Chinese Journal of Catalysis 39 (2018) 982–987

available at www.sciencedirect.com

ScienceDirect

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

Article

CoNiP/NC polyhedrons derived from cobalt-based zeolitic imidazolate frameworks as an active electrocatalyst for oxygen evolution

Jintang Li *, Guiqing Du, Xian Cheng, Pingjing Feng, Xuetao Luo

Fujian Key Laboratory of Advanced Materials, College of Materials, Xiamen University, Xiamen 361005, Fujian, China

ARTICLE INFO

Article history:
Received 19 December 2017
Accepted 21 January 2018
Published 5 May 2018

Keywords:
ZIF-67
Carbonization
Phosphorization
Electrocatalyst
Oxygen evolution reaction

ABSTRACT

The oxygen evolution reaction (OER) plays an important role in the development of energy conversation and storage technologies including water splitting and metal-air batteries, where the development of electrocatalysts is paramount. In this study, cobalt-nickel phosphide/N-doped porous carbon polyhedron electrocatalysts (CoNiP/NC) were prepared by a facile two-step carbonization method and subsequent phosphorization calcination in an Ar atmosphere using cobalt-based zeolitic imidazolate frameworks (ZIFs) as precursors. Among the electrocatalysts obtained by controlling the carbonization and phosphorization temperature, the CoNiP/NC700 catalyst, where 700 refers to the calcination temperature (°C), exhibited superior electrocatalytic activity for the OER with an onset overpotential of approximate 220 mV and an overpotential of approximate 300 mV in alkaline solution at a current density of 10 mA/cm^2. The CoNi/NC and Co/NC Samples were also tested for comparison and CoNiP/NC exhibited the better electrocatalytic activity at all the temperatures tested. The superior electrocatalytic activity of the phosphorization hybrid material can be attributed to the superior synergistic effect of Co, Ni, P and C due to their strong electron coupling interactions. The interconnected amorphous carbon anchored the active Co compounds to avoid aggregation and maintained conducting channels for electron transfer. The composite electrocatalyst prepared herein is a promising candidate for use in electrocatalytic OERs.

1. Introduction

Recently, the depletion of fossil fuels and the associated exponential rise in global warming have stimulated considerable interest in alternative sources of renewable energy production and conversion [1,2]. The oxygen evolution reaction (OER), a half reaction involving electrochemical water splitting, has attracted considerable attention due to its critical role in water splitting and metal–air batteries and for hydrogen production and metal regeneration [3,4]. High electrochemical overpotential typically results from the kinetically sluggish four-electron oxidation reaction at the anode [5]. Ruthenium and iridium oxides have been developed as the most efficient electrocatalysts for the OER to date due to their low overpotentials and high proton mobility efficiency. However, their high cost, scarce reserves, and poor durability considerably prohibit more extensive applications [6]. To reduce the reaction overpotentials and obtain good reaction rates with reduced input energy, the

---

* Corresponding author. Tel: +86-18030105513; E-mail: leejt@xmu.edu.cn

This work was supported by National Natural Science Foundation of China (51204143, 51334004) and the Scientific and Technological Innovation Platform of Fujian Province (2006L2003).

DOI: 10.1016/S1872-2067(18)63030-X | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 39, No. 5, May 2018

development of effective non-precious metal electrocatalysts with high activity and low cost is required [7]. To date, some efficient alternatives OER catalysts in alkaline electrolytes using noble metal-based non-precious electrocatalysts including layered double hydroxides [8,9], sulfides [10,11], transition-metal oxides [12], hydroxides [13], metal free catalysts [14] and phosphate [15] have been reported [16].

