Journal of Power Sources 203 (2012) 274–281

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

High performance dye-sensitized solar cells based on platinum nanoparticle/multi-wall carbon nanotube counter electrodes: The role of annealing

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ARTICLE INFO

Article history:
Received 3 June 2011
Accepted 15 November 2011
Available online 23 November 2011

Keywords:
Annealing
Dye-sensitized solar cell
Multi-wall carbon nanotube
Platinum nanoparticle
Surface roughness

ABSTRACT

A composite film is coated on the FTO using a solution, containing a synthesized dispersant, poly(oxyethylene)-segmented imide (POEM), dihydrogen hexachloroplatinate (H_2PtCl_6), and multi-wall carbon nanotube (MWCNT); the thus coated FTO is used as the counter electrode (CE) for a dye-sensitized solar cell (DSSC). The annealing temperature of the composite film, in the range of 110–580 °C, is found to be crucial for optimizing its catalytic ability to obtain the best possible performance for the DSSC. About 47% loss in mass for the POEM/H_2PtCl_6/MWCNT composite is observed from 110 to 390 °C, due to not only the progressive formation of PtNPs from H_2PtCl_6 but the decomposition of POEM. Therefore, the efficiencies (η) of DSSCs applying these CEs are enhanced from 1.28 ± 0.08% (110 °C) to 8.47 ± 0.21% (390 °C). The mass of the composite loses dramatically under heating above 390 °C, due to the decomposition of MWCNTs. The η decreases to 7.77 ± 0.15% at 450 °C because the decrease in surface roughness of film. PtNPs grow in sizes from 450 to 580 °C, resulting in the further decrease in catalytic ability of film and the observed η from 7.77 ± 0.15% to 7.19 ± 0.21%.

1. Introduction

The counter electrode (CE), a key component in a dye-sensitized solar cell (DSSC), has the essential function of conversion of triiodide (I_3^-) into iodide (I^-) in the electrolyte of the cell, and thereby completes the cycle of operation of the cell [1,2]. Due to its extraordinary catalytic ability and conductivity, platinum (Pt), is usually employed as the catalytic film on the conducting substrate of a CE. The platinized CE not only reduces the voltage loss, resulting from the charge-transfer overpotential at it, but also reflects the light falling on it [3]. Therefore, a Pt-based CE is of pivotal importance for a high performance DSSC. Several techniques, such as magnetron sputtering, electro-deposition, and thermal decomposition have been employed for the deposition of a Pt film on the CE substrate of a DSSC [4–7]. Papageorgiou et al. [6] have reported about a high performance DSSC; the CE of the pertinent cell was coated with a nanoparticles-film of Pt, through thermal decomposition. The catalytic Pt films, consisting of platinum nanoparticles (PtNPs) were obtained from the Pt precursor, dihydrogen hexachloroplatinate (H_2PtCl_6) [8].

Recently, some carbon materials and conducting polymers were used as efficient catalysts on the CEs of DSSCs [9,10]. Carbon nanotubes (CNTs) have long since been explored as promising materials in electrochemistry, owing to their electrical, mechanical, and thermal properties [11,12]. CNTs are efficient catalysts for I_3^- reduction in a DSSC; such cells exhibit a competitive performance, with reference to the DSSCs based on Pt CEs [13–17]. We have prepared a nanocomposite film for a CE by using a synthesized polymer, poly(oxyethylene)-segmented imide (POEM); the film consisted of PtNPs and multi-wall CNTs (MWCNTs) [18].

The present work deals with a DSSC, consisting of a CE with a catalytic layer of PtNP/MWCNT. Because of the coexistence of three components in the deposition solution, i.e., H_2PtCl_6, MWCNTs, and POEM, we determined most suitable annealing temperature for PtNP/MWCNT-coated CE. The variations in the catalytic film, e.g., surface morphology, crystalline size of the PtNPs, amount of POEM

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doi:10.1016/j.jpowsour.2011.11.031

in the film, and consequent variation in the power-conversion efficiency (η) of the pertinent cell, due to the variation in the annealing temperature of the catalytic film, are studied. The DSSC assembled with the PtNP/MWCNT-CE, in which the CE was annealed at the optimal temperature, has shown an η of $8.47 \pm 0.21\%$. The nanocomposite film was characterized at various annealing temperatures, using spectroscopic and electrochemical techniques.

