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Preparation and characterization of polyaniline film on stainless steel by electrochemical polymerization as a counter electrode of DSSC

Qi Qin, Jie Tao*, Yan Yang

College of Material Science and Technology, Nanjing University of Aeronautics and Astronautics, 29 Yudao Street, Nanjing 210016, PR China

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ABSTRACT

Polyaniline (PANI) films were electrodeposited on stainless steel 304 (SS) from 0.5 M H_2SO_4 solution containing 0.3 M aniline by potentiostatic techniques to prepare a low cost and non-fragile counter electrode in dye-sensitized solar cell (DSSC). The compact layer, micro-particles, nanorods and fibrils were observed on the top of PANI films with different applied potentials (E_{appl}) by SEM. Then the conductivity and electrochemical test illuminated that a polyaniline film with the highest conductivity and best electrocatalytic activity for I_3^-/I^- reaction was electrodeposited at 1.0 V E_{appl}. Finally, the photoelectric measurement showed that the energy conversion efficiency of DSSC with the PANI electrode was increased with the E_{appl} decreasing. And the efficiency of DSSC with PANI counter electrode at 1.0 V was higher than that with Pt electrode, owing to the loosely porous structure, high conductivity and excellent catalytic activity of PANI electrode.

1. Introduction

Dye-sensitized solar cells are one of the most promising photovoltaic devices owing to their high conversion efficiency and low cost [1–4]. The photovoltaic device is composed of a photo electrode and a counter electrode. In general, platinum thin films formed on transparent conductive glass substrates by vacuum vapor deposition or sputtering are used as the counter electrodes of DSSC. However, the platinized counter electrodes on conductive glasses are expensive and frangible [5,6]. Therefore, we consider using the stainless steel as the substrates, and employing a conducting polymer to replace Pt counter electrode in order to reduce the production cost of DSSC.

Recently, polyaniline is one of the most potential conducting polymers as counter electrodes due to its easy synthesis, high conductivity, and unique redox properties [7–10]. Among the previous research, there were many reports on PANI electrodeposited on the surface of stainless steel in the application of corrosion protection or supercapacitor. Sazou et al. reported polyaniline coating on stainless steel by potentiodynamic and potentiostatic deposition for a potential application to corrosion control [11]. Zhang et al. prepared a series of polyaniline/carbon nanotube array composite electrodes by cyclic voltammetry electrodeposition, to improve the capacitive performance of PANI/CNTA composites [12]. However, there were few reports about the PANI electrodeposited on SS as the counter electrode of DSSC in the previous researches. Wu et al. just studied the PANI counter electrode coated on conductive glasses using a chemical synthesis method [5], but the insoluble PANI was unable to form a compact and even film on the glass by the dip-tugging method. The electrochemical synthesis of PANI has the advantage of a direct and controllable synthesis on the surface of conducting substrates. Hence, to prepare polyaniline film by electropolymerization is explored in this study. The PANI films are synthesized on the surface of stainless steel 304 by potentiostatic techniques to construct counter electrodes for DSSCs, and the photoelectric performances of DSSCs with these PANI electrodes are also discussed.

2. Experimental

2.1. Materials

Aniline (An, analytical grade from Sinopharm Chemical Reagent Co., Ltd.) was purified by distillation under reduced pressure prior to usage. Analytical grade reagents, H_2SO_4, titanium (IV) chloride, iodine, lithium perchlorate, acetonitrile, ethanol and acetone (Sinopharm Chemical Reagent Co., Ltd.) were used without any pretreatment. All solutions were prepared from de-ionized water. Stainless steel 304 sheets (Haimen Senda Decoration Material Co., Ltd., China) were used for PANI deposition. Anhydrous lithium iodide, 4-*tert*-butylpyridine, 1-methyl-3-propylimidazolium iodide, methoxy-propionitrile were

* Corresponding author. Tel.: +86 13347800587; fax: +86 2552112626.
E-mail address: taojie@nuaa.edu.cn (J. Tao).

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provided by Fluka Chemical Corporation. TiO_2 electrode and N719 dye was the commercial product purchased from Hepta Chroma Solar Tech. Co., Ltd. (Dalian, China). Platinized counter electrode prepared on FTO conducting glass (Dyesol Limited, Australia) was used in the contrast test.

2.2. Preparation of PANI/SS electrodes

Stainless steel 304 sheets were rinsed with de-ionized water and immersed in ethanol ultrasonically for 15 min, then immersed in acetone ultrasonically for 15 min before PANI electropolymerization. One SS sheet was used as working electrode for PANI deposition. The deposited area was 1 cm^2 with other area insulated by adhesive tapes. And the counter electrode was a similar SS sheet with a larger area. PANI was electrodeposited on the surface of SS by potentiostatic method at different constant potentials (0.9 V, 1.0 V, 1.1 V, and 1.2 V) for 4000 s in a 0.3 M aniline/0.5 M sulphuric acid (H_2SO_4) electrolyte solution. Finally, PANI modified SS electrode was immersed in 0.5 M H_2SO_4 statically in order to expel aniline monomer and oligomer PANI from the polymeric film and then rinsed with de-ionized water for several times and dried in a vacuum at 60 °C for 24 h.

