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Seasoning effect of dye-sensitized solar cells with different counter electrodes

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Abstract Time dependent characteristics of the dye sensitized solar cells (DSSCs) having different counter electrodes were studied. For this study, three different types of counter electrodes CNT, sputtered platinum and electroplated platinum were used. Electrochemical impedance spectroscopy was used to study the aging effect of three counter electrode through measuring electrochemical properties of counter electrode/electrolyte interface as a function of time.

In the case of DSSC with CNT counter electrode, photoelectric conversion efficiency was almost constant. On the other hand, DSSC with sputtered Pt/electroplated Pt counter electrode, decline in efficiency was observed.

EIS measured that, decline in efficiency of sputtered Pt/electroplated Pt DSSC was due to increase in the series resistance.

Keywords Dye-sensitized solar cell · Counter electrode · Pt · CNT · Impedance spectroscopy

1 Introduction

A dye-sensitized solar cell (DSSC) is a sort of electrochemical photovoltaic battery using the photo-absorption properties of special dyes, the high surface area of TiO_2 nanoporous electrode and redox reactions of iodide ions in electrolyte [1]. In such cell, the redox reactions occur on the interfaces of electrolyte/counter electrode and electrolyte/dye molecule. The reaction on the surface of counter electrode is the reduction of tri-iodide such as $I_3^- + 2e \rightarrow 3I^-$, while the oxidation of iodide occurs on the dye molecule. The efficiency and properties of DSSC are deeply affected by the reduction rate on the counter electrode and the properties of counter electrode materials. The materials used for the good counter electrode should have a good catalytic effect on the reduction of tiiodide, high surface area, and high electric conductivity. The widely used counter electrodes are various Pt thin films deposited on a transparent conducting oxide (TCO) coated glass substrate. These Pt films can be prepared by sputtering, electro-deposition and screen printing [2, 3]. Carbon materials can be used for commercial DSSC because of their low price; although its properties are inferior to Pt. Recently there is a great interest in the carbon nanotube (CNT) having good catalytic effect and high electric conductivity [4, 5].

One of the main problems to delay the commercialization of DSSC is the stability of the cell. The efficiency of DSSC often rapidly drops with time in the initial several days after manufacturing due to the degradation of dye molecules and the reaction of electrolyte with sealing materials or counter electrode.

In this study we investigated the initial stability of DSSC with two Pt counter electrodes prepared by sputtering and electro-deposition and tried to find the causes of efficiency drop by the counter electrode. Especially, the possibility of CNT as the new long stable counter electrode materials was estimated comparing to its electrochemical performance to those of Pt.

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2 Experimental procedure

2.1 Construction of DSSC

Nanoporous TiO_2 film was fabricated by screen-printing method. TiO_2 paste for screen printing was prepared by mixing TiO_2 nano powder (Degusa P25) with α-terpineol. Nanocrystalline TiO_2 paste was coated on F doped SnO_2 glass (FTO) having the sheet resistance 12 ohm/sq, 80% optical transmittance in the visible region. The film was sintered at 480°C for 1 h in air. For adsorbing photo sensitized dye on the TiO_2 surface, TiO_2 electrodes were immersed in a solution of red dye ($RuL_2(NCS)_2$[L = 2,2′-bipyridine-4,4′-dicarboxylic acid] (N3) for 24 h at room temperature, and rinsed in ethanol.

Dye-adsorbed TiO_2 electrode and counter-electrode were assembled as a sandwich type cell, and then the assembled cell was filled with the redox electrolyte containing I^-/I_3^- redox couple. The electrolyte introduced into the cell by capillary effect through thin gap, having approximately 50 μm thickness between two electrodes. The gap was sealed with small amount of sealing materials, Amosil 4 (Solaronix SA). Structure of dye-sensitized solar cell is shown in Fig. 1.

2.2 Preparation of counter electrode

Pt counter electrodes were coated on FTO by electro-deposition and sputtering methods, respectively. In the case of electro-deposition method, platinum plate ($3 \times 3\,cm^2$) and FTO side 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 s in a 0.002 M H_2PtCl_6 aqueous solution.

The 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.