2. Experimental

2.1. Materials

MWCNTs (diameter = 40–60 nm, length = 0.5–10 μm) were received from Seedchem Company Pty., Ltd., Melbourne Vic, Australia. H_2PtCl_6 (ACS regent, Premion, 99.95%) and sodium borohydride ($NaBH_4$, 98%) were purchased from Alfa Aesar Chemical Co. Anhydrous LiI, I_2, acetonitrile (ACN) and poly(ethylene glycol) (PEG, M.W. = 20,000 g mol^{-1}) were received from Merck. Titanium(IV) isopropoxide (TTIP, +98%), 4-*tert*-butylpyridine (TBP, 96%), and *tert*-butanol (TBA, 99.5%) were obtained from Acros. 3-methoxypropionitrile (MPN, 99%) was a product from Fluka. *cis*-Bis(isothio-cyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II)bis- tetrabutylammonium (so-called N719), and 1,2-dimethyl-3-propylimidazolium iodide (DMPII) were obtained from Solaronix S.A., Aubonne, Switzerland.

2.2. Preparation of nanocomposite PtNP/MWCNT counter electrode

Poly(oxyethylene)-segmented imide polymer (POEM) was synthesized by mixing poly(oxyethylene)-diamine (POE2000, M.W. = 2000 g mol^{-1}, waxy solid, melting point = 37–40 °C, amine content 0.95 meq. g^{-1} with an average 39 oxyethylene and 6 oxypropylene units in the structure) and 4,4′-oxydiphthalic anhydride (ODPA, 97% purity, Aldrich Chemical Co.). The use of POE-backboned polymer dispersant allows the non-covalent blending of PtNPs with MWCNTs; the amphiphilic solvating property of POEM is required for high dispersibility of PtNP/MWCNT composite in the solution. The POEM polymer was synthesized through the reaction of POE2000 with ODPA at a molar ratio of 6:5; the following procedure is adopted. POE2000 (10.00 g, 5 mmol) in tetrahydrofuran (THF, TEDIA Company Inc.) (15 mL) was poured into a 100 mL three-necked, round-bottomed flask, equipped with a magnetic stirrer, nitrogen inlet-outlet lines, and a thermometer; a solution of ODPA (1.29 g, 4 mmol) in THF (10 mL) was added to the reactor through a funnel in a drop-wise manner. During the addition, the mixture was stirred vigorously and the reactor was maintained at 150 °C for 3 h. The product was subjected to rotary evaporation under a reduced pressure and was finally recovered as a yellowish waxy solid. During the process, samples were taken periodically and characterized by using a Fourier transform infrared (FTIR) spectroscopy. The FTIR spectra shows that the absorption peaks of anhydride at 1780 cm^{-1} (s) and 1850 cm^{-1} (w) disappeared at the expense of the peaks at 1713 and 1773 cm^{-1} for the asymmetric stretch of imide. The characteristic absorption of oxyalkylene was observed at 1100 cm^{-1}. The combination of PtNPs with MWCNTs was accomplished through an *in situ* reduction of H_2PtCl_6 in the presence of MWCNTs in the dispersant POEM in an aqueous medium. The MWCNTs (0.036 g) were first dispersed in 7.11 g of deionized water in a vial and sonicated under a VCX 500 Ultrasonicator at ambient temperature for 15 min. The resulting solution was dark black with some solid precipitate at the bottom of the container, indicating a low degree of dispersion. In a separate glass container, POEM (1.0 g) and H_2PtCl_6 (1.00 g, 2.4 mmol) were dissolved in 5.14 g of deionized water, and the contents were added to a solution of MWCNTs/deionized water (7.11 g). A homogenous suspension of MWCNTs was obtained by mixing them in the presence of POEM and H_2PtCl_6. PtNPs were then generated by slowly adding 0.7 wt% of $NaBH_4$ (0.007 g) into 1 g deionized water (due to the reduction of H_2PtCl_6). This dispersion was further stirred for several hours at ambient temperature and monitored for the attachment of PtNPs on the surfaces of MWCNTs, using a transmission electron microscopy (TEM). The prepared solution was then spin-coated on a fluorine-doped SnO_2 glass substrate (FTO, surface resistance = 15 Ω sq.$^{-1}$, Solaronix S.A., Aubonne, Switzerland), in which 2000 rpm were used for 30 s. FTO glasses coated with the nanocomposite films were annealed at various temperatures of 110, 200, 390, 450, and 580 °C for 20 min. Thus, the fabrication of PtNP/MWCNT counter electrode (PtNP/MWCNT-CE) was accomplished.

