Extended Abstracts of the 2010 International Conference on Solid State Devices and Materials, Tokyo, 2010, pp513-514

Application of a Porous Titanium Film to a Counter Electrode of a Dye-sensitized Solar Cell

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Introduction

Recently dye-sensitized solar cells (DSCs) [1] attract great interest for its easy preparation, low cost and relatively high energy conversion efficiency η. A DSC consists of a dye-coated titanium dioxide (TiO_2) particle layer on a transparent conductive oxide (TCO) glass substrate, an electrolyte with iodide/triiodide ions and a counter electrode. A TCO glass substrate on which a platinum (Pt) layer of several hundred nm in thickness is deposited is generally used as a counter electrode. The performance of a DSC depends on various factors. A series resistance is one of the most important factors and a large series resistance R_s causes a decrease in the fill factor (*FF*) leading to deterioration in the energy conversion efficiency η [2-4]. The conventional Pt/TCO counter electrode has generally a large resistance. The series resistance R_s mainly consists of three factors [5]. One is a resistance of charge transfer process in an electrolyte, another is a resistance at the TiO_2/electrolyte and electrolyte/counter electrode interfaces and the other is the sheet resistance of TCO. Therefore, it is quite important to develop a novel counter electrode with a low resistance at electrolyte/counter electrode interface and without a TCO substrate for reducing a series resistance R_s. On the other hand, the high corrosion resistance is required of a counter electrode because triiodine ions are reduced to iodine ions at the electrolyte/counter electrode interface. Therefore, the porous titanium (Ti) is a promising material for the counter electrode because the large surface of the porous material reduces the interface resistance and because Ti is highly corrosion resistant metal and inexpensive compared to Pt. Here, in this study, we developed a porous Ti counter electrode and the surface of porous Ti is coated with a very thin Pt layer. A glass substrate on which aluminum (Al) was deposited was used instead of a TCO glass substrate. Finally, the performance of the DSC using a porous Ti counter electrode was compared with that of the DSC using a conventional Pt/TCO counter electrode.

2. Experimental

2.1. Preparation of the counter electrode of DSC

An Al film of about 200 nm in thickness was deposited on a glass substrate (Asahi Glass Co. Ltd, Japan) by the vacuum evaporation method. The Ti layers were deposited on the Al layer using the DC magnetron sputtering method. The structure of the Ti layer was controlled by an argon (Ar) pressure. The dense (not porous) Ti layer was deposited on the Al-deposited glass substrate at an Ar pressure of 0.08 Pa to prevent the Al layer from dissolving to an electrolyte. After depositing the dense Ti layer, a porous Ti layer was deposited on it at an Ar pressure of 1 Pa. The porosity of the Ti film were controlled by etching technique by a hydrofluoric acid solution (HF) (Stella Chemifa Corporation, Japan) of 1.36 % and a mixture of TiW-I (mixture of hydrogen peroxide and boric acid, chelating agent) and TiW-II (ammonia water) (Wako Pure Chemical Industries, Ltd., Japan). Finally, Pt was deposited on the porous Ti surface by thermal decomposition of H_2PtCl_6. In order to form a conventional Pt/TCO counter electrode an RF magnetron sputtering process was applied to deposit Pt on TCO (Asahi Glass Co. Ltd, Japan). Hitachi SU8000 FE-SEM (field emission scanning electron microscope) was used to observe the structures of the counter electrode.

2.2. Preparation of the TiO_2 electrode and Fabrication of DSC

TiO_2 paste was prepared using the ratio of TiO_2 nano-particle: poly-ethylene glycol (PEG): acetyle acetone: triton x100: H_2O = 300:150:30:15:1000 and was milled for 6 hours. The TiO_2 paste was applied to a TCO glass surface in the area of 5×5 mm^2. The sample (TiO_2/TCO) was annealed at 400ºC for 1 hour followed by at 500ºC for half an hour. N719 dye molecules were adsorbed on the TiO_2 layer for 24 hours. Finally the TiO_2 electrode and counter electrode were assembled. To prevent the short circuiting, these electrodes were kept isolated from each other by a polymer spacer. After filling an iodide/triode ion redox couple electrolyte in the interface between the two electrodes, the DSCs were characterized under the illumination of AM 1.5 (100mW) using a solar simulator.

