



High performance carbon black counter electrodes for dye-sensitized solar cells



Chia-Shing Wu, Ting-Wei Chang, Hsisheng Teng, Yuh-Lang Lee*

Department of Chemical Engineering, National Cheng Kung University, Tainan, 70101, Taiwan

ARTICLE INFO

Article history:

Received 3 February 2016

Received in revised form

29 May 2016

Accepted 6 September 2016

Keywords:

Carbon black

Poly(vinylidene fluoride)

Counter electrode

Doctor blade

Thermal treatment

ABSTRACT

Carbon black (CB) thin films are prepared using a doctor blade process and utilized as counter electrodes (CEs) of dye-sensitized solar cells (DSSCs). Poly(vinylidene fluoride) (PVDF) is used as a binder to regulate the viscosity of the CB paste to facilitate the doctor blade process. The PVDF is then removed via thermal treatment at 350 or 450 °C. The effects of CB composition (8–15 wt%) and the heat-treatment temperature on the electrochemical properties of the CB electrodes are studied, as well as on the performance of the corresponding DSSCs. The results show that, after the heat treatment, all CB films demonstrate a mesoporous structure. Film thickness increases with increased CB concentration. CB films heat-treated at 350 °C exhibit low electrochemical activity, high charge transfer resistance, and poor performance when utilized in DSSCs. These results are attributed to the presence of residual PVDF. By elevating the treating temperature to 450 °C, PVDF is completely removed and the electrochemical properties of the resultant CB films resemble closely those of platinum (Pt) film. The DSSCs using these CB CEs achieve conversion efficiencies (8.27–8.35%) comparable to cells using Pt (8.29%).

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1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted considerable attention due to their potential for high conversion efficiency, positioning them to be a viable alternative to traditional solar cells [1–3]. In the DSSC structure, the counter electrode (CE) acts as a catalyst to reduce the oxidized species of redox couples. Platinum (Pt) is the most common material used as the CEs of DSSCs. Platinum has high catalytic activity towards I_3^- and has been demonstrated as an efficient material for achieving high-performance DSSCs [4–6]. However, the high cost of Pt limits its practical application for the mass production of DSSCs.

In addition to Pt, a variety of alternative materials, including carbon [7–15], conducting polymers [16–19], metal sulfides [20–26], and metal carbides/nitrides/oxides [27–29], have also been applied as the CEs of DSSCs. Among these materials, carbon has the advantages of low-cost, environmental friendliness, and high corrosion resistance. Therefore, carbon is a promising material to supplant Pt, and has attracted much interest in the literature. In early 2003, carbon black (CB) films were prepared and employed as

the CE of DSSCs [8,30,31]. However, efficiency was very low (3.89%) [31]. In the later studies, carbon-related materials including carbon nanotubes [32], graphine [33], and reduced graphine oxide [34] were tested as DSSC CEs. Furthermore, carbon materials were also combined with other materials to fabricate composite CEs such as CB/TiO₂ [31,35], CB/Pt [36], Pt/carbon nanotubes [37], and Pt/graphene [38]. These studies demonstrated that DSSCs using carbon-based CEs as electrodes can achieve performance comparable to Pt [35,37]. However, high performance was obtained only for the composite electrodes. For the CEs prepared by pure carbon materials, it is still difficult to compete with Pt.

In this study, carbon black (CB) was utilized to prepare pure carbon CEs, aiming not only to fabricate high efficiency CEs, but also to develop a process suitable for mass production of DSSCs. Commercially available nano-size scale CB was utilized as the main component. PVDF was used as a binder to regulate the viscosity of the CB paste for the doctor-blade process. After printing a film on a fluorine-doped tin oxide (FTO) glass substrate, the film was heated in an oven under argon atmosphere to remove the PVDF, forming a pure CB film with a mesoporous structure. Carbon films with various thicknesses were prepared by controlling the composition of the CB pastes and their effects on cell performance were studied. The present study demonstrates that the CEs prepared by CB can achieve performance comparable to sputtered-Pt CEs.

* Corresponding author.

E-mail address: yilee@mail.ncku.edu.tw (Y.-L. Lee).

2. Experiments

2.1. Materials

TiO₂ pastes PST-18NR and 400C (Catalysts & Chemicals Industries Co., Ltd.), lithium iodide (99.99%), iodine (99.99%), 4-tert butylpyridine (TBP) (99%), 1-propyl-2,3-dimethylimidazolium iodide (DMPII) (99.5%), guanidine thiocyanate (99%), lithium perchlorate (98%), CB (Printex L, Degussa), [NBu₄]₂[*cis*-Ru(4,4-Hdcbpy)₂(NCS)₂] N719 dye, and PVDF (MW: 60000 g/mol, Polysciences, Inc.) were acquired from commercial sources. The detail properties of then CB used in this work were given in the [supplementary information](#).

2.2. Preparation of dye-sensitized TiO₂ photoanodes

The main and scattering layers were prepared by screen printing pastes containing 20- and 400-nm TiO₂, respectively, followed by a gradual sintering process. Then, the TiO₂ films were immersed in an ethanol solution containing 0.5 mM N719 dye for 24 h at room temperature, followed by rinsing with ethanol.

2.3. Preparation of electrolyte

An acetonitrile solution containing 0.1 M LiI, 0.03 M I₂, 0.5 M TBP, 0.1 M guanidine thiocyanate, and 0.6 M DMPII was used as the DSSC electrolyte in this work.

