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Preparation of the working electrode of dye-sensitized solar cells: Effects of screen printing parameters

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ABSTRACT

The working electrode films of dye-sensitized solar cells are screen printed using a stainless steel cloth screen or a stencil screen. The as-prepared films and the corresponding cells are characterized and evaluated. The films prepared using the stainless steel cloth screen are thinner than those prepared using the stencil screen under the same screen printing conditions. Thus, while the stainless steel cloth screen is suitable for multi-layer film preparations, the stencil screen is ideal for mono-layer film preparations. Provided that the total working electrode film thickness is about the same, a three-layer working electrode prepared using the stainless steel cloth screen gives a cell with the conversion efficiency of 5.46% and a mono-layer working electrode prepared using the stencil screen gives a cell with the conversion efficiency of 5.30%. When using the stainless steel cloth screen for the working electrode preparation, a low squeegee angle and a low printing speed gives a porous thick film, which is ideal for dye absorption.

1. Introduction

High efficiency dye-sensitized solar cells (DSSCs) have been intensively studied since they were initially introduced by Grätzel's group [1,2]. Although some modifications have been proposed, a DSSC typically has a sandwich structure: a dye-adsorbed porous TiO_2 film coated on the transparent-conductive-oxide (TCO) covered substrate as the working electrode, a catalytic/conductive counter electrode and an electrolyte between two electrodes. When photons excite the TiO_2 absorbed dye molecules, the excited electrons inject into the conduction band of TiO_2 and the electrons are delivered to TCO through the networking of TiO_2. The electrons are delivered to the counter electrode through the external loop, and reduce the redox mediator in the electrolyte at the counter electrode. The reduced ion further regenerates the oxidized sensitizer and develops the complete electric loop [3,4]. The highest reported conversion efficiency for a DSSC cell is 12.3% [5]. Because of the attractive high conversion efficiency and easy fabrication process, many studies have been carried out to improve the photovoltaic performances of DSSCs [6–11]. Methods were also proposed for fast DSSC fabrications [12–14].

Although the doctor-blade technique is commonly used for the small area DSSC working electrode preparation in laboratories, other reliable working electrode preparation methods are required for large area DSSC commercialization. One of the most reliable DSSC working electrode preparation methods for commercialization is the screen printing technique [15–17]. The screen printing technique uses a squeegee and a screen to prepare a film on a flat substrate. When applying the screen printing technique for the DSSC working electrode preparation, the coating paste containing the TiO_2 nanopowders, the organic solvents and the binder solutions are coated on the pre-cleaned TCO deposited substrate. The coated wet film on the substrate is dried and sintered to form the nanoporous TiO_2 layer. Although it is known that the film thickness and uniformity are affected by the squeegee printing speed, the printing pressure, the coating paste viscosity, the surface properties of the substrate, the types of the squeegee and the screen and etc, only limited work has been carried out to study the effects of the paste composition on the properties of the porous TiO_2 film [15,16]. The influences of the screen printing parameters on the photovoltaic characteristics of the corresponding DSSCs are not fully understood. In this study, the effects of the squeegee speed, the squeegee printing pressure (angle) and the screen types

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on the properties of the working electrode and the photovoltaic performances of the corresponding cells are investigated.

2. Materials and method

2.1. TiO_2 working electrode preparation

The TiO_2 working electrode was prepared using the P200 paste (mass fraction of anatase TiO_2 powders = 15% to 20%, mean particle size = 20 nm to 50 nm, Everlight Chemical Industrial Corp., Taiwan) or the self-prepared P25 and P90 pastes. The compositions of P25 and P90 pastes are shown in Table 1. All chemicals listed in Table 1 were used as received from the supplier without any further treatments. When preparing P25 and P90 pastes, the chemicals in Table 1 were sealed in a 250 ml milling jar together with 25 g 2 cm zirconium milling balls. The chemicals were homogenized in a planetary ball mill rotating at 300 rpm for 2 h (PM-100, Retsch, Germany) and the pastes were thereby obtained.

Two screens were used for the film preparation: the stainless steel cloth screen (mesh = 200) and the stencil screen. The film prepared using the stainless steel cloth screen and P200, P25, or P90 paste are named SP200, SP25 and SP90, respectively. The film prepared using the stencil screen and P200 paste is named TP200. The stainless steel cloth consists of stainless steel wires of the diameter of 0.04 mm. The aperture size is 0.087 mm × 0.087 mm and the opening ratio is 0.47. The stencil screen has an opening of 10 mm × 10 mm and a thickness of 0.06 mm. A 70° rubber squeegee was used in the screening printing process. The gap between the substrate and the screen was set as 3.6 mm and 0 mm when using the stainless steel cloth screen and the stencil screen, respectively.