3. Result and Discussions

3.1. Formation of a Porous Ti film

Figures (a) and (b) show FE-SEM images of the top view and the cross-section of an alternative counter electrode of a DSC which consists of a combination of porous and dense Ti films on an Al coated glass substrate after the treatment with diluted HF (1.36%) solution and a mixture of TiW-I and TiW-II (10:1 w/w) solution, respectively. From Fig. 1, we can see that the porous structure of Ti with large surface area was formed and

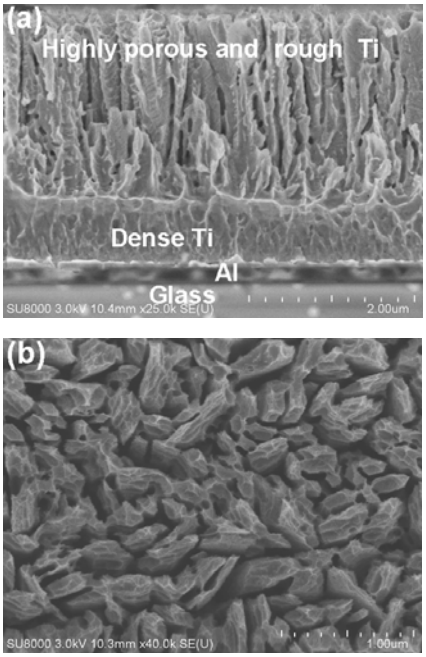

Fig. 1. FESEM images of (a) cross-sectional and (b) top surfaces of a Ti film as a new counter electrode.

that the Al layer was completely covered with the dense Ti layer.

3.2 Photovoltaic performance of DSC using the porous Ti counter electrode

Figure 2 shows a comparison of the photovoltaic performances of the DSCs using the porous Ti counter electrode (solid line) and using a conventional a Pt counter electrode (broken line). From Fig. 2, we can see that the porous Ti counter electrode was stably worked as a counter electrode without dissolution of Al to an electrolyte and that the DSC using porous Ti counter electrode showed higher open circuit voltage (V_{oc} = 0.65 V), larger short circuit current density (J_{sc} = 6.1 mA/cm^2), higher fill factor (*FF* = 0.65), and a better conversion efficiency (η = 2.6 %) than the DSC using a conventional Pt/TCO counter electrode (V_{oc} = 0.63 V, J_{sc} = 5.4 mA/cm^2, *FF* = 0.55, η = 2.0 %). The improvement of the conversion efficiency is mainly associated with a larger fill factor and a larger short circuit current. The large surface area of the porous Ti counter electrode decreased the resistance of the reduction process at the electrolyte/counter electrode interface and the Al layer instead of a TCO layer also decreased a series resistance. The decrease of the series resistance R_s led to the improvement of the fill factor. According to the single diode model, the improvement of short circuit current by the decrease in a series resistance cannot be explained although it has been reported [3-5]. This indicates that it is necessary to elucidate the detail of the photovoltaic mechanism of the DSC.

4. Conclusions

We formed a porous Ti film on an Al-deposited glass

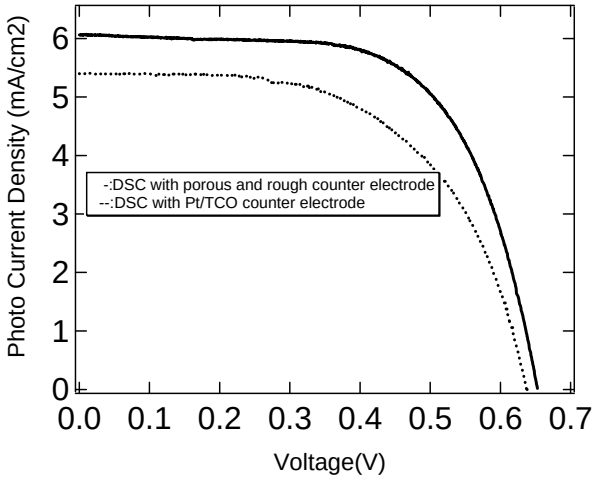

Fig. 2. *I-V* Characteristics of DSCs using porous Ti counter electrodes (solid line) and using Pt/TCO counter electrode (broken line).

substrate using the DC magnetron sputtering method and the etching technique with diluted HF and TiW-I-II solutions, and applied it to a counter electrode for a DSC. We demonstrated that the porous Ti counter electrode improved the conversion efficiency of a DSC compared to a conventional Pt/TCO counter electrode and that it was stable without dissolution of Al to an electrolyte. The large surface area of the porous Ti film decreased the series resistance of the DSC to improve the conversion efficiency. Our results indicate that the composite film of the porous and dense Ti and Al layers is one of the most promising candidates of a counter electrode for a DSC.

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