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Porous amorphous FeCo alloys as pre-catalysts for promoting the oxygen evolution reaction

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ABSTRACT

The design and development of efficient electrocatalysts composed of earth-abundant elements for oxygen evolution have gained significant attention. In this study, a FeCo alloy electrocatalyst with an amorphous and porous structure was designed and prepared. The electrochemical test results showed that the amorphous alloy product with a Co:Fe molar ratio of 2:1 showed an optimal intrinsic catalytic activity for oxygen evolution. At a current density of 10 mA cm⁻², only a small overpotential of 290 mV was required in a KOH solution (1 mol L^{-1}), which is much lower than that for the monometallic catalyst (428 mV for amorphous cobalt for the same current density). The bimetal composition of this catalyst induced a strong synergistic effect. Moreover, it exhibited an amorphous and porous structure with a large number of exposed active sites along with high conductivity. These factors contributed to the excellent catalytic performance of this catalyst. This study provides an insight into the design of advanced oxygen evolution reaction catalysts.

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1. Introduction

Oxygen evolution reaction (OER; $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ in acid and $40H^- \rightarrow 0_2 + 2H_2O + 4e^-$ in base) is a critical process for various energy-related applications such as electrochemical watersplitting, electrocatalytic CO₂/N₂ reduction, and rechargeable metal-air batteries [1]. For the generation of one oxygen molecule, O-H bond breaking and O-O bond formation are required. The entire process involves the transfer of four electrons, and hence shows sluggish kinetics [2,3]. Oxygen evolution often requires a high overpotential to achieve a considerable current density. Thus, the development of efficient electrocatalysts is imperative to decrease the reaction overpotential and to accelerate the reaction rate. Ru- and Ir-based compounds such as RuO₂ and IrO₂ are widely used as traditional OER electrocatalysts. These electrocatalysts exhibit excellent catalytic performance in acidic solutions [4]. However, the high cost, scarcity, and instability in basic solutions of these electrocatalysts limit their large-scale applications. Recently, transition metal-based compounds especially Ni-based and Cobased compounds have been developed as cheap OER catalysts with high efficiency [5–9].

Among transition metal-based OER catalysts, bimetal (especially FeCo-based) oxides, hydroxides, oxyhydroxides, and sulfides are extensively investigated owing to their high electrocatalytic activity and natural abundance [10-14]. Generally, for an excellent electrocatalyst, at least three factors should be considered. The first factor is the intrinsic catalytic activity of the surface-accessible metal centers, which act as catalytic active centers. The intrinsic catalytic activity of the metal sites of an electrocatalyst depends on its electronic structure, which is affected by the synergistic effect between its constituents [15,16]. Coupling of iron and cobalt can tune the adsorption energies of the intermediates (including O and O–O species formed during the OER process) formed at the metal sites to the optimal state [17-19]. FeCo-based composites show improved catalytic activities as compared to their monometallic counterparts, although the nature of the actual catalytic active centers (Fe or Co sites) is not clear [20]. The second factor is the number of exposed metal active centers; the larger is the number of exposed active centers, the higher is the catalytic activity. The number of exposed metal active centers can be increased by designing micro/nanostructures and by tuning the catalyst microscale size [21]. Open porous structures contain a large number of







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exposed metal centers [22–24]. Conductivity is another important factor for an electrocatalyst. Conductive species such as graphene and carbon nanotubes are added to catalysts in order to improve their conductivity [25]. Till date, various FeCo-based catalysts have been prepared and investigated for oxygen chemistry. For example, composite materials derived from FeCo-metal organic frameworks [26,27] and FeCo-based alloys encapsulated in carbon [28] have been demonstrated to be effective catalysts for oxygen chemistry.

