The Characteristic Analysis of the Sputter-deposited Pt Thin film for the Dye-sensitized solar Cell

色素増感太陽電池のスパッタ蒸着による白金薄膜の特性分析

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Dye-sensitized solar cells consist of the photo electrode of TiO_2/dye layer, the platinized counter electrode and the redox electrolyte. After light absorption, the electrons from excited dye are transferred to the external load through the TiO_2 network. The oxidized dyes are recovered by the electron injection from an electrolyte. In the operation, Pt catalyst plays an important role in the smooth electron supply to electrolyte for a high performance. In this work, the Pt thin films by various fabrication methods were characterized. I-V data, electrochemical impedance, and cyclic voltammetry were analyzed for the verification.

1. Introduction

Dye-sensitized solar cells (DSCs) have been considered as a possible alternative to current silicon based photovoltaic devices because of their advantages of high efficiency, simple fabrication process and low production cost [1,2]. Typical DSCs consist of a dye-sensitized nano-porous TiO₂ film interpenetrated by a redox electrolyte. After light absorption, electrons from excited dye molecules are transferred to the conduction band of TiO_2 , and diffuse through the TiO_2 network to the contact electrode. The oxidized dye molecules are recovered by the electron supply from electrolyte. Especially, the counter electrode, as one important component in DSCs, are usually constructed of conductive glass substrates coated with Pt films due to its superior catalytic activity for I^{-}/I_{3}^{-} redox couple. Pt counter electrode is fabricated by various methods such as sputter, electroplating, thermal depositions and so on [3-5]. In this work, the property of Pt thin films according to the fabrication methods was investigated. In order to verify each property, the effect in terms of the photovoltaic performance, the electrochemical impedance and the cyclic voltammetry was examined.

2. Experimental

DSCs used in this work were fabricated as follows. FTO substrates were used as the transparent conductive oxide (TCO) to make the photo and counter electrodes. The substrates were cleaned by sonicating in ethyl alcohol. And a nano-porous TiO_2 with a thickness of about 50 µm

was pasted onto the FTO substrate. The film was sintered at 450°C for 30min and the sintered photo electrode was soaked in a 0.2mM N719 dye solution for 24h. For the counter electrode, Pt thin films were deposited by three methods; sputtering, solution, and paste depositions. For the sputter deposition, Pt thin film was deposited by radio frequency sputtering at a power of 150W and a working pressure of 2.4×10^{-3} Torr. For the solution deposition, 10mM H₂PtCl₆ solution in the isopropanol was spin-coated on the FTO substrate with the rotating speed of 3,000 rpm and sintered at 450°C for 30 min. For the paste deposition, Pt precursor paste was deposited by the doctor blade method and sintered at 400°C for 30 min. Deposited films were morphologically characterized by the field emission scanning electron microscopy (FE-SEM). After that, the photo and counter electrodes were sealed and completed by injecting a redox electrolyte.

The photovoltaic performance was measured under 1 sun. The irradiated cell area was 0.25cm^2 . The I-V data were used to calculate the short-circuit current density (J_{SC}), open-circuit voltage (V_{OC}), fill factor (*FF*) and the overall efficiency (η). The electrochemical impedance spectroscope (*EIS*) and the cyclic voltammogram (*CV*) were analyzed by the electrochemical analysis instrument. In order to characterize Pt counter electrode, CV was operated at the scan rate of 10mV/s and the potential region from -1V to 1V. EIS spectra were measured over a frequency range from 10mHz to 1MHz. The applied bias voltage and AC amplitude are set at V_{OC} of DSC and 10mV, respectively.

3. Results and discussion



Fig.1. FE-SEM images of Pt thin films deposited by (a) sputter, (b) solution, (c) paste deposition

Figure 1 shows FE-SEM images of Pt thin films by various deposition methods. The thickest film was coated by doctor blade method. Therefore, FTO structure was not shown unlike other two films. However, different thickness was not affected because the performance of DSC didn't dependent on the thickness of Pt thin film [3]. And the sputter deposition made the roughest film and the lowest transmittance while other two films were transparent.



Fig.2. Cyclic voltammetry of Pt films

Figure 2 shows CV of different Pt films. In the CV, the peak values of negative and positive pairs mean the activity of $I_3^-+2e^-\rightarrow 3I^-$ and $3I^-\rightarrow I_3^-+2e^-$ reactions, respectively. That is, the catalytic reaction was the most active in the case of the sputter deposition and the solution deposition had the worst catalytic reaction.



Fig.3. Electrochemical impedances according to Pt films

And the charge transportation at the counter electrode was compared by EIS analysis. Figure 3 shows a Nyquist diagram of EIS. Two semicircles are attributed to the charge transportation at the counter electrode and the electron transfer at the TiO₂/dye/electrolyte interface in the high and middle frequency ranges, respectively [6]. In figure 3, the second semicircles were similar each other

because the experimental condition was identical except for the fabrication of Pt thin film. However, the first semicircles related to the charge transportation at the counter electrode were much different. The results were almost same with the above-mentioned CV analysis. The charge transportation was the best on the sputtered Pt film and the worst on the solution coated Pt film.

The sputtered Pt thin film had the most active catalytic reaction and the best charge transportation based on the CV and EIS. Finally, the photovoltaic performance was measured. Table I shows their performance. As follow above results, DSC with the sputtered Pt film had the best performance while DSC with the solution deposited film had the worst performance. That is, their different catalytic activity made different performance. And their different catalytic activity came from the roughness of surface because the rough film has wider surface for the active catalytic reaction.

Table I. The performance of DSCs with different Pt films

	$V_{OC}(V)$	$J_{SC}(mA/cm^2)$	FF	η(%)
Sputtering	0.73	12.96	0.65	5.47
Pt Solution	0.73	11.58	0.43	3.65
Pt Paste	0.73	12.99	0.50	4.72

4. Conclusion

In this work, the different platinized counter electrodes were fabricated by various deposition methods such as sputter, solution, and paste deposition. The CV and EIS analysis were verified their catalytic activities and charge transportation at the counter electrode, respectively. As a result, the sputtered Pt film had the most active catalytic reaction and the best charge transportation. And the good catalytic activity and charge transportation made the photovoltaic performance enhanced. Consequently, the performance of DSC with sputtered Pt counter electrode was the best based on above-mentioned properties.

References

- [1] B.O'Regan, M.Grätzel: Nature **353** (1991) 737.
- [2] M. Grätzel: Nature **414** (2001) 338.
- [3] X. Fang, T. Ma, G. Guan, M. Akiyama, E. Abe: J. Photochem. Photobio. A: Chem. **164** (2004) 179.
- [4] P. Li, J. Wu, J. Lin, M. Huang, Z. Lan, Q. Li: Electrochim. Acta 53 (2008) 4161.
- [5] N. Papageorgiou: Coordin. Chem. Rev. 248 (2004) 1421.
- [6] N.Koide, A.Islam, Y.Chiba, L.Han: J. Photochem. Photobio. A: Chem. **182** (2006) 296.
- [7] H. Seo, M. Son, J. Hong, D.Y. Lee, T.P. An, H. Kim, H.J. Kim: Sol. Energy 83 (2009) 2217.