively. In this figure it can be estimated that the surface of electro-deposited electrode has more enlarged surface area than that in the case of sputtered one.

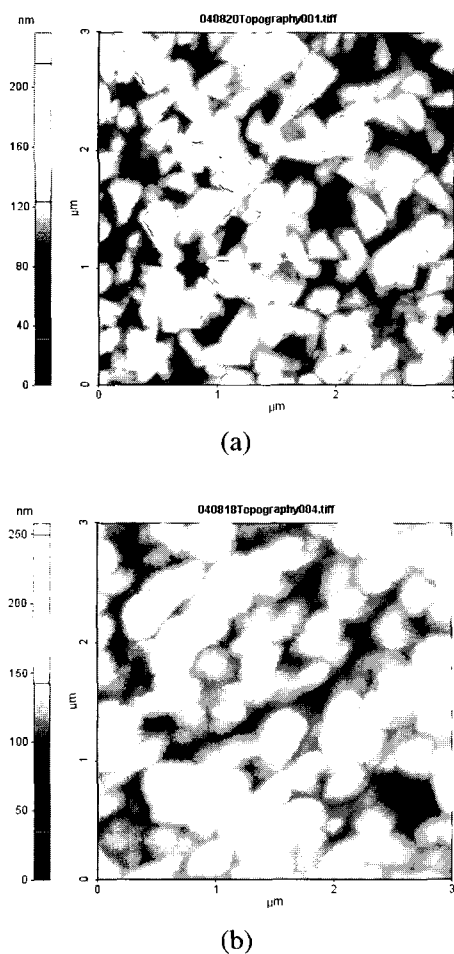


Fig. 3. The surface morphologies of Pt electrode deposited by electro-deposition (a) and sputtering (b), measured by AFM.

A cyclic-voltammetry measurement is helpful to understand the microscopic electrochemical surface reactions at the electrode. A reduction process occurs at the interface between the counter electrode surface of DSSC and electrolyte. The reduction reaction of an iodine ion in electrolyte can be rewritten as:



Figure 4 presents the cyclic voltammetric behaviors of the Pt electrodes coated by the electro-deposition and sputtering at a scan rate of 100 mV/s. Here, a peak in negative potential is corresponding to reduction of I_3^- ion.

In cyclic voltammogram, peak area and current density for reaction usually increases with the increase of reaction rate. The absolute value of peak potential is related to the reaction limit of potential[10,11]. The more the peak potential is big, the better reaction potential range the electrode has. In comparison of two curves, in Fig. 4, it was shown that the electro-deposited Pt electrode had higher area, higher current density and little lower peak potential of reduction reaction than those of the sputtered electrode. This means that the electro-deposited electrode has much higher apparent catalytic reactivity than that in the case of sputtered one. It is considered that such enhanced reactivity found in the electro-deposited sample is related to an increase in effective surface area by nanostructure morphology of electrodes as shown in Fig. 2 and 3.

Figure 5 presents the complex-plane impedance plots for Pt electrodes. The result of impedance experiment shows the typical plot corresponding to an equivalent circuit composed with the resistance of electrolyte, the capacitance of electrical double layer (EDL), and the complex resistance of EDL in the boundary of electrode and electrolyte. In Nyquist plot, frequency increases

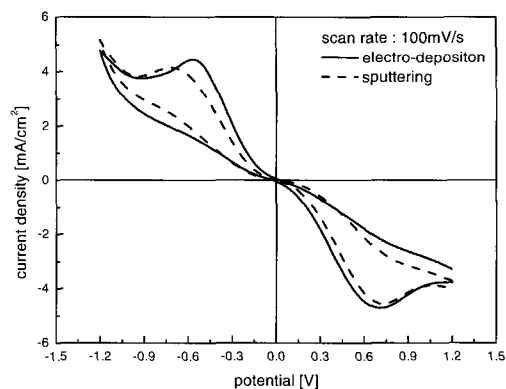


Fig. 4. The cyclic-voltammogram of Pt electrodes. Sweep rate is 100 mV/s.

