



Electrodeposited ternary iron-cobalt-nickel catalyst on nickel foam for efficient water electrolysis at high current density



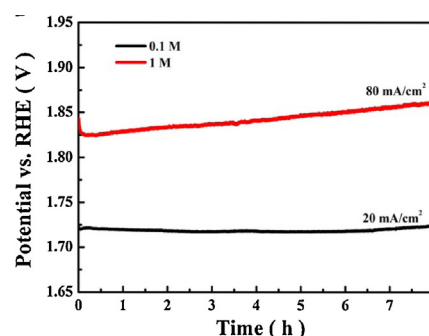
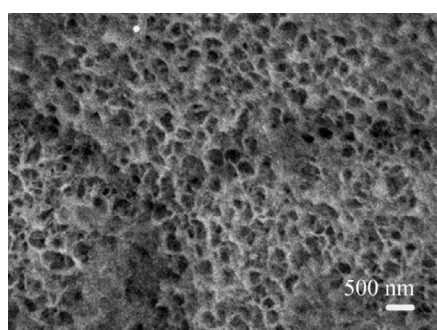
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HIGHLIGHTS

- FeCoNi/NF electrode is successfully prepared via one-step electrodeposition method.
- The FeCoNi/NF nanosheets exhibited relatively high activity and good stability for water electrolysis.
- The electrode has stable performance even at high current density of 300 mA/cm² for a long time.

GRAPHICAL ABSTRACT



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ABSTRACT

It is very important to develop efficient and stable oxygen evolution catalyst with low-cost and earth abundant elements for large scale hydrogen production from water electrolysis. In this article, a ternary FeCoNi oxygen evolution catalyst was prepared by simple electrodeposition on nickel foam. The composition and structure of the catalyst was characterized by SEM, TEM, XRD and XPS. The performance of the catalyst was measured in alkaline solution. The results show that the ternary catalyst has behaved high activity and stability for water electrolysis. The onset overpotential is as low as 0.20 V (vs. RHE) and the overpotential is as low as 0.37 V (vs. RHE) at the high current density of 300 mA/cm² when the catalyst was employed as an anode for water electrolysis. Moreover, the stability of the anode is very good at high current density. The potential retains at almost the same value after more than 8 h continuous electrolysis and the SEM measurement confirms that the catalyst was not decomposed or exfoliated from the nickel foam.

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1. Introduction

Facing the energy and environmental issues, human beings are intensively stimulated to explore new clean and sustainable energy [1,2]. Hydrogen is widely considered as a potential and ideal energy carrier and can be acquired from water splitting by photoelectrochemical or electrochemical methods [3–9]. Water splitting through oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) plays a vital role in achieving efficient conversion and storage of solar and (or) electric energy into chemical fuels [10,11]. However, the sluggish kinetics [12,13] of OER has a main limitation because the disruption of O–H bond and the combination of O–O bond are a multi-step proton-coupled electron transfer process [14]. As a result, high overpotential is typically required, which leads to low energy conversion efficiency. In order to overcome this problem, it is necessary to employ an effective oxygen evolution catalyst (OEC) to accelerate the reaction, reduce the overpotential and improve the efficiency of energy conversion.

Up to now, the most active OEC is Ir- or Ru- based [15–17] compounds, but the high cost and scarcity restrict their large-scale application [18]. Therefore, extensive researches have focused on the development of alternatives based on low-cost and earth abundant transition metals [19,20], which are sufficiently active and stable in long-term oxidation conditions for OER. For instance, iron, cobalt, manganese and nickel-based OECs including their simple [21,22], mixed-metal oxides [23,24], phosphide [25], hydroxide [26], boride [27], perovskite [28] or sulfide [29,30] are developed during the past decades. Among these OECs, Markovic et al. [31] previously reported Ni based OEC with high activity. However, the recent reports have demonstrated that binary NiCo mixed OEC has shown better performance in comparison to the parent metal catalysts. Nevertheless, the maximum specific OEC of binary NiCo nanohybrid only reaches 23 mA/cm² at 1.70 V [32]. It has also been found that the catalyst consisting of Fe can promote the charge transport between the binary NiCo catalyst and the electrolytes, but only a few works related to ternary FeCoNi as OER catalyst are reported [33,34]. On the other hand, the most catalysts reported in the literatures are powders [35], which need assembly onto conductive substrates for water electrolysis. In this process of assembly, polymeric binder employed will unavoidably reduce the contact area between electrolyte and catalytic active site leading to lower electrochemical activity. Moreover, the stability of the electrode is relatively poor because the glued catalysts tend to readily detach from the substrate, especially at high current density.

