Electrochimica Acta 247 (2017) 835–842

Contents lists available at ScienceDirect

Electrochimica Acta

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

A NiFe-Based Hierarchically Structured 3D Electrode by Hydrothermal Deposition for Highly Efficient Water Oxidation

Weiqiang Tang, Shangshang Zuo, Jianying Wang, Yongli Mi, Zuofeng Chen*

Shanghai Key Lab of Chemical Assessment and Sustainability, School of Chemical Science and Engineering, Tongji University, Shanghai 200092, China

ARTICLE INFO

Article history:
Received 20 April 2017
Received in revised form 9 July 2017
Accepted 12 July 2017
Available online 14 July 2017

Keywords:
FeOOH
nickel foam
oxygen evolution reaction
hydrothermal deposition
electrocatalysis

ABSTRACT

Herein, nanostructured FeOOH supported on the 3D nickel foam (FeOOH-NF) was prepared by a facile one-pot hydrothermal deposition. A series of analytical techniques indicate formation of a layered uniform nanosheets from the underlying nickel foam which incorporate *in situ* generated FeOOH. Thanks to the synergistic interaction between Fe and Ni and the good electrical connection between the active catalyst and conductive substrate by the direct growth, the hierarchically structured electrode exhibits high electrocatalytic performance for the oxygen evolution reaction (OER) in alkaline solution with low overpotential, small Tafel slope and excellent long-term durability. In 1 M KOH, a current density of 20 mA/cm^2 is achieved at an overpotential of only 210 mV with a Tafel slope of 29 mV/decade, which is competitive or superior to various electrocatalysts on the 3D nickel foam under similar conditions. Considering the simple and facile electrode preparation, the low cost and environmental friendliness of the electrode materials, and the excellent catalytic performance, the FeOOH-NF electrode would be a promising anode candidate for the OER in large scale water electrolysis.

1. INTRODUCTION

Hydrogen represents a potential clean energy vector and its increasing importance can be attributed to the anticipated severe shortage of fossil fuels and the problem of global warming by mass utilization of fossil fuels [1–3]. To date, water electrolysis using renewable energy sources (wind, solar, or hydro) is the most sustainable route for H_2 production [4,5]. The key factor determining the energy efficiency of water electrolysis is usually the oxygen evolution reaction (OER) at the anode. The rate of the OER is typically limited by the intrinsically sluggish reaction kinetics, which requires loss of $4e^-$and $4H^+$ from two water molecules with concomitant formation of an O—O bond ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$) [6–10]. So far, iridium and ruthenium oxides represent the most efficient and benchmark electrocatalysts for the OER. However, these metals are rare elements, and the scarcity and high cost of these noble metals have greatly hampered their practical applications on a large scale [11–13]. In the past decade, considerable researches have been carried out to develop inexpensive and efficient OER electrocatalysts to replace the noble metals.

Owing to its natural abundance and environmental friendliness, iron-based materials are attractive electrocatalysts for the OER. For example, the FeOOH as electrocatalyst holds great promise for the OER because of its open structure [14–19]. However, the poor electrical conductivity of FeOOH remains a major challenge which limits its electrocatalytic performance [20]. Hybridizing FeOOH with other conductive materials such as the nickel foam will be an efficient way to improve the electrocatalytic performance. The good electronic/ionic conductivity and 3D macroporous framework of nickel foam are favorable factors for the enhancement of the OER activity. In addition, the synergistic interaction between Fe and Ni will possibly enhance the catalytic performance. Indeed, mixed-metal materials containing iron group elements (Fe, Co, Ni) have been generally acknowledged as one of the most competent electrocatalyst candidates for the OER in aqueous alkaline media [21–24].

In this study, we report the fabrication of nanostructured FeOOH supported on the 3D nickel foam (FeOOH-NF) through a facile hydrothermal deposition. Compared to other deposition strategies such as electrodeposition [25], pulsed-laser deposition [26], photochemical metal-organic deposition [27], etc., the hydrothermal deposition could be carried out by a simple step and on a large scale (one pot) with no need to use expensive instrumentation. A layered nanosheets-like film is developed from the underlying nickel foam with *in situ* generated FeOOH

* Corresponding author.
E-mail address: zfchen@tongji.edu.cn (Z. Chen).

http://dx.doi.org/10.1016/j.electacta.2017.07.075
0013-4686/

incorporated, which renders a hierarchically structured 3D integrated electrode. The direct growth of the hybrid active catalyst from the underlying conductive substrate can eliminate the use of other conductive agents and binders, which ensures good electrical contact between the electrocatalyst and the conductive substrate. Electrochemical measurements show that the FeOOH-NF electrode exhibits high catalytic activity and durability, which make it a promising electrocatalyst candidate for high-performance OER in scale-up application.

2. EXPERIMENTAL

2.1. Chemicals

Ferric chloride ($FeCl_3 \cdot 6H_2O$, 99%), sodium nitrate ($NaNO_3$, 99%) and potasium hydroxide (KOH, 99%) were obtained from Fisher Scientific. Nickel foam (NF, thickness ~0.5 mm, bulk density ~0.56 g/cm^3) was obtained from Shanxi Lizhiyuan Material of Battery Co. Ltd (China). All chemicals used in this study were of analytical grade and were used without further purification. All electrolyte solutions were prepared by ultrapure water (18 MΩ·cm) unless stated otherwise.