from right to left. The resistance of electrolyte and the complex resistance are defined at a point that a half circle meets with x-axis ($y = 0$) at high frequency region and low frequency region, respectively. However, in Fig. 5 the complex resistance was not directly determined from the measured curve because the diffusion rate of iodide ion controlled the whole reaction rate at low frequency region. At diffusion-controlled region an impedance curve appears as linear line. In this case, the complex resistance can be determined by extrapolation of half circle measured at reaction-controlled region. In Fig. 5, it is shown that electro-deposited Pt has lower complex resistance than that in the case of the sputtered Pt. From these results, we can regard that the electro-deposited electrode with enlarged surface area has higher

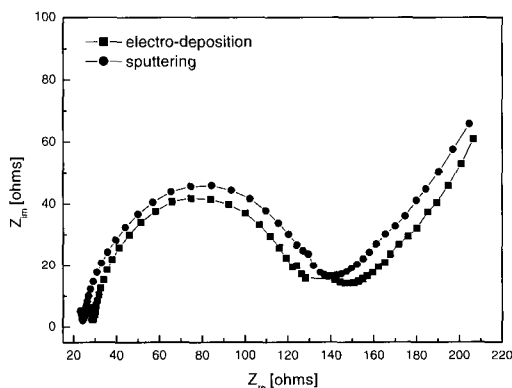


Fig. 5. Nyquist plot of ac impedance spectroscopy of Pt electrodes. Z_{im} and Z_{re} mean imaginary and real part of impedance, respectively.

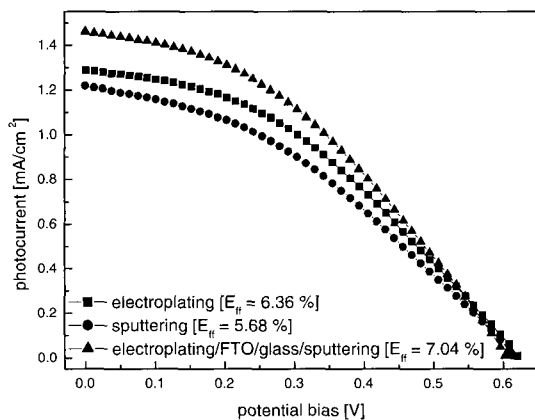


Fig. 6. J-V plots of DSSC having the electro-deposited electrode and the sputtered electrode together with the electrode of composite structure.

electrochemical activity than the electrode having smooth surface morphology. i.e. the case of the sputtered electrode.

The solar cell efficiency is not only affected by the electrochemical reaction rate at the surface of electrode, but also electrical conductivity and the reflectivity of electrode. Therefore, the effectiveness of an electrode for the application to DSSC should be tested in a normal solar cell. Figure 6 shows the J-V curves of DSSC with the two Pt electrodes. The DSSC with electro-deposited Pt electrode shows more enhanced performance, as expected from electrochemical experiments. Besides both electrodes mentioned above, the third electrode, having the composite structure, was additionally prepared. Pt composite electrode consists of sputtered one, following electrodeposited layer. In this electrode, one side contact with electrolyte has the electro-deposited electrode and the other side has the high reflectivity coating film such as sputtered Pt or thermal evaporated Al. Using Pt composite electrode, dye-sensitized TiO₂ dye-sensitized solar cell was assembled and I-V measurement was carried out. It is expected that the composite electrode bring about the effect of combining the high electrochemical reactivity of electrodeposited electrode and the high reflectivity of rear film. As expected, the efficiency of this cell is measured as best, as shown in Fig. 6.

4. CONCLUSION

In this study, the electrochemical behavior of the electro-deposited electrode was compared with that of the sputtered Pt electrode. The electrochemical reactivity of the Pt electrodes was determined by the cyclic-voltammetry and ac impedance spectroscopy. It was confirmed that the electro-deposited Pt electrode had better electrochemical properties of DSSC than in the case of the sputtered electrode. This is likely that enlarged area of surface in electro-deposited Pt electrode comparison with sputtered Pt electrode play a key role in enhancing electrochemical properties.

In order to verify the above-mentioned effect of two Pt electrodes, DSSC with the two kinds of electrodes were constructed and I-V characteristics were measured. As results of the I-V test, the electro-deposited Pt electrode shows more enhanced performance and higher opto-electric conversion efficiency than in the case of the sputtered Pt electrode, as expected from electrochemical experiments.

In conclusion, it is considered that characteristics of the electro-deposited Pt electrode having higher surface area as counter electrode of DSSC is superior to the sputtered electrode.

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