Electrodeposition [36–39] is an easily and versatile method, which can be used to accurately control the nucleation and growth process to acquire catalysts with different purity, structure and morphology. Moreover, electrodeposition as a scalable process is used in many industrial fields, which makes it very convenient for large scale application [40]. To improve the electrocatalytic OER efficiency, it is crucial to effectively increase the surface area for catalyst loading. Hence, the three-dimensional (3D) structure [41–45] (like nickel foam (NF) [46] or aerogels [47]) is emergent. The porous nickel foam is a low cost and conductive metal with a large electro-

active surface area, which is ideal for using as substrates to load catalysts and increasing active sites [48].

Based on the above consideration, herein, we designed and deposited the amorphous ternary FeCoNi catalyst on the NF as the OER electrode via one-step electrodeposition. The results indicate that the ternary FeCoNi coated NF exhibits very high activity and stability toward water splitting in alkaline electrolyte. The electrode can carry a high current density of 300 mA/cm² at a low overpotential of 0.37 V (vs. RHE). Moreover, the stability of the anode is very outstanding and the potential is maintained almost constant for 8 h at high current density.

2. Experimental section

2.1. Materials

All reagents in this study were analytical grade and without further purification prior to use. Ferric nitrate (Fe(NO₃)₃·9H₂O), Cobalt nitrate (Co(NO₃)₂·6H₂O), Nickel nitrate (Ni(NO₃)₂·6H₂O), Potassium hydroxide (KOH), hydrochloric acid (HCl), absolute ethanol (C₂H₅OH) and acetone (C₃H₆O) were gained from Sinopharm Chemical Reagent Co., Ltd. Ultrapure water was used throughout the experiments. NF (thickness: 1.6 mm, bulk density: 0.45 g/cm³) and graphite rod (GR) were obtained from Ailantian Advanced Technology Materials Co. Ltd. Nickel sheet (NS) and copper sheet (CS) were gained from Sinopharm Chemical Reagent Co., Ltd. Fluorine-doped tin oxide (FTO) with 4 × 1 cm² dimensions (14 Ω/square) was obtained from Huanan Xiangcheng Technology Co., Ltd.

2.2. Preparation

The FeCoNi catalyst was deposited on NF substrate via a simple electrodeposition process. Before the synthesis, the NF (approximately 1 cm × 4 cm) was degreased with acetone in an ultrasound bath for 15 min, etching with 2 M HCl aqueous solution under ultrasonic vibration for 15 min to remove the possible surface oxide layer, subsequently washed with ultrapure water and absolute ethanol to ensure the clean surface, then dried in air.

The electrodeposition was employed with a standard three electrode electrochemical cell at –1.0 V (vs. Ag/AgCl) at room temperature, while a clean NF was used as working electrode, a platinum wire as the counter electrode and a Ag/AgCl (3 M KCl) as the reference electrode. The solution contained certain amount of Fe(NO₃)₃·9H₂O, Co(NO₃)₂·6H₂O and Ni(NO₃)₂·6H₂O as electrolyte. After 300 s electrodeposition, FeCoNi catalyst was successfully loaded to the surface of NF. In order to obtain the optimal composition of the plating solution, we systematically adjusted molar ratios of Fe³⁺, Co²⁺ and Ni²⁺ maintaining the total concentration of plating solution at 6 mM. After electrodeposition, the NF was carefully removed from the electrolyte, rinsed three times with ultrapure water and absolute ethanol, and dried in air.

In addition, the single component (Fe, Co, Ni), double components (FeNi, FeCo, CoNi) and triple components (FeCoNi) catalysts

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