Though crystalline OER electrocatalysts have been extensively investigated, amorphous electrocatalysts exhibit several advantages [29–31]. Amorphous materials only bear a short-range order with irregular boundaries and are composed of randomly arranged atoms. This structural feature generates a large number of defects, which act as catalytic active sites and facilitate the diffusion of ions through the catalyst layer. For example, amorphous CoO_x clusters [32], amorphous NiO_x decorated on NiSe₂ [33], and amorphous FeO_x-based products [34,35] have been identified to be highly efficient OER catalysts.

In this study, we designed and prepared porous and amorphous FeCo bimetal alloys for application as OER electrocatalysts in basic solutions. We used NaBH₄, which is a strong reducing agent, to reduce Co(II)/Fe(III) species. Owing to the strong reducing ability of NaBH₄, the obtained metallic samples showed amorphous features, which improved their catalytic activity. The obtained products showed a large number of open pores on the surface, thus exposing a large number of metal sites during the catalysis. The strong synergistic effect between the cobalt and iron sites in these bimetal samples improved the intrinsic catalytic activity of the metal centers. The bimetal samples showed high conductivity. The amorphous FeCo alloy with the Co:Fe molar ratio of 2:1 showed excellent OER electrocatalytic activity with an overpotential of 290 mV at a current density of 10 mA cm⁻². This alloy also showed excellent stability, as revealed by the *i*-*t* test results.

2. Experimental section

2.1. Reagents and chemicals

Nafion solution (5 wt%) was purchased from Alfa Aesar. All the other chemical reagents used in this study were obtained from Sinopharm Chemical Reagent Co., Ltd. The chemicals used in this study were of analytical grade and were used as-received without any further purification.

2.2. Synthesis of amorphous alloys

The synthesis was carried out as follows: the aqueous solutions of $CoCl_2$ (1 mL, 1 mol L^{-1}) and $FeCl_3$ (1 mL, 1 mol L^{-1}) were added to 2 mL of an aqueous solution of $Na_3Co(NO_2)_6$ (0.5 mol L^{-1}). The resulting mixture was stirred at room temperature for 8 h. A dark red viscous liquid was obtained. A NaBH₄ solution (100 mL, 2 mol L^{-1}) was then added to the reaction mixture under vigorous stirring. This resulted in the formation of a black product. At the same time, a lot of gases were released. The black solid product (amorphous alloy) showed strong magnetism and was adsorbed on a magnetic sticker. After 0.5 h of reaction, the product was separated using a magnet or by centrifugation and was then washed with water and ethanol. The resulting sample was labeled as *a*-Co₂Fe (based on the molar ratio of Co:Fe) and was dried at 60 °C.

For comparison, the Co:Fe molar ratios of 1:0, 5:1, 7:2, and 1:2 were also used by changing the concentrations of the CoCl₂ and/or FeCl₃ aqueous solutions while keeping the total metal ion concentration and other conditions constant. The products obtained at the Co:Fe molar ratios of 1:0, 5:1, 7:2, and 1:2 were labeled as a-Co, a-Co₅Fe, a-Co₇Fe₂, and a-CoFe₂, respectively.

2.3. Characterization

The morphologies of the prepared samples were examined using scanning electron microscopy (SEM, REGULUS-8230), while their crystal phase structures were investigated using X-ray powder diffraction (XRD, MAP18XAHF). The Fourier transform infrared (FT-IR) spectra of the samples were recorded on a Nexus 870 spectroscope. The sizes and microstructures of the samples were examined using transmission electron microscopy (TEM, JEOL JEM 2100). The X-ray photoelectron spectroscopy (XPS) analysis of the samples was carried out on a Thermo Scientific Ka photoelectron spectroscope. The magnetic properties of the samples were evaluated using an MPMS XL-7 superconducting quantum interference device (SQUID). The N₂ adsorption-desorption behaviors of the samples were investigated using an ASAP 2010 sorption analyzer. The metal molar ratios of the samples were determined using a Vista-MPX inductively coupled plasma optical emission spectrometer (ICP-OES).