The influence of the squeegee printing angle on the corresponding DSSC performances was tested using SP200 films with the squeegee printing speed of 11 mm/s and the squeegee printing angles of 37° and 60° (Fig. 1). Since the same rubber squeegee had been used, a higher squeegee printing angle implies a smaller squeegee pressure acting on the screen. The influence of the squeegee speed on the corresponding DSSC performances was tested using SP200 films with the squeegee angle of 37° and the squeegee printing speeds of 11 mm/s and 55 mm/s.

2.2. DSSC preparation and evaluation

After printing, the wet film was dried and sintered in an oven. The oven was heated from room temperature to 500 °C with a heating rate of 4 °C/min and maintained at 500 °C for 1 h. This printing–drying–sintering process was repeated until the desired film thicknesses/layers have been achieved. The TiO_2 film with the desired thickness was immersed in a 0.3 mM D719 (Everlight Chemical Industrial Corp., Taiwan) acetonitrile solution for 24 h to allow the absorption of the dye molecules. The counter electrode was fabricated by spin-coating H_2PtCl_6 solution (5 mg/ml of isopropanol) on the pre-cleaned FTO conducting glass surface (10 Ω-cm), followed by reduction at 400 °C for 20 min. The dye-absorbed working electrode and the counter electrode were sealed by Surlyn® film of thickness 125 μm. The electrolyte of 0.5 M 4-tert-butyl-pyridine with a purity of 96.0%, 0.05 M I_2 with a purity of 99.8%, 0.5 M LiI with a purity of 98.0% and 0.6 M tetrabutylammonium iodide with a purity of 98.0% in acetonitrile was injected into the gap between the electrodes.

The photovoltaic performances of the DSSCs were evaluated. The size of the active area was 10 mm × 10 mm. The photocurrent–voltage curve of the cell was carried out at 25 °C using a 180 W xenon lamp of the intensity of 100 mW/cm^2 under one sun condition (AM 1.5 radiation) in a solar simulator (YSS-50AAA, Yu-Yi, Taiwan). The morphology of the printed film was observed by field-emission SEM (FE-SEM, S-5000N, Hitachi, Japan) and the 5-time average film thickness was measured by α-step (ET-3000, Kosaka, Japan). The BET specific surface area and the average pore size of the film were measured by Micromeretics ASAP 2020 (USA) using 99.999% nitrogen as the absorption gas. The haze value of the coated film on the FTO glass was measured by a haze meter (TC-H III, Tokyo Denshoku, Japan). The amount of dye adsorption on the film was also determined by a desorption method [12]. The dye of the dye-adsorbed working electrode was desorbed into a 0.1 M NaOH solution in de-ionized water. The absorption spectra of the desorbed-dye NaOH solution were then measured using an UV–vis spectrophotometer (Jasco V-650 spectrophotometer, Japan) to determine the amount of the dye adsorbed on the nanoporous TiO_2 layer.

Table 1
The compositions of the P25 and P90 pastes.

Paste	P25	P90
TiO_2	P25[a]	P90[b]
Powder (g)	10.00	8.00
Ethyl cellulose (g)	0.60	0.60
Isopropyl alcohol (ml)	10.0	10.0
α-Terpineol (ml)	30.0	30.0
Titanium (IV) isopropoxide (g)	2.00	2.00
Triton X-100 (g)	1.00	1.00
PEG 20000 (g)	3.00	3.00
4-Hydroxybenzoic acid (g)	0.25	0.25
Paste viscosity (cps)	27,500	21,500

[a] P25 (anatase 80% + rutile 20%, mean size = 21 nm, Degussa).
[b] P90 (anatase 90% + rutile 10%, mean size = 14 nm, Degussa).

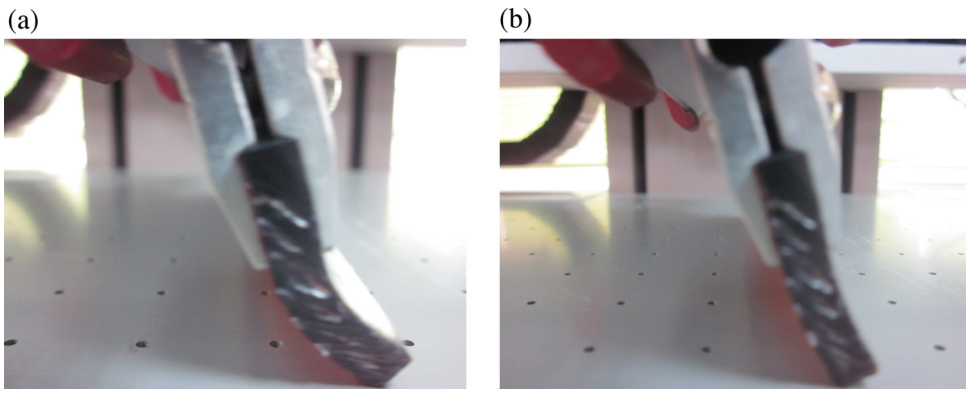

Fig. 1. The squeegee printing angle of (a) 37° and (b) 60°.