Among different electrocatalysts for OER, metal–organic frameworks (MOFs), and in particular zeolitic imidazolate frameworks (ZIFs), have gained attention as novel sacrificial templates to construct efficient porous carbon-based electrocatalysts [17]. These materials have been widely used in gas storage or separation [18], catalysis [19], CO_2 reduction [20], and water-splitting [21] because of their excellent chemical and physical properties including high specific surface area, large number of active sites (an active site means the point where catalysis reaction can happen) [22], and tunability of both metals and ligands in the MOFs [23]. MOFs have been used as precursors to synthesize OER catalysts because of their controllable porous structure and nearly infinite design possibilities. In addition, various MOF-derived carbon-based porous metal compounds can be obtained through direct carbonization without further processing or templating. Among cobalt-based MOF materials, ZIF-67 is one of the most investigated MOFs and offers a large number of active cobalt sites. For example, carbonization of ZIF-67 results in a porous Co@N-doped carbon composite (named N/Co-doped PCP//NRGO), which is very active toward the water splitting reaction [24]. In this study, we demonstrate a facile MOF-derived approach for the effective synthesis of OER electrocatalysts in 1.0 mol/L of KOH, producing CoNiP/NC derived from ZIF-67 and doped with nickel through a two-step carbonization and phosphorization calcination precedure in Ar atmosphere. Compared to a previous report of the phosphatization of sodium hypophosphite [25], the strategy described herein of simultaneous carbonization and phosphorization calcinations of Ni-doped ZIF-67 can more easily yield CoNiP/NC hybrid composites. These results suggest that the MOF-derived CoNiP/NC is a promising electrocatalysts for the OER for water splitting in alkaline electrolytes. The N-doped cobalt nickel phosphorus porous carbon electrocatalysts CoNiP/NC, and CoNiP/NC700, where 700 referrs to the calcination temperature (°C), exhibited superior activity towards oxygen evolution with an onset overpotential of approximately 220 mV and an overpotential of approximately 300 mV in alkaline solution at a current density of 10 mA/cm^2. The better electrocatalytic activity of the hybrid material can be attributed to the superior synergistic effect of Co, Ni, P and C due to their strong electron coupling interactions. The interconnected amorphous carbon anchored the active Co compounds preventing aggregation and afforded conducting channels for electron transfer.

2. Experimental

2.1. Formation of CoNiP/NC

In total, 0.5 g of ZIF-67 particles were dispersed in 200 mL of ethanol containing 1 g of nickel nitrate hexahydrate. After stirring for 30 min, the ZIF-67Ni yolk-shelled particles were formed, collected by centrifugation (at 9000 r/min for 10 min), and dried at 50 °C for 5 h. Subsequently, the CoNi/NC*x* , which *x* refers to the calcination temperature (°C), were obtained by annealing the as-obtained yolk-shelled particles at temperatures of 600, 700, 800, 900, and 1000 °C for 3 h at a ramp rate of 5 °C/min under an Ar atmosphere. To obtain CoNiP/NC*x*, 50 mg CoNi*x* and 1.0 g sodium hypophosphite were placed at two separate positions in a combustion boat and subjected to phosphidation at 300 °C for 2 h at a ramp rate of 5 °C/min under an Ar atmosphere.

2.2. Characterization

The obtained samples were characterized using powder X-ray diffractometry (XRD, Bruker-AxsD8) with Cu K_α radiation (λ = 0.15406 nm) at 2θ = 5°–70°, operating at a voltage of 40 kV and current of 40 mA. The morphologies of the samples were characterized by field emission-scanning electron microscope (FE-SEM, Hitachi SU-70) operating at 10 kV. The samples used for SEM imaging were gold sputtered prior to analysis. X-ray photoelectron spectroscopy (XPS) data were acquired on an ESCALAB 250Xi X-ray photoelectron spectrometer (Thermo Scientific) using Al K_α radiation.

2.3. Electrochemical measurements

Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) measurements were performed on an Autolab electrochemical workstation (NOVA 1.9). To prepare the electrodes for OER testing, 5 mg of active material was added to a mixture of 1.9 mL ethanol and 0.1 mL Nafion solution with sonication for 60 min. Subsequently, the catalyst (20 μL) was pipetted out and dropped onto a glassy carbon electrode with a diameter of 5 mm and fully dried at room temperature for 12 h before measurements were taken (loading of ~0.255 mg/cm^2). The electrochemical cell was assembled as a conventional three-electrode system with electrochemical workstation in KOH solution 1.0 mol/L. The counter and reference electrodes were composed of a Pt foil and an Ag/AgCl-saturated KCl electrode, respectively, and a glassy carbon electrode (GCE, 5 mm in diameter) was used as the working electrode. All measured potentials were normalized to the reversible hydrogen electrode (RHE) by adding a value of (0.197 + 0.059 pH) V. A scan rate of 10 mV/s was used in the linear sweep voltammetry to

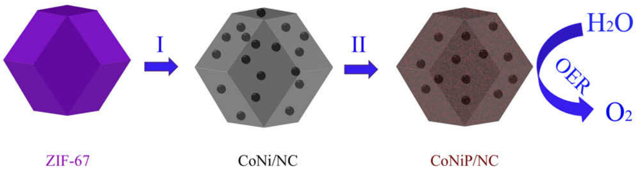

Fig. 1. Schematic diagram illustrating the OER catalytic principles on CoNiP /NC polyhedrons. Step I: transformation of ZIF-67 into CoNi/NC by a facile etching and deposition process and carbonization; Step II: formation of CoNiP/NC by phosphatizing CoNi/NC.