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Electrochemical impedance analysis on the additional layers for the enhancement on the performance of dye-sensitized solar cell

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ABSTRACT

A dye-sensitized solar cell is one of the representative photochemical solar cells. It has been actively studied and its performance has been much enhanced so far. For better performance, various additional layers such as compact, barrier, and light scattering layers have been applied. Compact and barrier layers suppress the charge recombination with redox electrolyte and light scattering layer improves the light harvesting. Although it was confirmed that these layers were clearly effective for the performance enhancement, there is still a variety of opinions concerning their electrochemical impedance analyses. Therefore, this work tried to analyze their effect on the internal impedance using electrochemical impedance spectroscopy. The most widely used materials were employed for the fabrication of additional layers. $TiCl_4$ and $Zn(NO_3)_2{\cdot}6H_2O$ aqueous solutions, and a 400 nm sized TiO_2 were used for compact, barrier, and light scattering layers, respectively. The photovoltaic characteristics confirmed their effect on the performance and their impedance spectra were analyzed according to high, middle, and low frequency bands. As a result, these layers mainly affected the impedance in the middle frequency range because the change of TiO_2/dye/electrolyte interface was significantly associated with this impedance. Finally, all three layers were applied to a single cell and the performance was considerably increased with reduced charge recombination and improved light harvesting.

1. Introduction

Dye-sensitized solar cells (DSCs) have attracted considerable attention in photovoltaic researches [1–5]. Its simple fabrication process and low manufacturing cost are advantageous in photovoltaics [6–10]. It has a sandwich structure that the redox electrolyte is filled between TiO_2/dye layered photo electrode and platinized counter electrode. Its working mechanism differs from conventional photovoltaic devices because the charge generation, extraction, and collection are separated. After absorption of incident photons, the electrons are photogenerated from excited dye molecules and injected to the conduction band of TiO_2. These electrons diffuse to the transparent conductive oxide (TCO), which is connected to the external circuit. The oxidized dye molecules are recovered by electrons supplied from the redox electrolyte and the electrolyte is regenerated by the electrons received from the counter electrode. This is one complete cycle. But this system has some drawbacks such as contact between TCO/TiO_2, and charge recombination, to suppress the performance of the solar cell. Therefore, to overcome these drawbacks and to improve the performance of the cell, many researches have investigated additional layers such as compact, barrier, and light scattering layers [8,11–18]. Fig. 1 shows the structural diagram of DSC with these layers. Compact layer is effective at the interface of TCO/TiO_2 to block the charge recombination and improve the contact between TCO and TiO_2 [8,11–13]. Barrier layer also suppresses the charge recombination at the TiO_2/electrolyte interface and increases photocurrent [14–16]. Light scattering layer re-supplies transmitted light to TiO_2/Dye layer and light harvesting of DSC is enhanced [17,18]. According to previous reports, it was obvious that they contributed to the performance enhancement. However, these layers were not impedance-analyzed clearly in previous researches. In this work, additional layers were clearly analyzed by electrochemical impedance spectroscopy (EIS). The performance enhancement with each layer was also elucidated separately on the basis of impedance analysis. Finally, the performance of all the three layers present in a single cell was also investigated. These layers were fabricated by general fabrication methods. Compact and barrier layers were fabricated by wet processes. $TiCl_4$ aqueous solution was spin-coated on TCO for a compact layer and zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$) aqueous solution was dip-coated on TiO_2 for barrier layer [13,16]. A 400 nm sized TiO_2 was used for the light scattering layer [17,18]. In order to analyze precisely, the photovoltaic performance, incident photon to current conversion efficiency (IPCE), and EIS were examined.

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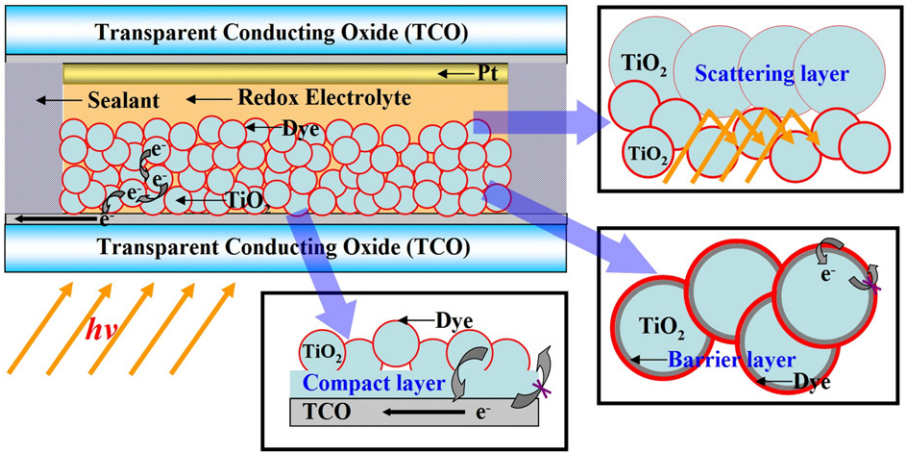


Fig. 1. Structural diagram of a DSC with compact, barrier, and light scattering layers.

