Journal of Power Sources 360 (2017) 232–242

Contents lists available at ScienceDirect

Journal of Power Sources

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

Hollow platinum alloy tailored counter electrodes for photovoltaic applications

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HIGHLIGHTS

- Hollow PtNi alloy CEs are synthesized using ZnO nanostructure templates.
- The PtNi alloy electrode has high electrocatalytic activity to redox electrolyte.
- A promising cell efficiency of 8.74% is determined on the optimal DSSC.
- The dissolution-resistance of PtNi alloy electrode is markedly enhanced.

ARTICLE INFO

Article history:
Received 13 January 2017
Received in revised form
1 June 2017
Accepted 7 June 2017

Keywords:
Solar cells
Counter electrodes
Binary alloy electrocatalysts
Energy conversion

ABSTRACT

Without sacrifice of photovoltaic performances, low-platinum alloy counter electrodes (CEs) are promising in bringing down the fabrication cost of dye-sensitized solar cells (DSSCs). We present here the realization of ZnO nanostructure assisted hollow platinum-nickel (PtNi) alloy microstructure CEs with a simple hydrothermal methods and maximization of electrocatalytic behaviors by tuning Zn precursors. The maximal power conversion efficiency is up to 8.74% for the liquid-junction dye-sensitized solar cells with alloyed $PtNi_{0.41}$ electrode, yielding a 37.6% cell efficiency enhancement in comparison with pristine solar cell from planar Pt electrode. Moreover, the dissolution-resistant and charge-transfer abilities toward I^-/I_3^- redox electrolyte have also been markedly enhanced due to competitive dissolution reactions and alloying effects.

1. Introduction

Dye-sensitized solar cell (DSSC) has suffered significant increase in cell efficiency since the birth of prototype created by O'Regan and Grätzel [1]. Till now, the maximal power conversion efficiency has been raised to as high as 14.3% [2], arising from structural optimization of three components including dye-sensitized photoanodes, redox electrolytes, and counter electrodes (CEs). Notably, the CEs serve as mediators for collecting photogenerated electrons from external circuit and catalyzing the reduction reaction of $I_3^- + 2e^- = 3I^-$. Therefore, ideal CEs are considered to have high catalytic activity toward I_3^- reduction reaction, low charge-transfer resistance, and persistent stability. As a preferred electrode material, platinum (Pt) on account of its excellent electrocatalytic activity for I^-/I_3^- redox couples is the most common CEs to catalyze the reduction reaction of I_3^- ions for a DSSC [3]. However, the high cost of precious metal Pt has been the major burden for commercial DSSC. A golden rule of developing commercial photovoltaics includes high efficiency, good long-term stability, cost-effectiveness, and environmentally-friendliness. Apart from CEs, electrolytes and photosensitizers have also been replaced with cost-effective aqueous systems or natural dyes, respectively [4–7]. Therefore, low-Pt and Pt-free CEs including compounds [8–10], conducting polymers [11–15], carbonaceous materials [16–19], and alloy materials [20–22] are promising in reducing fabrication cost without sacrificing catalytic activity. The standard of selecting alternative CEs are placed on satisfactory electrocatalytic activity toward I_3^- reduction reaction, high conductivity for collecting electrons from external circuit, and good long-term stability. However, conducting polymers are always organic semiconductors, arising from delocalized electrons on their conjugated structures [11], and suffer desorption reactions and structural collapse during the complicated electrocatalytic processes [23]. Carbonaceous materials

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http://dx.doi.org/10.1016/j.jpowsour.2017.06.022
0378-7753/

display rapid electron transportation ability, two of the challenges for these species are unsatisfactory catalytic capability and electrochemical corrosion [24]. Therefore, our focus will be placed on alloy species owing to excellent electrocatalytic activity for I^-/I_3^- redox couples, high conductivity and good long-term stability. Therefore, alloy materials have been the better choice as the CEs in comparison with other materials. Previously, Tang et al. have pioneerly reported Co-Ni alloy CEs for 8.39%-efficiency DSSC [20]. The remaining problem for such alloys is the dissolution in liquid electrolyte owing to negative Gibbs free energy ($\Delta_r G_m$) for the reaction between transition metals and I_3^- species. An efficient route for overcoming this issue is the alloying of Pt and transition metals to form competitive dissolution reactions. Among various PtM alloy materials, the PtNi alloy is beneficial of catalyzing the reduction reaction from I_3^- to I^- ions [25,26], having better long-term stability and excellent charge-transfer ability. Previously, Pt-Ni nanoparticles [27], nanoframes [28], and nanofilms [29] have been made as CE materials for DSSC applications. High power conversion efficiencies are also determined on the corresponding devices because of superior catalytic activity and matching work functions.

Aligned one-dimensional (1D) CEs can maximize the electron transfer and therefore I_3^- reduction. In this fashion, the optimization of topographies of CEs could enhance solar cell performances by increasing the specific surface area for electrolyte adsorption [30]. Additionally, CEs with different morphologies could change the reaction area for I_3^- reduction reaction and the electron transfer distances at electrolyte/CE interface [30]. However, it is still a challenge to tune aligned CEs by a direct strategy, therefore we present here the realization of well-aligned PtNi microstructures using polymorphous ZnO nanostructures as templates. ZnO is controllable in morphology and size by adjusting growth temperature and pH during a commonly used hydrothermal method [30–33]. The maximal solar-to-electric conversion efficiency is as high as 8.74% for $PtNi_{0.41}$ based solar cell, demonstrating a 37.6% enhancement in cell efficiency in comparison with DSSC from Pt electrode.