2.4. Preparation of carbon black and platinum counter electrodes

CB CEs were prepared using pastes containing CB and PVDF. Briefly, 10 wt% PVDF was first dissolved in *N*-methyl-2-pyrrolidone and then 8–15 wt% CB was added to the polymer solutions and mixed to form homogeneous pastes. The CB/PVDF pastes were doctor bladed onto FTO substrates using 60- μ m films as spacers. The CB/PVDF films were then heat-treated at 350 °C or 450 °C in nitrogen atmosphere to decompose the PVDF. For preparing Pt CEs, a direct-current sputter coater (Cressington 108 Auto Sputter Coater, Ted Pella, USA) was employed at a base pressure of 10⁻² Torr. The sputtering current was controlled at 40 mA, which corresponds to a deposition rate of 0.11 \pm 0.005 nm/s. The deposition time was 105s.

2.5. Fabrication of DSSCs using carbon-black-based counter electrodes

Dye-sensitized TiO₂ photoanodes and CEs were sandwiched using a 60- μ m-thick sealing spacer. Two holes were left in the CE for injection of electrolyte. These holes were sealed using polyimide tape after electrolyte injection. The performance of the cells was measured under one-sun illumination from a solar simulator (AM1.5, 100 mW cm⁻²) (San-Wi Electric, class 3A, XES-301S). The current-voltage (*I*-*V*) characteristics of the cells were recorded using an Eco Chemie Autolab potentiostat/galvanostat. At least three samples were prepared for each condition and the average values were calculated for comparison.

2.6. Experimental details of the CV measurements

The cyclic voltammetry (CV) measurement was conducted in an electrochemical cell with three-electrode configuration, including an Ag/AgCl reference electrode and a Pt counter electrode. The potentiostat was supplied by CH Instruments Inc. (model CHI627D). Acetonitrile was used as the solvent to prepare the electrolyte containing 10 mM LiI, 1 mM I₂ and 0.1 M LiClO₄. The experiment

was performed at room temperature with a scanning rate of 50 mV/s.

3. Results and discussion

3.1. Thermal decomposition temperature of PVDF

PVDF was used as a binder to regulate the viscosity of CB pastes to facilitate the doctor blade process. However, PVDF exhibits poor conductivity and the presence of PVDF will inhibit charge transfer. Fortunately, PVDF is easily removed via thermal treatment. Thermogravimetric analysis was performed on the PVDF and the result (shown in [Fig. S1](#), in Supporting Information: SI) reveals that the thermal decomposition temperature (*T*_d) of PVDF is around 425 °C. Therefore, the CB/PVDF films were thermally treated at 450 °C for 30 min to remove PVDF. Furthermore, a lower heat-treatment temperature (350 °C) was also tested to investigate the effect of residual PVDF on the performance of the CEs.

3.2. Surface morphology and thicknesses of the films

The surface morphologies of the films were investigated using scanning electron microscopy (SEM) and the thicknesses measured by an alpha-step profilometer. The SEM images obtained from the 350 °C and 450 °C heat-treated films, as well as the film without heat treatment are shown in [Fig. 1](#). Note ribbon-like phases corresponding to PVDF can be observed on the film without heat treatment in [Fig. 1a](#). After heat treatment [[Fig. 1b,c](#)], the PVDF phases disappear and the films demonstrate a mesoporous structure with grain sizes of ca. 50–100 nm. It was found that all the heat-treated films have similar surface morphologies, independent of the CB compositions and treating temperatures. For film thickness (shown in [Table S1](#), SI), the films heat-treated at 350 °C and 450 °C have nearly identical thicknesses. The films prepared using 8 wt% CB paste have a thickness of ca. 4.8 μ m. Increasing CB composition leads to an increase of film thickness and a value of ca. 12 μ m was measured for the 15 wt% films. The results indicate that the thickness of a CB film can be controlled by varying the CB concentration in the paste. Furthermore, the similar film thicknesses and film morphologies obtained for the two treating temperatures imply that PVDF is also removed at 350 °C. However, it is certain that all PVDF molecules are removed completely.

To check the residual PVDF, the 15 wt% CB films were subjected to energy-dispersive X-ray spectroscopy (EDS) analysis and the atomic percentage of fluorine was used to evaluate the composition of PVDF. The CB film without heat treatment was found to have a fluorine composition of 15.8%. After 350 °C heat treatment, the concentration decreases to 5.7%. That is, a large amount of PVDF was removed, but some still exist in the film. For the 450 °C treated films, no fluorine can be detected, confirming the complete removal of PVDF.

3.3. Catalytic activity of the CB films

Cyclic voltammetry (CV) was utilized to investigate the catalytic activity of the CB CEs. [Fig. 2](#) shows the CV spectra measured in the electrolyte containing the I₃⁻/I⁻ redox couple. For sputtered-Pt, two pairs of redox peaks were observed. These can be attributed to the redox reactions of I₃⁻/I⁻ (0.08 and 0.38 V) and I₂/I₃⁻ (0.6 and 0.8 V), respectively. For the CB films heat-treated at 350 °C ([Fig. 2a](#)), the high potential redox-peaks (I₂/I₃⁻) are very similar to those of the Pt film, indicating the similar activity of these films to this reaction. However, for the low potential redox peak (I₃⁻/I⁻), which is responsible for the reactions in DSSCs, the current densities greatly decrease, especially for the reduction reaction. Furthermore, the

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