2.4. Electrochemical measurements

Electrochemical tests were carried out at room temperature on an CHI 650E electrochemical analyzer with a KOH aqueous solution (1 mol L^{-1}) as the electrolyte. A typical three-electrode system consisting of a Hg/HgO electrode (1 mol L^{-1} of KOH) as the reference electrode, a glassy-carbon electrode (3 mm in diameter) as the counter electrode, and the electrocatalyst-modified glassy-carbon electrode (3 mm in diameter) as the working electrode was used.

The working electrode was prepared using a procedure reported in our previous study [21,36]. The catalyst ink was prepared by mixing 4 mg of the catalyst and 3.5 mg of acetylene black in a mixture composed of 1 mL of ethanol and 15 µL of 5 wt% Nafion under ultrasonication. Then, the catalyst ink (5 µL) was carefully loaded on the glassy-carbon electrode, which was then dried at room temperature. The loading density of the catalysts on the working electrode was determined to be ~0.28 mg cm⁻². In this manuscript, all the potentials are reported with respect to the reversible hydrogen electrode (RHE), according to $E_{vs. RHE} = E_{vs. Hg/HgO} + E_{Hg/HgO}^{\Theta} + 0.0591pH$ (in volts). $E_{Hg/HgO}^{\Theta}$ is the potential of the Hg/HgO electrode (1 M NaOH, 0.098 V).

The as-prepared electrodes were activated by 1000 cyclic voltammetry (CV) cycles over the potential range of 0.1-0.9 V vs. Hg/ HgO. The linear sweep voltammetry (LSV) curves of the samples were recorded at a scanning rate of 5 mVs⁻¹. The LSV curves were not corrected with the *iR* potential drop. The Tafel slopes of the samples were calculated directly from their polarization curves by plotting their overpotential against log(j), where *j* is the current density. The durability of the electrodes was tested by i-t method and by obtaining the polarization curves before and after 3000 CV cycles.

3. Results and discussion

3.1. Morphology and structure

The amorphous alloys were synthesized at room temperature. NaBH₄, which is a strong reducing agent with a standard electrode potential of -1.24 V, was used to reduce the involved metal ions. Be noted that the cobalt and iron species can catalyze the hydrolysis of BH₄, thus generating hydrogen [37,38]. For the synthesis, Na₃Co(NO₂)₆ was used as a cobalt source. The NO₂ ligands are coordinated by the involved metal ions, thus modulating the formation rate of the alloys.

The amorphous products were examined using XRD. The XRD patterns of the products are shown in Fig. 1. The XRD patterns did



Fig. 1. XRD patterns of the synthesized products.

not show any peaks, confirming the formation of amorphous or poorly crystalline products. This also confirms the strong reducing ability of NaBH₄, as quick formation of the alloys with the amorphous structure was observed. Unlike NaBH₄, which produces amorphous FeCo alloys, hydrazine when used as the reducing agent causes the formation of crystalline FeCo alloys [39].

The microstructures and particle sizes of the samples were examined using SEM. The SEM images of *a*-Co and *a*-Co₂Fe are shown in Fig. 2. The *a*-Co and *a*-Co₂Fe samples showed similar structural features. Both the samples were composed of irregular particles. The particle sizes of both the samples were found to be within the range of 100–300 nm. The samples showed porous structural features. As indicated by the arrows in Fig. 2b and d, the samples showed pores with the size of about 50 nm. The *a*-Co₅Fe, *a*-Co₇Fe₂, and *a*-CoFe₂ samples also showed similar porous structures. The corresponding SEM images are shown in the supporting information (Fig. S1).

The microstructures of the amorphous samples were further examined using TEM. The TEM images of the *a*-Co and *a*-Co₂Fe samples are shown in Fig. 3. The TEM images showed lower contrast regions (Fig. 3a and e), confirming the presence of pores or voids in the samples. These structural features were further examined by high-resolution TEM (HRTEM) (Fig. 3b and f). The HRTEM images of the *a*-Co and *a*-Co₂Fe samples are shown in



Fig. 2. SEM images of a, b) a-Co; c, d) a-Co₂Fe.