2.2. Apparatus

Scanning electron microscope (SEM) images, energy dispersive X-ray (EDX) elemental analysis data and EDX mapping images were obtained at Hitachi S-4800 (Hitachi, Japan) equipped with a Horiba EDX system (X-max, silicon drift X-Ray detector). The time for EDX mapping images is 10 min. Transmission electron microscopy (TEM) images were obtained using JEM-2100, JEOL. The catalysts were scraped from the nickel foam substrate and dispersed in the absolute ethanol uniformly, and a drop of the mixture was dried on a carbon-coated copper grid for analysis. The catalyst deposited on the nickel foam was imaged through a dark field optical microscope (Olympus BX51) fitted with an Olympus DP27 camera. The magnification is 1000 (100 × 10) times of the original size. Powder X-ray diffraction (XRD) was measured by Bruker Foucs D8 via ceramic monochromatized Cu Kα radiation of 1.54178 Å, operating at 40 kV and 40 mA. The scanning rate was 5° per min in 2θ and the scanning range was from 10 − 80°. X-ray photoelectron spectroscopy (XPS) for elemental analysis was conducted on a Kratos Axis Ultra DLD X-ray Photoelectron Spectrometer. Infrared spectroscopy (IR) spectra were recorded in the wavenumber range of 400–4000 cm^{-1} on an Alpha Centauri IR spectrophotometer by use of KBr pellets. Raman spectroscopy was conducted on a confocal microscope laser Raman spectrometer (Rainshaw invia). The amount of FeOOH deposited on the nickel foam was determined by the inductively coupled plasma optical emission spectroscopy (ICP-OES) using the Perkin Elmer ICP-OES Optima 8300. The iron concentration was obtained using the working curve method.

Electrochemical measurements were performed on a CHI 660E electrochemical workstation (Chenhua Corp., Shanghai, China). The three-electrode system consisted of a working electrode, a platinum plate counter electrode, and a saturated calomel reference electrode (SCE). Prior to measurement, the platinum plate counter electrode was treated by soaking in 1 M hydrochloric acid to remove any deposition. Unless stated otherwise, all potentials in cyclic voltammetry and controlled potential electrolysis were reported *vs.* the reversible hydrogen electrode (RHE) without *iR* compensation. All experiments were performed at 22 ± 2 °C.

2.3. Procedures

The FeOOH integrated nickel foams were prepared by a facile one-pot hydrothermal deposition strategy. A teflon-lined stainless steel autoclave was filled with 20 ml aqueous solution containing various amounts of ferric chloride and sodium nitrate (the molar ratio of $FeCl_3$:$NaNO_3$ is 15:100). Several pieces of 1 × 2 cm^2 nickel foams were immersed in the solution. The autoclave was then sealed and maintained at 95 °C for a certain period of time before being cooling down to room temperature. A uniform nanosheets-like catalyst film with incorporated iron oxyhydroxides (FeOOH) was formed on the nickel foam surface. The hydrothermally treated nickel foams were washed with distilled water and then dried at 50 °C in an oven.

The FeOOH integrated FTO (F-doped SnO_2) electrode was prepared by a similar procedure with the nickel foam substituted by FTO substrate. A typical FeOOH-FTO electrode was prepared with a solution mixture of 15 mM $FeCl_3$ and 100 mM $NaNO_3$ for 40 min.

2.4. Tafel plot

The current-potential data of the FeOOH-NF electrode were obtained by linear sweep voltammetry (LSV) at a very slow scan rate (0.1 mV/s). The Tafel slope was obtained from the LSV plot using a linear fit applied to points in the Tafel region. The solution resistance measured prior to the data collection (using *iR* test function) was used to correct the Tafel plot for *iR* drop.

2.5. Calculation of ECSA

The electrochemically active surface area (ECSA) of the nickel foam is evaluated by measuring their double layer charging capacitance in 1 M KOH solution. Briefly, a potential range where no apparent Faradaic process occurred was determined by using the cyclic voltammetry (CV). The charging current (i_c) in this

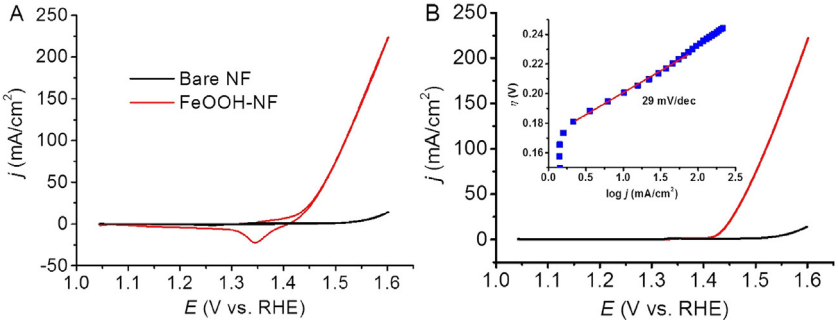

Fig. 1. (A) CVs of a bare nickel foam and a FeOOH-NF electrode in 1 M KOH at 2 mV/s. (B) LSVs of a bare nickel foam and a FeOOH-NF electrode in 1 M KOH at 0.1 mV/s. The insert shows the Tafel plot of a FeOOH-NF electrode.