Electrochimica Acta 280 (2018) 1–8

Contents lists available at ScienceDirect

Electrochimica Acta

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

Fe^{3+} doped amorphous $Co_2BO_y(OH)_z$ with enhanced activity for oxygen evolution reaction

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ARTICLE INFO

Article history:
Received 5 February 2018
Received in revised form
27 April 2018
Accepted 7 May 2018

Keywords:
$(Co_{0.7}Fe_{0.3})_2BO_y(OH)_z$
Oxygen evolution reaction
3d electron density
Mössbauer spectrum

ABSTRACT

Achieving efficient oxygen evolution reaction (OER) is crucial for advancing energy storage and conversion technologies. Several methodologies have been developed to expedite the OER process. However, producing catalysts with excellent performance still remains challenging. Herein, we successfully achieve an enhanced OER performance in amorphous $(Co_{1-x}Fe_x)_2BO_y(OH)_z$ (x = 0, 10, 20, 30, 40 and 50%) by improving electrode kinetics. The incorporation of Fe^{3+} not only improves the charge transfer rate, but also modulates the absorption ability of Fe^{3+} ions to hydroxyl, as evidenced by the decrease of 3d electron density from the Mössbauer measurement. As a consequence, $(Co_{0.7}Fe_{0.3})_2BO_y(OH)_z$ shows a superior electrocatalytic performance with a current density of 10 mA cm^{-2} at an overpotential of 308 mV and a Tafel slope of 39 mV dec^{-1}, which are smaller than those observed for undoped parent catalyst $Co_2BO_y(OH)_z$ and commercial IrO_2. Moreover, $(Co_{0.7}Fe_{0.3})_2BO_y(OH)_z$ catalyst has a high stability in OER electrocatalytic process. The current density still remains about 70% after continuous electrocatalytic reaction for 12 h. $(Co_{0.7}Fe_{0.3})_2BO_y(OH)_z$ used as anode also catalyzes overall water splitting reaction to give a current density of 20 mA cm^{-2} at 1.62 V when taking Pt/C catalyst as cathode. The present study provides an effective approach to design new metal-based electrocatalystsby introducing foreign cation to alter outer electron density and further modulating the electrochemical activity.

1. Introduction

Electrochemical water splitting, as a clean and efficient energy conversion technique to produce hydrogen, has attracted widespread interests [1–3]. However, oxygen evolution reaction (OER), $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$, is a half reaction of the electrochemical water splitting that needs substantial overpotential to reach the required current density, which heavily hinders the efficiency of water electrolysis [4–6]. Until now, RuO_2 and IrO_2 have been considered as the state-of-the-art excellent OER catalysts [7,8], while their scarcity and prohibitive cost limit their wide applications in industrial electrolysis of water [9]. Therefore, new noble metal free catalysts are urgently required to meet the development concerns of advanced energy storage and conversion technologies.

Amorphous boron based materials, as a new class of electrocatalysts, gradually come to the scope of researchers [10–14]. Boron has less valence electrons, which could affect the electronic states of active metals to generate a significant enhancement in catalytic activity [15,16]. Over the past few years, amorphous boron based materials such as cobalt boride [17], nickel boride [18] have been proved to show a promising electrochemical activity for OER. For example, Schuhmann and co-workers reported that amorphous cobalt boride could be a good OER electrocatalyst owing to its diminished thermodynamic and kinetic barrier of the hydroxylation reaction induced by boron [17]. Nevertheless, their unsatisfying OER activity still needs to be optimized due to the simple electronic structure and poor conductivity.

Doping is a widely applied technology to achieve the material with desirable functions [19–21]. Various metal dopants, such as Fe^{3+} [22], Ag^+ [23] and Zn^{2+} [24–26], etc., have been selected to optimize the electronic structure and thus to improve the OER activity of inorganic materials. Interestingly, the electrochemical process for iron doped catalyst is efficiently modulated, and the observed activity is often better than that of the corresponding single-metal catalyst. It is highly possible that the incorporation of Fe^{3+} into 3d transition-metal materials can facilitate the formation

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https://doi.org/10.1016/j.electacta.2018.05.065
0013-4686/

of high-chemical-valence OOH-like species or exert synergistic effect on the instinct materials. For example, Chen's group reported that Fe^{3+} doped cobalt oxide altered the nature of Co^{2+} in the lattice through the electronic interaction and geometrical confinement, thus resulting in a strikingly high activity [27]. Li and his co-workers found that a stable Fe-NiOOH layer was formed on the surface of the Fe doped Ni_2P by electrochemical activation, thus promoting the charge transfer ability and surface electrochemically active sites generation [28]. Even though some progresses have been achieved, few works directly probe the chemical environment of the Fe after doping, nor reveal the relationship between the chemical environment of the Fe and the OER activity, especially for metal-nonmetal materials. Extending such investigations is helpful to find new noble metal free catalysts and further recognize the role of Fe in metal—nonmetal materials, such as metal boron based compounds.

In this work, we successfully synthesized different contents of Fe^{3+} doped amorphous nanoparticles of $(Co_{1-x}Fe_x)_2BO_y(OH)_z$ (x = 0, 10, 20, 30, 40 and 50%). By varying the doping amount of iron, 30% Fe^{3+} doped sample was found to exhibit the optimal OER activity. The required overpotential to reach a current density of 10 mA cm^{-2} is 308 mV, which is superior to its parent material $Co_2BO_y(OH)_z$ and benchmarks commercial IrO_2. The impressive electrocatalytic performance was attributed to the enhanced conductivity, exposure of ion-accessible sites and the electron transfer between Fe and B. Mössbauer measurement was utilized to investigate the chemical environment of Fe. The quantity of Fe^{3+} with a lower electron density was found to have a strong correlation with the OER activity. This work provides a guidance for introducing foreign cation to alter outer electron density and further modulating the electrochemical activity.