2. Experimental details

DSCs were fabricated as follows. Fluorine-doped tin oxide (FTO) substrates (13 Ω/sq., Hartford Glass Co. Inc.) were used as TCO to make the photo and counter electrodes. They were cleaned by sonicating in ethanol and dried using a stream of nitrogen. For the compact layer, a 50 mM $TiCl_4$ aqueous solution was spin-coated on the cleaned FTO substrates with a rotating speed of 3000 rpm for 60 s. A $TiCl_4$ solution was prepared by slowly adding $TiCl_4$ (89545, Fluka) to distilled water in an ice bath [8,19]. After that, $TiCl_4$ coated FTO substrates were sintered at 500 °C for 30 min. A uniform and nano-porous TiO_2 (Ti-Nanoxide T/SP, Solaronix) layer with a thickness of approximately 50 μm was pasted onto the substrate by the doctor blade method. The deposited film was sintered at 450 °C for 30 min, and then its thickness was lowered to 10 μm. The thickness was measured by an α-step surface profiler (KLA Tencor Co., USA). For the barrier layer, FTO/TiO_2 substrates were dipped into a 50 mM $Zn(NO_3)_2{\cdot}6H_2O$ aqueous solution for 10 min and sintered at 450 °C for 30 min [16]. For the light scattering layer, a 400 nm sized TiO_2 (PST-400C, CCIC) was pasted on the FTO/TiO_2 substrate and sintered at 450 °C for 30 min [17,18]. Its thickness was about 1.7 μm. The formation of FTO/TiO_2/ZnO was ascertained by measuring X-ray diffraction (XRD, X'pert PRO MRD, Philips) under optimized operating conditions of 30 mA and 40 kV. Prepared electrodes were immersed in a 0.2 mM N719 dye (cis-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-discarboxylato)-ruthenium(II)-bis-tertabutylammonium, $RuC_{58}H_{86}N_8O_8S_2$) solution for 24 h. Excess dye molecules were removed by rinsing with ethanol. For the counter electrode, a 10 mM H_2PtCl_6 solution in the isopropanol was spin-coated on the FTO substrate with a rotating speed of 3000 rpm for 60 s and sintered at 400 °C for 30 min. After that, the photo and counter electrodes were sealed using a thermoplastic hot-melt sealant (SX 1170-25, Solaronix) with a thickness of 25 μm. The sealed cells were completed by injecting a redox electrolyte through a pre-drilled hole into the counter electrode. The redox electrolyte consisted of 0.5 M LiI, 0.05 M I_2 and 0.5 M 4-tertbutylpyridine in acetonitrile. A standard DSC without any additional layers was fabricated as a reference.

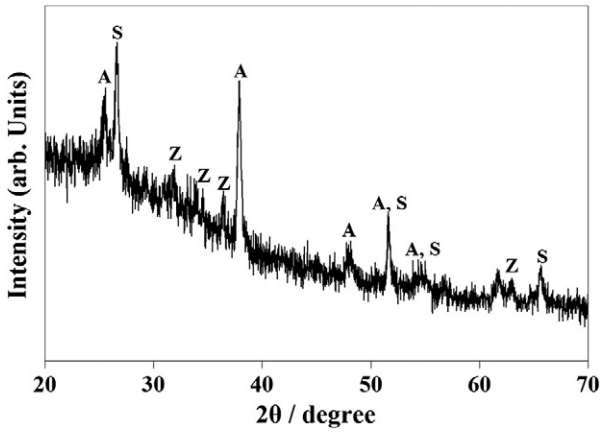
Before their characterization, DSCs were stored in the dark under open-circuit conditions for 24 h to allow the electrolyte to penetrate into the TiO_2 pores. The photovoltaic performance was measured under 1 sun (air mass 1.5, 100 mW/cm^2) by a source meter (Model 2400, Keithley Instrument, Inc.) and IPCE (SM-250-P1, Bunkoukeiki) was measured in the wavelength range from 250 to 900 nm. During their irradiance and characterization, DSCs were covered with a black mask fitting the irradiated cell area of 0.20 cm^2. Current–voltage (I–V) characteristic curve and Eq. (1) were used to calculate the short-circuit current (I_{SC}) and density (J_{SC}), open-circuit voltage (V_{OC}), fill factor (FF) and an overall efficiency (η). The electrochemical properties were investigated using EIS (SP-150, Biologic SAS). Impedance spectra were measured in the frequency range from 10 mHz to 1 MHz at room temperature under irradiation. The applied bias voltage and AC amplitude were set at V_{OC} of DSC and 10 mV, respectively. The electrical impedances were characterized using a Nyquist diagram.

$$\eta = \frac{P\max}{Pin} \times 100 = \frac{FF \cdot Voc \cdot Jsc}{Pin} \times 100(\%). \quad (1)$$

3. Results and discussion

Fig. 2 shows XRD patterns of TiO_2 coated with ZnO on FTO substrate. The phase of anatase TiO_2 denoted as 'A' was 25.2°, 37.7°, 48.0°, 52.0°, and 54.9° (JCPDS No. 89-4921) [14,15]. 'S' denoted peaks at 26.1°, 52.0°, and 65.9° attributed to SnO_2 from FTO [14]. The diffraction peak at 31.8°, 34.4°, 36.2°, and 63.2° denoted as 'Z' corresponded to the reflection of ZnO (JCPDS No. 79-0208) [14,15]. XRD results confirmed the presence of both TiO_2 and ZnO materials on the FTO substrates.

Fig. 3 shows I–V characteristic curves of a standard DSC and DSCs with additional layers. It was clear that all additional layers contributed to the performance enhancement. A DSC with the compact layer had 0.72 V of V_{OC}, 12.42 mA/cm^2 of J_{SC}, 0.71 of FF, and 6.36% of efficiency and a DSC with the barrier layer had 0.75 V of V_{OC}, 12.25 mA/cm^2 of



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