In this experiment, CNT powder was prepared by Carbon Nanotech Co. using Fe caltalysis by thermal chemical-vapor process and was multi-wall type of carbon nanotubes having 10–20 nm in diameter and 5 μm in length. Mixture of CNT powder, de-ionized water and Carboxyl Methyl Cellulose were mechanically ball-milled for 24 h. CNT paste was coated on FTO glass (9 × 9 mm), using doctor blade method and then dried at 70°C for 10 h in air. CNT film thickness is approximately 20–25 μm.

2.3 Measurement of electrochemical properties

To characterize CNT and Pt electrodes, electrochemical impedance spectroscopy (EIS) was executed. The EIS measurement was performed with a Galvanostat/Potentiostat (EG&G 273A) and a Lock-in amplifier (EG&G 5210). All measurements were carried out in room temperature.

3 Results and discussion

Figure 2 shows seasoning effect of opto-electric conversion in three kinds of DSSC having two Pt counter electrodes and CNT counter electrode. The I-V measurement of DSSC was conducted after 24 h from the time of electrolyte injection for waiting the consolidation of sealing adhesive. In Fig. 2, in the case of CNT counter electrode, the efficiency of DSSC slightly changes within several days. However, in the case of two Pt counter electrodes, the rapid degradation of efficiency occurred, showing stability as low values after 3 days. From these results, it is found that DSSC having CNT counter electrode has more stability than that in the case of Pt counter

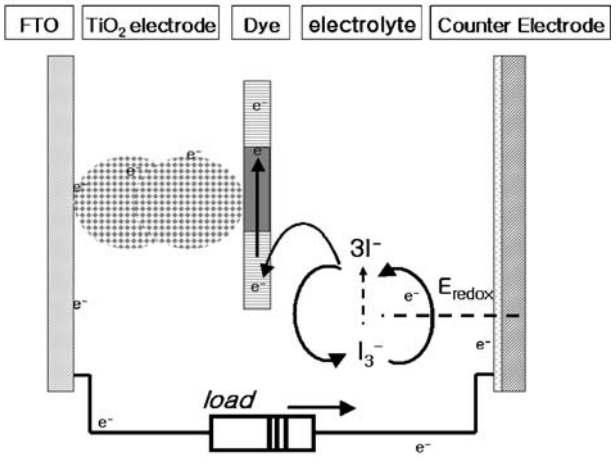


Fig. 1 Schematic diagram of dye sensitized solar cell

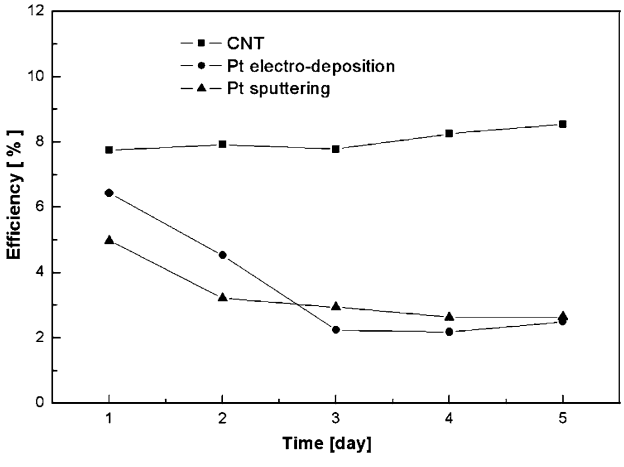


Fig. 2 Variation of efficiency of DSSC using Pt electrodes and CNT electrode with time

electrodes. Also, higher efficiency of DSSC was observed in the case of CNT counter electrodes.

To understand change of DSSC efficiency with aging time, the electrochemical impedance spectroscopy (EIS) and the surface morphologies of the Pt and CNT electrodes were employed.

The FE-SEM image of Pt film deposited by an electro-deposition method is shown in Fig. 3(a). It was found that the 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 Pt coated film is almost similar to that of FTO glass substrate. Figure 3(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 electrode. Figure 3(c) shows the surface morphology of CNT film prepared by the doctor-blade method. The FE-SEM image of CNT film shows severely tangled structure of CNT combined with CMC solution. From such CNT film, we may expect the larger surface area than that in the case of Pt film, especially. Also, CNT itself has good electrical conductivity, i.e. $10^{-4}\Omega\cdot$cm. The sheet resistance of CNT-coated layer on FTO glass was measured as the value of $10\Omega/\square$ by 4-point probe method. This means that CNT electrode may be used as a good counter electrode of DSSC in the standpoint of conductivity.