2. Experimental Section

2.1. Preparation of materials

Fe^{3+} doped $Co_2BO_y(OH)_z$ catalysts were synthesized through a facile liquid-phase method by dripping aqueous sodiumborohydride ($NaBH_4$) into different molar proportional aqueous mixtures of cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$) and ferric chloride hexahydrate ($FeCl_3 \cdot 9H_2O$). Boron is involved in the reaction. Amorphous boron compounds are thereby produced due to the coprecipitation of B. In a typical synthesis procedure, calculated amounts of hydrated $CoCl_2$ and $FeCl_3$ were dissolved into the deionized water with the total amount of metal ions at 0.01 mol. Then the obtained aqueous solution was transferred into a three-neck round-bottomed flask and deaerated with the aid of a vacuum set-up, flushed with argon. This process was carried out under 0° C using an ice-bath. 2 M $NaBH_4$ (in 0.2 M NaOH) maintained in ice-bath advance was slowly added into the round-bottomed flask by means of a syringe. As the drip went on, bubbles kept coming out and a dark precipitate was observed. When the bubbles stopped, the precipitate was collected by centrifugation and washed with large amounts of deionized water, followed by ethanol. The products were directly dried in vacuum under ambient temperature for 12 h without any heat-treatment. Using the similar procedure, the catalysts with different Fe contents were prepared, named as $(Co_{1-x}Fe_x)_2BO_y(OH)_z$, where x varied from 10% to 50%. We also synthesized 30% Ni^{2+} doped sample with the same method, named as $(Co_{0.7}Ni_{0.3})_2BO_y(OH)_z$ accordingly.

2.2. Sample characterization

Powder X-ray diffraction (XRD) was recorded on a D/MaX2550 diffractometer (Cu Kα, λ = 1.5418 Å) at 40 kV and 15 mA. The morphologies and EDS mappings of the samples were observed by field-emission scanning electron microscopy (SEM) Hitachi S-4800 and JSM 7800, respectively. Transmission electron microscopy (TEM) was taken on Tecnai G2S-Twin F20 apparatus. The chemical compositions of the samples were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES) on an OPTIMA 3300DVinstrument (Perkin Elmer). The test results show that the molar ratio of metal elements to B is closer to 2. X-ray photoelectron spectroscopy (XPS) measurements were carried on an ESCALAB 250Xi spectrometer with a Mg Kα radiation. All the spectra were calibrated using the C 1s photoemission line at a binding energy of 284.8 eV. ^{57}Fe Mössbauer spectra of samples were recorded on an Oxford MS-500 model constant acceleration Mössbauer spectrometer (with a 1024 multichannel analyzer) with ^{57}Co/Pd source at room temperature. The isomer shift (IS), quadrupole splitting (QS), and magnetic hyperfine (H_{hf}) were calculated respecting to α-Fe.

2.3. Electrochemical measurement

Electrochemical tests were carried on the catalyst films with glassy carbon electrode (GCE) as support. Prior to the coating of the catalyst, the glassy carbon electrodes (5 mm diameter) were polished with Al_2O_3 paste (0.05 mm) and washed ultrasonically with deionized water. Catalyst inks were prepared by dispersing 4 mg of the sample into a mixture of 50 μL of 5% Nafion solution, 450 μL of deionized water and 500 μL of ethanol under sonication for 30 min. The 10 μL catalyst ink was dripped onto the GCE to a form a catalyst film with a loading density of 0.2 mg cm^{-2}. Then the black catalyst films were dried at room temperature. In this work, all the electrochemical measurements were performed with Hg/HgO as a reference electrode and graphite as a counter electrode and a rotation speed at 1, 200 rpm [29]. The potentials were displayed versus reversible hydrogen electrode (RHE) by the RHE calibration: $E(RHE) = E(Hg/HgO) + 0.098 + 0.059 \times pH$, where pH = 14 in 1.0 M KOH solution. The linear polarization curves (LSVs) were recorded from 0.3 V to 0.8 V vs. Hg/HgO at a scan rate of 5 mV s^{-1} with iR corrected. Before the iR corrected LSVs recording, we tested the LSVs at 30 mV s^{-1} until stable LSVs curves were obtained. CV curves were measured in oxygen saturated 1.0 M KOH between 1.1 V and 1.6 V at 1 mV s^{-1} to determine the redox potential. Electrochemical impedance spectroscopy (EIS) measurements were tested at 1.6 V vs. RHE (i.e., η = 370 mV) in the frequency range of 10^{-2} Hz to 10^5 Hz with an amplitude of 5 mV. Chronoamperometry was tested at an applied potential of 1.55 V vs. RHE at pH = 14 to study the durability of the electrocatalysts. Cyclic voltammetry (CV) measurements with different scan rates (40, 80, 120, 160, 200 mV s^{-1}) were used to determine the electrochemical double layer capacitances (EDLC, C_{dl}).

2.4. Overall water splitting measurement

The catalyst inks were prepared by the similar method as abovementioned. Overall water splitting was estimated in a two-electrode system by using 30% Fe^{3+} doped amorphous catalyst as anode and Pt/C (Pt 10%) catalyst as cathode on carbon fiber paper with a loading density of 1 mg cm^{-2}.

2.5. Calculations

Calculation of mass activity, specific activity, and TOF are shown as below:

The values of mass activity (A g^{-1}) are calculated based on the