Fig. 3c and g, respectively. No clear lattice fringes were observed for the samples. A few regions showed a presence of lattice fringes. This indicates that the samples were mainly composed of amorphous constituents. The amorphous structure of the samples was further examined by obtaining their selected area electron diffraction (SAED) patterns (Fig. 3d and h). The amorphous structure creates a large number of exposed metal sites as catalytic centers, which improves the catalytic properties of the material [29,40]. The results discussed thus far confirm the formation of amorphous and porous products using the room-temperature synthesis route developed in this study.

To determine the specific surface areas of the synthesized amorphous and porous products, their N₂ adsorption-desorption isotherms were obtained. Fig. 4a shows the N₂ adsorptiondesorption isotherms of the *a*-Co and *a*-Co₂Fe samples. As can be observed from the figure, the samples showed type-III adsorption curves. The N₂ adsorption amount increased monotonically with an increase in the relative pressure, indicating the presence of pores in the samples. The Brunauer-Emmet-Teller (BET) specific surface areas of the a-Co and a-Co₂Fe samples were estimated to be 58.1 and 127.1 m² g⁻¹, respectively. The a-Co₂Fe sample showed higher specific surface area than the *a*-Co sample. These specific surface area values are much higher than those of metal oxide nanoparticles $(\langle 20 \text{ m}^2 \text{ g}^{-1})$ [41]. The pore diameters of the samples were determined using the BJH method. Both the samples showed a pore diameter of about 40 nm. This value is consistent with the TEM and SEM results.

The ICP analysis results revealed that the *a*-Co₂Fe sample showed a composition of Co18Fe. This is consistent with the cobalt and iron dosages used in the preparation process. XPS was employed to further examine the surface compositions and chemical states of the samples (Fig. 5). The high-resolution Co 2p spectrum of *a*-Co showed two typical bands at 781.0 and 796.7 eV corresponding to Co 2p3/2 and Co 2p1/2, respectively. The spinorbit splitting of 15.7 eV (796.7-781.0 eV) indicates that the sample surface consisted of cobalt species with the +2 oxidation state [42]. The Co 2p spectrum of the sample showed two satellite peaks at 786.5 and 803.2 eV [43]. In the case of the a-Co₂Fe sample, the Co XPS band showed a slight blue-shift of ~0.5 eV (Fig. 5a). This indicates the presence of strong electronic interactions between the Fe and Co sites. Fig. 5b shows the Fe 2p XPS spectrum of *a*-Co₂Fe. The Auger peak of cobalt was observed in the Fe 2p binding energy range, causing the distortion of the spectrum. The two bands at 711.8 and 725.3 eV suggest the presence of iron species with the +3oxidation state in the sample [44,45]. The Auger peak of cobalt and the satellite peak of Fe $2p_{3/2}$ were observed at 714.6 and 719.3 eV, respectively. Fig. 5c shows the high-resolution O 1s spectra of the samples. The spectra could be fitted into three bands at 530.7, 531.7, and 532.6 eV corresponding to the M-O species, defect sites with low oxygen coordination, and adsorbed –OH or H₂O, respectively [46-48].

The surface oxygen species of the samples were analyzed by obtaining their FT-IR spectra over the wavenumber range of $4000-400 \text{ cm}^{-1}$. As can be observed from Fig. 6, the two samples showed similar IR bands. The broad and intense peak at 3423 cm^{-1} corresponds to the O–H stretching vibration, while the band at 1064 cm⁻¹ corresponds to the O–H or H₂O species on the surface of the samples. The band at 1623 cm⁻¹ can be attributed to the bending vibration of absorbed H₂O [49]. These hydrophilic groups on the surface will enhance the electrolyte wetting of the surface of the samples, thus improving their electrocatalytic performance.

