



Contents lists available at ScienceDirect

Journal of Energy Chemistry

journal homepage: www.elsevier.com/locate/jechem<http://www.journals.elsevier.com/journal-of-energy-chemistry/>

Annealing temperature dependent catalytic water oxidation activity of iron oxyhydroxide thin films

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ARTICLE INFO

Article history:

Received 11 January 2017

Revised 28 March 2017

Accepted 1 April 2017

Available online xxx

Keywords:

Iron oxyhydroxide/oxide electrocatalyst

Electrodeposition method

Water splitting

Linear sweep voltammetry (LSV)

X-ray photoelectron spectroscopy (XPS)

ABSTRACT

Nanostructured iron oxyhydroxide (FeOOH) thin films have been synthesized using an electrodeposition method on a nickel foam (NF) substrate and effect of air annealing temperature on the catalytic performance is studied. The as-deposited and annealed thin films were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (FE-SEM) and linear sweep voltammetry (LSV) to determine their structural, morphological, compositional and electrochemical properties, respectively. The as-deposited nanostructured amorphous FeOOH thin film is converted into a polycrystalline Fe₂O₃ with hematite crystal structure at a high temperature. The FeOOH thin film acts as an efficient electrocatalyst for the oxygen evolution reaction (OER) in an alkaline 1 M KOH electrolyte. The film annealed at 200 °C shows high catalytic activity with an onset overpotential of 240 mV with a smaller Tafel slope of 48 mV/dec. Additionally, it needs an overpotential of 290 mV to drive the current density of 10 mA/cm² and shows good stability in the 1 M KOH electrolyte solution.

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1. Introduction

With the increasing consumption of fossil fuels and growing concern about global warming, renewable energy sources must become a viable option for fossil fuel technology [1]. Solar and wind are primary renewable energy sources; however these sources are intermittent and require conversion into renewable fuels [2]. Electrochemical water splitting has been considered as an efficient path to produce hydrogen fuels and to store electricity from renewable sources, such as wind and sunlight [3]. Electrochemical water splitting has two main half-cell reactions, one at the cathode where hydrogen evolution reaction (HER) occurs and another at the anode where the oxygen evolution reaction (OER) occurs [4]. The HER is relatively easy; however the OER is more complicated and kinetically sluggish as it requires more overpotential than the theoretical potential value (1.23 V) [5]. Therefore, an electrocatalyst is needed to reduce overpotential and to increase the reaction rate [6]. Currently, precious metals such as Ru and Ir-based oxides exhibit good OER activity. However, due to their scarcity and high-cost, their practical applications are greatly hampered [7]. Ac-

ordingly, tremendous efforts have been undertaken to develop inexpensive, highly durable and readily available electrocatalysts for use as electrode materials in the OER to replace noble metal catalysts. Recently, great progress has been made in developing oxides and hydroxides based on earth abundant transition metals (Ni, Co, Fe, Mn) as OER electrocatalysts [8–15].

Among the various transition metal oxides/hydroxides investigated as OER electrocatalysts, iron-based compounds can be considered as better alternatives for RuO₂ and IrO₂ due to being inexpensive, earth abundant and environmental friendly [16]. The iron oxides and hydroxides can be synthesized by various methods, such as chemical bath deposition (CBD) [17], successive ionic layer adsorption and reaction (SILAR) [18], hydrothermal [19], spray pyrolysis [20] and electrodeposition [21]. Among these methods, electrodeposition is a simple, scalable and low temperature versatile method that allows control over the thickness of the deposited layer simply by changing either the current or voltage [21]. The major advantage of this deposition method is that the material can be deposited on the desired conductive substrate without the need of a binder. Recently, iron oxide/hydroxide were used as OER electrocatalysts for water splitting. Trotochaud et al. [22] studied the OER electrocatalytic properties of spin coated FeO_x films and reported 405 mV as the onset potential. Smith et al. [23] synthesized amorphous FeO_x using photochemical metal organic

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deposition and reported 320 mV as the onset overpotential. Liu et al. [24] synthesized α -Fe₂O₃ nanorods by a hydrothermal method on carbon cloth which showed 330 mV as the onset potential in an alkaline electrolyte. Zhao et al. [10,16] reported the electrodeposition of iron-based compounds on an ITO substrate in aqueous and non-aqueous media. It has been observed that the aqueous deposited iron oxide shows an onset potential of 408.6 mV, whereas iron oxyhydroxide deposited in the latter medium shows an onset potential of 470 mV. Cao et al. [25] have electrodeposited an iron based thin film on an ITO substrate with an onset potential of 480 mV. Zou et al. [26] have electrodeposited an iron (oxy) hydroxide thin film on an Au substrate with an onset potential of 350 mV. Recently, three dimensional (3D) porous nanostructured nickel foam (NF) has been used for depositing efficient electrocatalyst materials due to its high surface area, excellent conductivity, and high number of exposed active sites favoring sufficient accessibility of the electrolyte for higher electrochemical performance [27,28].

In this manuscript, we have synthesized iron oxyhydroxide (FeOOH) thin films on nickel foam (NF) substrates by an electrodeposition method followed by air annealing at different temperatures. The impact of air annealing on the structural, morphological, and electrochemical properties of the thin films is studied. The FeOOH thin film exhibits a lower overpotential of 290 mV at a current density of 10 mA/cm² in 1 M KOH electrolyte solution. In addition, it exhibits excellent stability in the electrolyte for 11 h, indicating the promising material for OER electrocatalyst.