2. Experimental

2.1. Preparation of ZnO nanostructures

Using the peculiar merits of ZnO in tuning its nanostructures, a layer of Ni is covered on outward surface of ZnO nanostructures by an electrochemical method, subsequently, partial Ni species are displaced by H_2PtCl_6 to form ZnO supported PtNi electrodes. After dissolution of ZnO in acidic solution, the resultant hollow PtNi alloy CEs were obtained. In the current work, we were focusing on investigating the impacts on PtNi morphology on cell performances, therefore ZnO nanorods (NRs), nanoflowers (NFs), and nanosheets (NSs) were employed as templates for CEs. In details, ZnO NRs, NFs and NSs were prepared with a simple hydrothermal method by adjusting synthesis conditions. ZnO NRs were grown on an FTO glass substrate (12 Ω square^{-1}) by mixing 50 mL of 150 mM zinc nitrate [$Zn(NO_3)_2$] aqueous solution and 50 mL of 150 mM hexamethylenetetramine [HTMA, $C_6H_{12}N_4$, 99%] aqueous solution. The ZnO NFs were realized from 98 mL of 75 mM $Zn(NO_3)_2$, 98 mL of 75 mM HTMA and 2 mL of ammonia water [$NH_3 \cdot H_2O$, 25%], while ZnO NSs were from 98 mL of 75 mM $Zn(NO_3)_2$ and 2 mL of ammonia water [$NH_3 \cdot H_2O$, 25%]. The FTO glass substrates with FTO layer downward were immersed into abovementioned reagents and subsequently processed at 95 °C for 12 h, 90 °C for 8 h, and 175 °C for 24 h to prepared aligned ZnO NRs, ZnO NFs, and ZnO NSs, respectively. After cooling to room temperature, the resultant ZnO nanostructures were thoroughly rinsed by deionized water and dried in air.

2.2. Preparation of PtNi alloy CEs

The PtNi alloy CEs were prepared using a common electrochemical deposition method on a traditional three-electrode system using a Pt plate as counter electrode, FTO substrate supported ZnO nanostructure as a working electrode and a Ag/AgCl filled with 3 M KCl aqueous solution as a reference electrode. The electrochemical deposition of Ni layer was realized in a supporting electrolyte from 50 mM of nickel sulfate [$NiSO_4 \cdot 6H_2O$, 98.5%] and 20 mM of ammonium chloride (NH_4Cl). The deposition process was performed on a constant current density of 0.25 mA cm^{-2} for 600 s in air atmosphere. Subsequently, the ZnO supported Ni substrates were immersed into 1 mM chloroplatinic acid [$H_2PtCl_6 \cdot 6H_2O$, 37.0%] aqueous solution for 15 min. Finally, 2 mM H_2SO_4 aqueous solution was utilized to dissolute ZnO nanostructures and to obtain hollow PtNi alloy CEs. As a reference, the commercial Pt electrode deposited by a magnetron sputtering method was purchased from Yingkou OPV Tech New Energy Co., Ltd.

2.3. Assembly of DSSCs

A layer of mesoscopic TiO_2 film with an average thickness of around 10 μm was used as a photoanode by coating TiO_2 colloid onto FTO glass substrate. The colloidal TiO_2 was synthesized by a sol-thermal method according to the detailed procedures in previous literature [34]. The active area of TiO_2 film was controlled at 0.25 cm^2, subsequently, the FTO glass with TiO_2 film was calcined at 450 °C for 30 min in air atmosphere and sensitized by a 0.50 mM N719 dye (purchased from DYESOL LTD) ethanol solution for 24 h. The DSSC device was realized by injecting redox electrolyte containing I^-/I_3^- couples into interspace of a dye-sensitized TiO_2 anode and an alloy electrode. The solar cell was sealed with 30 μm-thickness Surlyn film by heat-pressing the device at 110 °C.

2.4. Electrochemical characterizations

The corresponding electrochemical performances of CEs including cyclic voltammetry (CV) curves, electrochemical impedance spectroscopy (EIS) plots, and Tafel polarization curves were performed on a conventional three-electrode CHI660E setup. The supporting electrolyte consisted of 50 mM LiI, 10 mM I_2, and 500 mM $LiClO_4$ in acetonitrile. In addition, the EIS measurements were recorded on a symmetric alloy electrode/electrolyte/alloy electrode architecture in a frequency range of 0.1 Hz–0.1 MHz and at an AC amplitude of 10 mV. Tafel polarization curves were also recorded on the same symmetric dummy cells at a scan rate of 10 mV s^{-1}. The 100-cycles CV curves of CEs were recorded in redox electrolyte at a scan rate of 50 mV s^{-1}. The 100-cycles Nyquist and Bode plots were determined on the symmetric dummy cells.

2.5. Photovoltaic measurements

The photocurrente-voltage (*J-V*) curves of solar cells were determined under irradiation of a simulated solar light (Xe Lamp Oriel Sol3A™Class AAA Solar Simulators 94023A, USA) from a 100 W xenon arc lamp in ambient atmosphere. Before measurement, the device was covered by a mask with an active area of 0.25 cm^2 to avoid the stray light. The EIS measurements were recorded on the frequency of 0.01–10^5 Hz at open-circuit voltage of each DSSC device under the condition of irradiation of a simulated solar light from a 100 W xenon arc lamp in ambient atmosphere. To control the results within experimental errors, each DSSC device was repeatedly measured at least ten times. Incident photo-to-current conversion efficiency (IPCE) plots were obtained at the short-circuit condition on an IPCE measurement systems (M260).