



# Cobalt-iron (oxides) water oxidation catalysts: Tracking catalyst redox states and reaction dynamic mechanism

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## ABSTRACT

Developing earth-abundant materials to replace the traditional noble metals in water splitting to meet industrial requirements remains a challenge. Cobalt-iron (oxides) have been widely studied as electrocatalysts for the oxygen evolution reaction (OER), yet our understanding of the OER dynamic reactivity related to the oxidation state changes as well the adsorption energies of surface species on the metal surface linked to the water oxidation are not well-documented. In this work, a facile chemical reduction process is developed for preparation of Co-only, Co<sub>3</sub>Fe<sub>7</sub> alloy, and Fe-only catalysts. We use X-ray photoelectron spectroscopy (XPS) and in-situ X-ray absorption spectroscopy (XAS) to evaluate metal valences and the dynamics of the oxidation state changes of the electrocatalysts in 0.1 M KOH solution, which disclose that about 20% of the Co centers get oxidized in Co-only from the oxidation state of +2 to +3/+4, while only 1% reach to +3 valence for the Co<sub>3</sub>Fe<sub>7</sub> catalyst under cyclic voltammetry (CV) operation. The small edge changes of Fe centers in Fe-only result in negligible changing the oxidation state. Density-functional theory (DFT) calculation predicts the mechanism of OER performance, which indicates that the OER activity largely relies on the metal oxidation states on the surface of catalysts. Co<sub>3</sub>O<sub>4</sub> on the surface of Co-only catalyst presenting the most positive d-band center and the fewest e<sub>g</sub> electron contributes to the highest OER activity. Fe-only coated by γ-Fe<sub>2</sub>O<sub>3</sub> shows the lowest OER performance due to the weakest oxygen adsorption energy of γ-Fe<sub>2</sub>O<sub>3</sub> as well as the poor electrical conductivity of FeOOH evolved after operation. Co<sub>3</sub>Fe<sub>7</sub> exhibiting medium OER activity is aroused by the co-existence of CoO and γ-Fe<sub>2</sub>O<sub>3</sub>, wherein Co<sup>2+</sup> is less active than Co<sup>3+</sup>. Introducing Fe in Co matrix could depress the formation of Co cations with high oxidation state in as-prepared catalysts, which is not favorable for oxygen production.

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## 1. Introduction

Hydrogen produced by water electrolysis offers the promise of a clean and sustainable energy for fossil fuels [1]. The hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) coherently processing through the electrolysis of water are important

support for a number of energy conversion and storage technologies [2–5]. Oxygen evolution reaction, as a half reaction of the water splitting process, remains the bottleneck of the whole process at present. The best electrocatalysts for OER are considered as the noble metal catalysts, such as RuO<sub>2</sub> and IrO<sub>2</sub>. But the low reserves and high cost inhibit their maximum applications. Therefore, the ongoing researches need to focus on exploring new non-noble-metal electrocatalysts with excellent electrocatalytic performance for OER. Co-based OER catalysts, e.g. Co-Fe (oxy) hydroxides, FeCoO<sub>x</sub> films, have attracted great interest in water splitting since Co catalysts are considered as the only known OER catalysts with reasonable activity in neutral media. To achieve structural atomic-level and chemical insight into the relation between structure, mechanism, and activity of OER performance

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in mixed Co-Fe catalysts, substantial work has focused on mixed-metal systems containing both Co and Fe. However, the contradictory conclusions are still in dispute that whether the Fe plays a positive effect in OER performance when incorporated in  $\text{CoO}_x$  because of the difficulty in quantifying the number of active sites, as well as the correlation between the chemical states and local atomic structure around metal centers. Hence, several studies have been conducted to illustrate the Fe effect in Co-based catalysts. Laouini et al. indicates that Co-ion could be partially replaced by Fe-ion in the cobalt cobaltite  $\text{Co}_3\text{O}_4$ , which give rise to an enhancement of OER activity [6]. Grewe et al. shows that the  $\text{Co}_3\text{O}_4$  doped with small amounts of iron could exhibit comparable water oxidation activity with noble metal due to the alteration of mesostructural symmetry [7]. Xiao et al. also reveals that the incorporation of Fe into  $\text{mCo}_3\text{O}_4$  ( $\text{Fe-mCo}_3\text{O}_4$ ) results in significantly enhanced catalytic activity due to unusual synergistic effect [8]. In the contrary, Kishi et al. investigates that the introduction of Fe in  $\text{Fe}_x\text{Co}_{3-x}\text{O}_4$  ( $0 \leq x \leq 2$ ) depress OER activity [9]. Recent study indicates that the intrinsic OER activity of  $\text{Co}_{1-x}\text{Fe}_x(\text{OOH})$  is 100-fold higher for  $x \approx 0.6$ – $0.7$  than for  $x = 0$  [10]. A more plausible explanation would seem to be that Fe incorporation in CoFe complex (substitutional doping of Fe in Co crystal lattice) related to strong electronic interactions between the two elements is thus important for enhancing OER catalytic activity, further giving rise to the possibility that Fe is the active site. Giving the above, diversity of fabrication protocols of Co-Fe mixture catalysts would influence the localized structure of catalysts, thus producing different active sites with changeable electrochemical behavior of  $\text{Co}_{\text{cat}}$ . Until now, the effect of Fe doping on the OER activity of amorphous Co as well as the relation between the 3d electron configuration and OER catalysis remain unresolved.