2.3. Preparation of TiO_2 photoanode and assembly of DSSC

In a sol–gel method, the TTIP was added into H_2O/HNO_3 at 88 °C for 8 h. The resultant solution was further subjected to 240 °C in an autoclave for 12 h to obtain nanocrystalline TiO_2. The TiO_2 solution was concentrated to 13 wt%. 30 wt% of PEG (with respect to TiO_2) was then added to the slurry. The paste was then doctor-bladed on the FTO, and the TiO_2/FTO was further annealed at 450 °C for 30 min. After repeating the coating and annealing twice, a light scattering layer (a layer of TiO_2 with particles of 300 nm) was coated on the TiO_2 film; the film was then again annealed at 450 °C for 30 min [19]. The TiO_2 film was shaved to obtain an active area of 0.16 cm^2, and then it was immersed in a solution of 0.3 mM N719 in ACN/TBA (equal volume) for 12 h. The dye-adsorbed TiO_2 photoanode was attached to a CE, using a 25 μm-thick Surlyn film as the spacer between the electrodes. The MPN-based liquid electrolyte containing 0.6 M DMPII, 0.1 M LiI, 0.05 M I_2, and 0.5 M TBP was then injected into the space separated by the Surlyn film (through the capillary effect).

2.4. Instrumentation

Thermo-gravimetric analyzer (TGA, TGA-7, PerkinElmer) was used for quantifying the loss in the weight percentage of the samples. The surface morphologies of the CEs were observed by field-emission scanning electronic microscopy (FE-SEM, Zeiss EM 902A). Energy dispersive spectrometer (EDS, NovaTM NanoSEM 230) and atomic force microscopy (AFM, NanoScope) equipped with a probe of tapping mode were used for estimating the contents of chlorine and the surface roughness of the CEs, respectively. The crystalline orientations and sizes of PtNPs were measured and calculated from X-ray diffraction (XRD, Philips, X'Pert) patterns. Cyclic voltammetry (CV, CHI, electrochemical workstation, model 440) was performed with a three-electrode cell for determining the active surfaces of the films. Surface of the DSSC was illuminated by a class A quality solar simulator (PEC-L11, AM 1.5G, Peccell Technologies, Inc.) and the incident light intensity (100 mW cm^{-2}) was calibrated with a standard Si cell (PECSI01, Peccell Technologies, Inc.). Photoelectrochemical characteristics of the DSSC were recorded with a potentiostat/galvanostat (PGSTAT 30, Autolab, Eco-Chemie, the Netherlands). Electrochemical impedance spectra (EIS) were obtained by the above-mentioned potentiostat/galvanostat equipped with an FRA2 module, under a constant light illumination of 100 mW cm^{-2}.

3. Results and discussion

The synthesized POEM dispersant has the chemical structure shown in Fig. 1. POEM was used for dispersing the inorganic