The presence of oxygen-containing species (oxides/hydroxides) can be attributed to the use of the alkaline NaBH₄ solution for the formation of the metallic alloys. Because of the strong reducing



Fig. 3. TEM and HRTEM images and SAED patterns of a-d) a-Co and e-h) a-Co₂Fe.



Fig. 4. a) N₂ adsorption-desorption isotherms and b) BJH pore size distribution curves the *a*-Co and *a*-Co₂Fe samples.



Fig. 5. XPS spectra of a-Co and a-Co₂Fe. a) High-resolution Co 2p, b) Fe 2p, and c) O 1s XPS spectra of the samples.

environment, the formed oxides/hydroxides showed a presence of large number of oxygen defects. On the other hand, the surface of these active alloy nanoparticles oxidized easily when exposed to air because of their high surface energy, forming a metal oxide or hydroxide layer on the surface to protect the metal core.

The prepared samples showed excellent magnetic properties and could be easily collected by a magnet (inset of Fig. 7). The magnetic properties of the a-Co and a-Co₂Fe samples were examined using a SQUID. As shown in Fig. 7, both the samples showed long and narrow magnetic hysteresis loops with small remanent magnetization (Mr) of 0.2–3.3 emu g⁻¹. The two samples also showed small coercive forces (Hc) of 7.0 Oe (for *a*-Co) and 54.0 Oe (for *a*-Co₂Fe) (the inset shows the magnified loops in the magnetic field range of \pm 600 Oe). This indicates that the samples were typical soft-magnetic materials [50,51]. The saturation magnetization values of the *a*-Co and *a*-Co₂Fe samples were 8.4



Fig. 6. IR spectra of the *a*-Co and *a*-Co₂Fe samples.



Fig. 7. Hysteresis loops of the *a*-Co and *a*-Co₂Fe samples over the magnetic field range of \pm 30000 Oe. The insets show the sample attracted by a magnet and the magnified loops over the magnetic field range of \pm 600 Oe.

emu g^{-1} and 31.8 emug⁻¹, respectively. The difference in the saturation magnetization values of the samples can be attributed to the difference in their compositions and metal contents [39].

3.2. Electrocatalytic performance for OER

To investigate the OER electrocatalytic performance of the asprepared amorphous catalysts, their electrochemical polarization tests were carried out in an 1 M KOH aqueous solution using LSV (Fig. 8). As shown in Fig. 8a, among all the samples, the *a*-Co₂Fe sample showed the smallest overpotential (η_{10}) defined by the potential at the current density of 10 mA cm⁻², which is a measure of the activity of OER catalysts [3]. The η_{10} value of the *a*-Co₂Fe catalyst was only 290 mV. This value is much smaller than those of the other catalysts (428 mV for a-Co, 343 mV for a-CoFe₂, 335 mV for *a*-Co₅Fe, and 340 mV for *a*-Co₇Fe₂) (Fig. 8a and c). This indicates that the optimum Co:Fe molar ratio was 2:1. It should be noted that the *a*-Co sample showed the largest overpotential among all the samples, indicating that the coupling of iron and cobalt improved the OER activity of the catalysts. In addition, the activity of the optimized a-Co₂Fe catalyst with a η_{10} value of 290 mV was superior or comparable to those of most of the reported FeCo-based electrocatalysts [52-56]. Table 1 compares the catalytic activities of the catalysts.

Fig. 8b shows the overpotential vs. log(j) curves of all the samples over the current density range of $1-10 \text{ mA cm}^{-2}$ (the plots in the current density range of 0.5-50 mA cm⁻² are shown in Fig. S2). From these curves, the Tafel slopes of the samples were determined. The a-Co₂Fe and a-CoFe₂ samples showed similar Tafel slopes of $62-67 \text{ mV dec}^{-1}$, which are lower than those of the other catalysts with higher cobalt contents (for example 90 mV dec $^{-1}$ for a-Co₇Fe₂). This indicates that the iron-rich catalysts showed faster OER kinetics. The overpotentials and Tafel slopes for the five samples are shown in Fig. 8c. The sample with the optimal Co:Fe ratio of 2:1 was found to be the best electrocatalyst. The mass activity of the catalyst with the optimum Co:Fe ratio was then estimated based on its current density at the overpotential of 350 mV, which was calculated to be 85.4 A g^{-1} . This value is about seven times higher than that of the monometallic catalyst, *a*-Co (12.4 A g^{-1} calculated at the same overpotential).