In the light of clarifying the role of Fe playing in OER catalysis on  $\text{CoFe}(\text{O})$  catalysts, we synthesized elemental Fe-only, Co-only, and  $\text{Co}_3\text{Fe}_7$  alloy nanochain networks at room temperature. The purpose of designing alloy of  $\text{Co}_3\text{Fe}_7$  is to establish a structure in which the Fe atoms were partially replaced by Co, and thus be able to evaluate the number of active sites by tracking OER dynamic process. The electrochemical behaviors of the three catalysts were connected with morphology, structure, and oxidation state changes that occur during OER catalysis. Furthermore, in order to clarify the correlation between the OER catalytic activity and the nature of the catalysts, we applied in-situ X-ray absorption spectroscopy (XAS) to track the metal valences and the dynamics of the oxidation state changes of the electrocatalysts during CV scanning. To further gain insight into the mechanism of OER performance, we calculated the d-band center to evaluate the adsorption energies for the surface intermediates on metal catalysts by density functional theory (DFT). Because of the nanochain-type architecture which could shorten the diffusion path of ions as well as the optimal oxygen adsorption energy, Co-only nanochain networks show a highest catalytic activity compared with Fe-only and  $\text{Co}_3\text{Fe}_7$  for OER in alkaline. A simple but plausible hypothesis was proposed to interpret the role of Fe in  $\text{CoO}_x$  with respect to the redox state and d-band center under OER condition.

## 2. Experimental

### 2.1. Sample preparation

All reagents were analytically pure and used without further purification. The cobalt-iron (oxides) nanochains were synthesized by a facile chemical reduction process [11]. 0.002 M  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and 0.004 M  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  were dissolved in 20 mL deionized water under vigorous stirring. Then 0.009 M  $\text{NaBH}_4$  was added to the

above solution as reducing agent. Excess amount of borohydride was used in order to completely reduce Co and Fe cations to metals. The product was magnetically separated and collected, washed with distilled water and anhydrous ethanol in order to remove  $\text{Cl}^-$  and  $\text{Na}^+$  ions and vacuum dried at room temperature to obtain black powders. For comparative studies, Fe-only nanochains and Co-only nanoparticles were also synthesized in a similar manner by using only  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  in the initial solution respectively. The crystalline Co-only nanoparticles were prepared by heating the as-prepared nanoparticles at 450 °C for 5 mins in Ar atmosphere. The diagram of the route that the catalysts were synthesized in the hydrothermal growth process is shown in Fig. S1.

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.jcat.2018.06.031>.

### 2.2. Sample characterization

The surface morphology, composition, and structure of the samples were characterized by field emission scanning electron microscopy equipped with EDX system (SEM, Hitachi S-4800, Japan), X-ray diffraction (XRD, D8 Advanced, Bruker, Germany), and transmission electron microscopy (TEM, JEM-2100F, Japan). Surface chemical analysis of cobalt-iron (oxides) nanochains was performed by X-ray photoelectron spectroscopy (XPS, PHIL1600ESCA). Total metal content in catalysts was analyzed using total reflection X-ray fluorescence (TXRF) spectroscopy.

### 2.3. Electrochemical measurements

The electrochemical experiments were carried out in a three-electrode cell using an electrochemical potentiostat (Biologic VSP-300) in  $\text{N}_2$  saturated 0.1 M KOH solution using a platinum net as counter electrode and an Ag/AgCl electrode as reference electrode. 4 mg of as-prepared catalysts were dispersed in mixture of distilled water (800  $\mu\text{L}$ ) and ethanol (200  $\mu\text{L}$ ). Then, 80  $\mu\text{L}$  of Nafion (5 wt%, Alfa Aesar) was added to the above solution. The mixed solution was sonicated at least 30 mins to form a homogeneous ink. 150  $\mu\text{L}$  of the mixed solution was drop-casted onto the glassy carbon electrode (GCE) with the work area of 0.2826  $\text{cm}^2$ . Then, the electrode was dried in drying oven at 303 K for 40 mins. The GCE coated by catalysts was served as the working electrode. All potentials were referenced to a reversible hydrogen electrode (RHE) by adding a value of  $(0.205 + 0.059 \times \text{pH} + E_{\text{Ag}/\text{AgCl}})$  V. The polarization curves for the OER were determined using cyclic voltammetry (CV) under a scanning rate of 10  $\text{mV s}^{-1}$ . Electrical impedance spectroscopy (EIS) was conducted under the following conditions: an AC voltage amplitude of 1.8 V vs. RHE and a frequency range of  $1 \times 10^5$ – $1 \times 10^{-2}$  Hz.

### 2.4. In-situ X-ray absorption

The spectrometer was connected via fiber optic cables to the electrochemical cell. Co and Fe K-edge XAFS spectra were performed on the 1W1B beamline of the Beijing Synchrotron Radiation Facility, China. Co K-edge was recorded from 7655 eV to 8095 eV and Fe K-edge in the range 7058 eV to 7428 eV in fluorescence mode with a step-size of 0.25 eV at the near edge. All samples for in-situ measurements were prepared by drop-casting on carbon fiber paper as the working electrode with a geometric area of 1  $\text{cm}^2$ , a Pt-wire was used as counter electrode, and an Ag/AgCl electrode as reference electrode. After the measurements, the spectrum can be used to estimate the edge position.

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