For EIS measurements, the structure of test cells was designed to be as similar as DSSC except replacing TiO_2 to Pt plate. Cells for EIS measurement consist of two main parts which relate to equivalent circuit as shown in Fig. 4. One part is parallel connection of resistance (Rp) and capacitance (C_B) for interfacial reaction. The other part is series connection of electrolyte resistance, electrode resistance, and interfacial resistance between electrode and TCO.

Here, Rp and C_B is related to reaction of Helmholtz double layer. Rs is related to total resistance of others except interfacial reactions. The value of Rs, series resistance of test cell, can be obtained from intercept point with zero imaginary part. Also, Rp is related to a region of relatively lower frequency. This value is determined by fitting the semi circle. Figure 5 show the Nyquist plots of as prepared cell (a) and 5 days old cell (b). In this figure, in the case of CNT electrode there is no significant change of impedance characteristics even if 5 days past. The value of Rs is approximately 22.5 ohm. However, in the case of Pt electrode, Rs was increased from 17.0 to 62.5 ohm. In the measured electrode part of test cell, Rs is strongly dependent on $R_{electrode}$ and $R_{electrode/TCO}$. In this case, we used same electrolyte and FTO glass. R_{Pt} increased with increasing aging time, since small amount of Pt particles detached

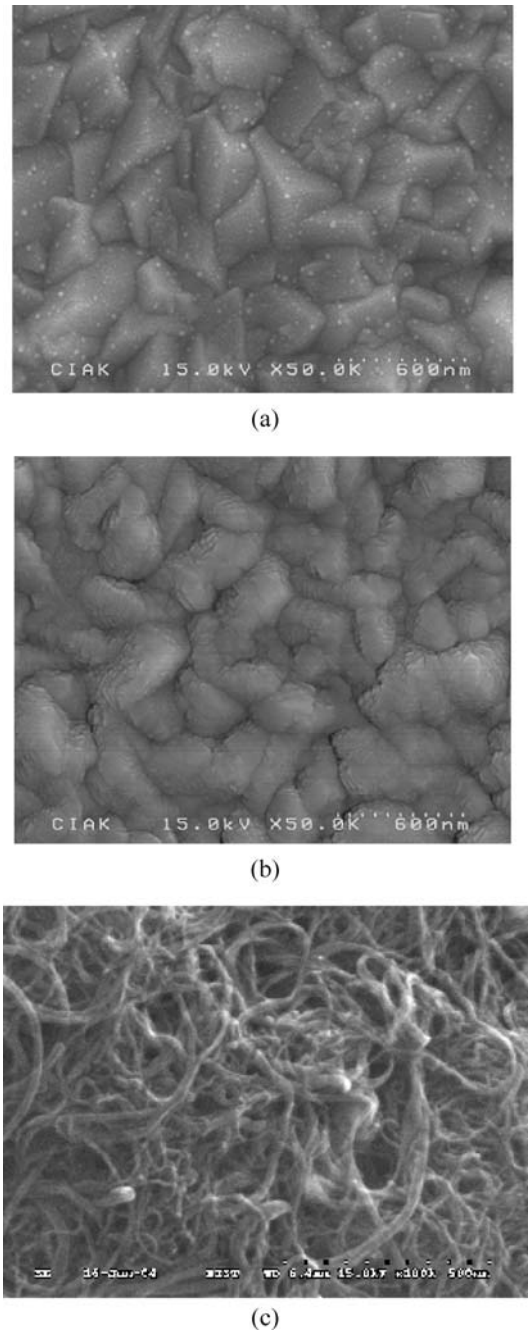


Fig. 3 The FE-SEM images of Pt films prepared by (a) electro-deposition (b) sputtering and CNT film by doctor-blade method (c)

from FTO substrate. Such phenomena were also reported in other studies [6, 7]. In Fig. 5 R_s decreased with increasing aging time, however, $R_{electrode}$ and Rs increased. In the case of CNT electrode, $R_{interface}$ (Rp) slightly decreased with increasing aging time. Controversially, in the case of Pt electrode, $R_{interface}$(Rp) remarkablely increased with increasing aging time. In the case of CNT electrode, Nyquist plot (Fig 5(a)) shows no significant increase in interfacial resistance. This means CNT and binder CMC are stable against electrolyte.