2. Experimental

The iron oxyhydroxide (FeOOH) thin films were synthesized using an electrodeposition method on the NF substrate from an aqueous electrolytic bath containing 0.01 M iron nitrate (Fe(NO₃)₃·9H₂O) at room temperature. The electrochemical cell contained a saturated calomel electrode (SCE) as the reference electrode, platinum as the counter electrode and NF with a deposition area of 1 × 1 cm² as the working electrode. Analytical reagent grade (AR) chemicals used for precursor solution preparation (supplied by Sigma-Aldrich). Prior to electrodeposition, NF was first cleaned with 1 M HCl solution with ultra-sonication for 15 min to remove the nickel oxide layer. After that, the NF was washed with acetone, ethanol and doubly distilled water for 15 min and then dried at 60 °C for 24 h. The adherent and uniform films were deposited at –1.0 V vs. SCE in potentiostatic mode for 300 s using a WonATech, WMPG1000 Multichannel Potentiostat/Galvanostat ver. 1.11. After film deposition, the deposited films were rinsed with double distilled water and then dried at room temperature. The films were then annealed in an air atmosphere at different annealing temperature ranging from 100 °C to 400 °C for 2 h. The resulting films were denoted as Fe-OH/NF-100, Fe-OH/NF-200, Fe-OH/NF-300, Fe-OH/NF-400, respectively. The as-deposited and annealed films were used for further characterization.

The structural and chemical properties of the as-deposited and annealed thin films were studied using high resolution X-ray diffraction (XRD) with Ni-filtered CuK α radiation ($k\alpha = 1.54056 \text{ \AA}$) (X_{pert} PRO, Philips, Eindhoven, Netherlands) and X-ray photoelectron spectroscopy (XPS, VG Multilab 2000, Thermo VG Scientific, UK) with a monochromatic Mg-K α (1253.6 eV) radiation source, respectively. The surface morphology and compositional analysis of the films was measured using an FE-SEM (field emission scanning electron microscope, Model: JSM-6701F, JEOL, Japan) attached to an energy-dispersive X-ray analysis (EDAX) system. Electrochemical measurements were made using a standard three electrode cell configuration with a 1 M KOH electrolyte solution using the as-deposited/annealed films as a working electrode, platinum as the counter electrode and SCE as the reference electrode. To evaluate the OER activities of all the films, linear sweep voltammetry (LSV)

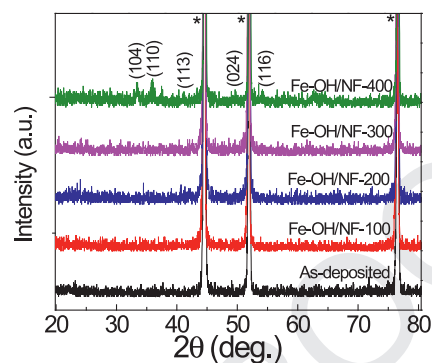


Fig. 1. XRD patterns of as-deposited and annealed FeOOH thin films at different temperatures.

was performed to acquire the polarization curve. All the potentials recorded in this work were vs. reversible hydrogen electrode (RHE) by the Nernst equation $E_{\text{RHE}} = E_{\text{SCE}} + (0.059 \times \text{pH}) + 0.24$ and the overpotential (η) was obtained by the equation: $\eta = E_{\text{RHE}} - 1.23 \text{ V}$ [29].

3. Results and discussion

Fig. 1 shows the XRD patterns of the as-deposited and air annealed thin films in the range of 100–400 °C for 2 h. The XRD spectra reveal the amorphous nature of the as-deposited and the annealed films up to 200 °C. However, for the films annealed above 200 °C, weak diffraction peaks corresponding to the (104), (110), (113), (024) and (116) planes are observed in the spectra indicating the formation of a crystalline α -Fe₂O₃ hematite phase. The observed crystalline phase matches with the JCPDS-89-0548 card and is in good agreement with the reported results [30, 31]. The intense and sharp peaks (indicated by *) in the XRD spectra are attributed to the NF substrate. Thus, it is clear that the crystallinity of the Fe₂O₃ films is enhanced with increasing the annealing temperature.

Fig. 2 shows the XPS spectra for the as-deposited and annealed thin films. In the survey spectra, the photoelectron peaks with binding energies (BEs) of 724 eV, 710 eV, 530 eV and 284 eV are observed, which could be assigned to the Fe 2p_{1/2}, Fe 2p_{3/2}, O 1s, C 1s, respectively (Fig. 2(a)). The high resolution XPS spectra for the Fe 2p and O 1s regions for all the films are shown in Fig. 2(c, d). The two major peaks of Fe 2p are centered approximately at 711.5 eV and 724.53 eV for the as-deposited film [32]. Interestingly, the BE values decreased with an increase in the annealing temperature, and the spectrum shows 710.7 eV and 724.12 eV for the film annealed at 400 °C [33]. The characteristic satellite peak is associated with Fe 2p_{3/2} and is located approximately at 8 eV higher than main Fe 2p_{3/2} peak [34]. The as-deposited film shows lowest BE peaks at 529.5 eV, 531 eV and 532.5 eV in the O 1s region and can be assigned to O²⁻, OH and chemically or physically adsorbed water respectively. The presence of –OH group suggests that the as-deposited film contain FeOOH phase [35]. Also Fe-OH/NF-100 and Fe-OH/NF-200 °C samples show similar peaks. The ratio of OH to O²⁻ is approximately 1, which indicates the presence of FeOOH phase in these samples. However, as annealing temperature increases, the –OH group peak is disappeared due to evaporation of hydroxide content from the film and single phase α -Fe₂O₃ is formed. Also, O²⁻ peak is slightly shifted monotonically toward the lower energy side.

Fig. 3 shows the SEM images of the as-deposited and annealed iron-based compound thin films deposited on NF substrates at different annealing temperatures. The as-deposited (Fig. 3(b)) and annealed films below 200 °C (Fig. 3(c, d)) show smooth, dense uni-

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