2.3. Assembling of DSSCs

Nano-TiO_2 electrode was treated with 50 mM $TiCl_4$ aqueous solution at 70 °C for 30 min and washed with distilled water. Then the porous TiO_2 electrode was sintered by anneal at 450 °C for 30 min. After cooling to 100 °C, the TiO_2 film was immersed in an ethanol solution of N719 dye (0.5 mmol/L) for 24 h. Finally, a dye-sensitized solar cell was assembled by injecting a drop of electrolyte with I_2 (0.05 mol/L), LiI (0.5 mol/L), 1-methyl-3-propylimidazolium iodide (0.4 mol/L), 4-*tert*-butylpyridine (0.5 mol/L) in methoxypropionitrile (5 mL) into the aperture between the TiO_2 porous film electrode and the PANI/SS electrode.

2.4. Characterization of PANI/SS electrodes

The morphology of PANI was characterized by SEM (LEO1550, GER). FTIR spectrum of the PANI was recorded in the range of 500–4000 cm^{-1} using FTIR spectroscopy (Perkin Elmer 1760, USA). The conductivity of PANI was measured by manual four probe instrument (MP 1008, WENTWORTH, UK). X-ray photoelectron spectroscopy analyses were conducted at a vacuum pressure of $(1.0–2.0) \times 10^{-9}$ Torr and an angle of incidence around 45°. The XPS spectra were obtained by an ESCA System PH I550 photoelectron spectrometer with an Al Kα source, operating at 300 W (10 kV). The binding energy scale was calibrated with reference to the C1s line at 284.6 eV. All the polymerization experiments and cyclic voltammogram measurements were performed on an electrochemical workstation (CHI660A, CH Instrument, China). For cyclic voltammogram method, the configuration of the electrochemical cell was in three-electrode system. The PANI/SS, Pt-foiled, and saturated calomel electrodes were employed as working, counter and reference electrodes. The electrolyte was an acetonitrile solution containing 10 mM LiI, 1 mM I_2, and 0.1 M $LiClO_4$. The electrochemical impedance spectroscopy (EIS) measurements were performed in a symmetric cell consisted of two identical counter electrodes with an electrochemical station (CHI660C, CH Instrument, China) at the frequency range of 0.1–10^5 Hz. The magnitude of the alternative signal was 10 mV. Photocurrent–voltage characteristics of the DSSCs were obtained by a Keithley model 2400 digital source meter using an Oriel 91192 solar simulator equipped with AM 1.5 filter and intensity of 100 mW/cm^2.

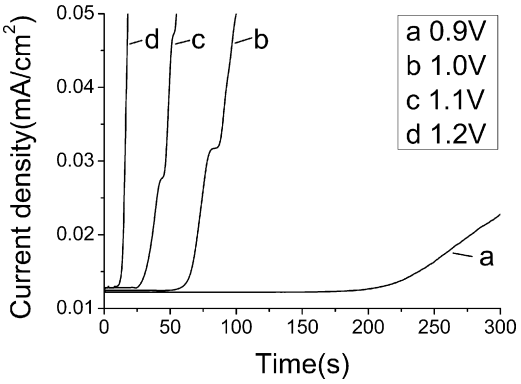

Fig. 1. Current–time transients traced during the PANI electrodeposition at different E_{appl}: (a) 0.9 V, (b) 1.0 V, (c) 1.1 V and (d) 1.2 V.

3. Results and discussion

3.1. Potentiostatic polymerization

Fig. 1 illustrates the current–time curves traced during the potentiostatic polymerization of PANI at different constant potentials. It is shown that PANI starts growing on the surface of SS electrode upon E_{appl} 0.9 V by potentiostatic deposition, and the deposition does not occur below 0.9 V E_{appl}. The process of PANI electrodeposited on SS goes through two steps [13]: the initial induction period and the rapid growth period. During the initial stage, the current density keeps steady for a long induction time (200 s) at the low E_{appl} (0.9 V), and this induction time is reduced as the E_{appl} becomes more positive. When the E_{appl} rises upon 1.0 V, the initial induction time is shortened within 50 s or so. It indicates that the nucleation rate at low potential is much slower than that at high potential. After the induction period, the current density increases and the deposition process of PANI enters the growth stage. This increase of anodic current depends on the oxidation of aniline to PANI during the growth process. Moreover, the current density increases more sharply as the E_{appl} exceeds 0.9 V, and the current density increasing rate rises along with the E_{appl} moving to positive potential. This phenomenon might be attributed to the fact that the growth rate of PANI at high E_{appl} (above 0.9 V) is much faster than that at low one.

3.2. Morphological properties

Fig. 2 shows the surface morphology of PANI/SS at different applied potentials. At the low E_{appl} (0.9 V), PANI nuclei grow on the bare electrode to form a compact layer, which adhered to the electrode surface strongly. Increasing the E_{appl} to 1.0 V, the particles with the diameter in range of 800 nm and some nanorods with an average diameter 200 nm both appear on the top of PANI nodules layer. These mixed PANI particles and rods represent an open porous structure, which is benefited for adsorbing more liquid electrolyte. As the E_{appl} shifts to more positive potential, the PANI particles disappear and the nanorods or fibrils emerge on the surface of PANI film. At 1.1 V E_{appl}, PANI mainly forms the thin nanorods with the length of 800 nm, and at the higher E_{appl}, PANI deposition shows an extensive fibril growth. This growth of PANI has no directional alignment and the nanorods or fibrils are non-uniform. It is clearly demonstrated that the formation of slender nanorods is preferred at low polymerization potential while the development of fibrils with larger diameter is more easily achieved at higher potential.

As mentioned above, the growth of PANI occurred in two separate stages: the initial induction stage, a strongly bound compact