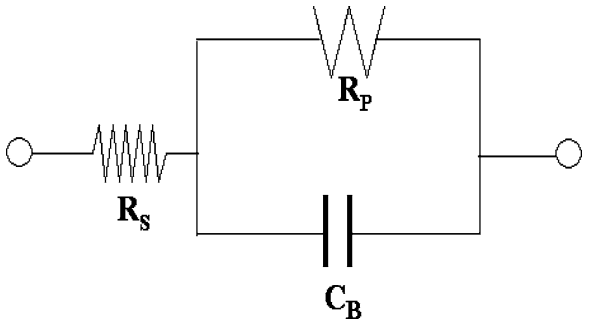
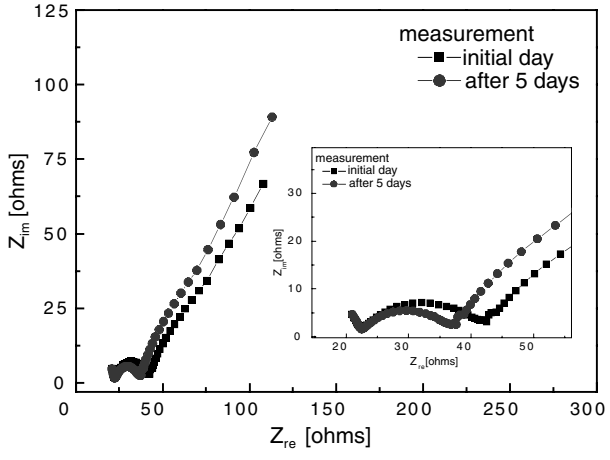


Fig. 4 Equivalent circuit of cell for EIS measurement



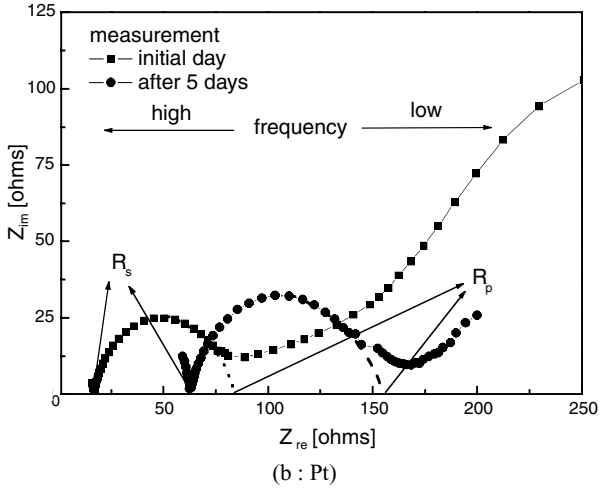


Fig. 5 Nyquist plots measured at the cell assembled day and after 5 days: CNT (a) and Pt (b)

also, there was no detachment of CNT from FTO glass, since good adhesion between CNT and FTO glass occurred.

From such effects, it is inferred that efficiencies of DSSCs having CNT counter electrode steadily maintained after 5 days. Also, in the case of Pt electrode, it is considered that efficiencies of DSSCs remarkably decreased with increasing aging time

Consequently, we confirmed that stability of CNT layer as counter electrode of DSSCs is superior to that used Pt electrode. However, in order to establish high stability of DSSCs having Pt counter-electrode, further research on adhesive between Pt (or CNT) and TCO layers is needed in near future.

4 Conclusion

In this study, DSSCs using three different counter electrode were fabricated to understand time-dependent characteristics. Here, three different types of counter electrodes were used; a multi-wall carbon-nanotube (MWCNT) film coated by Doctor blade method; a Pt-sputtered film (∼500 nm); a Pt-electroplated film (∼ 5 nm). Changes in efficiency of DSSC, electrochemical impedance spectroscopy (EIS) of counter electrodes were investigated with increasing aging time.

As results, DSSC having CNT counter electrode has higher efficiency and more stability than those in the case of two Pt counter electrodes. In EIS experiment, there is no significant change of impedance characteristics in CNT electrode even if 5 days past. However, in the case of Pt electrode, three times of increase in the value of series resistance was observed. It is supposed that this increase of resistance comes from the degradation of the adhesion between Pt (or CNT) and TCO layers. Therefore, the high stability of the interface between counter electrode and substrate is one of important factors for enhancing the stability of DSSC.

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