The activity of an electrocatalyst mainly depends on its active surface area and the intrinsic activity of each catalytic site. To investigate the origin of the improved catalytic activity for the sample with the optimum Co:Fe ratio, the electrochemical surface areas (ECSA) of the samples were determined by measuring their double layer capacitance (C_{dl}), which is proportional to the ECSA [61,62]. The C_{dl} values of the samples were obtained from their CV curves, which were recorded over the potential range not including the redox reaction at various scan rates (20, 40, 60, 80, and 100 mV s⁻¹) (Fig. S3). The C_{dl} values were calculated using the equation $C_{dl} = \frac{j_a - j_v}{2v} = \frac{Aj}{2v}$, where j_a and j_c are the anodic and cathodic current densities, respectively. As shown in Fig. 8d, the *a*-Co₂Fe sample showed the lowest C_{dl} value of 0.23 mF cm⁻² among all the samples. This indicates that the enhanced activity of the catalytic sites (not the active surface area) in *a*-Co₂Fe contributed to its excellent catalytic performance.

The ECSA values of the *a*-Co and *a*-Co₂Fe samples were calculated using the equation: ECSA = $A_{Geom} \times \frac{C_{dl}}{C_{dl-ref}}$, where C_{dl-ref} = 0.06 mF and A_{Geom} is the geometrical surface area of the electrode (0.0707 cm²) [61,62]. The ECSA values of the *a*-Co and *a*-Co₂Fe catalyst-loaded electrodes were 0.47 and 0.27 cm², respectively. Fig. 8e and f shows the LSV curves of the samples for the current densities normalized by their ECSA and BET surface areas. It can be observed that *a*-Co₂Fe showed much better electrocatalytic performance than *a*-Co irrespective of the current density. This confirms the conclusion that the *a*-Co₂Fe sample showed the best electrocatalytic activity among all the samples.

The results suggest that the bimetallic a-Co₂Fe sample showed a better catalytic activity than the monometallic sample, a-Co, mainly because of the enhanced activity of its catalytic sites. It is well-known that the surface of OER catalysts undergoes phase and composition changes during the OER operation because of the strong alkaline environment and high overpotentials used [30,63]. The catalyst surface then transforms into oxides/oxyhydroxides, which act as the actual catalytic active centers for the OER. The microstructure, defect states, and compositions of the oxides/oxyhydroxides formed *in situ* on the surface depend on the precursors used and induce different catalytic effects [63].

To examine the phase and microstructural changes of the catalysts during the OER operation, the *a*-Co₂Fe catalyst was recollected after the OER operation and was then subjected to XRD, SEM, TEM, and XPS analyses. After the OER operation, the catalyst did not show any XRD peak. This indicates that the catalyst was amorphous or weakly crystalline (Fig. 9a). The microstructure of the recollected catalyst was investigated by SEM and TEM (Fig. 9b–e). The microstructure of the recollected catalyst with thin sheet-like units was quite different from that of the original catalyst. This indicates the formation of active species during the OER process. The sheet-like units did not show any lattice fringes, suggesting the amorphous



Fig. 8. Electrochemical measurements of the as-prepared catalysts. a) LSV curves obtained at 5 mVs⁻¹ in a 1 M KOH solution; b) Tafel plots derived from the LSV curves over the current density range of 1–10 mA cm⁻²; c) Overpotentials (η_{10}) and Tafel slopes of all the investigated catalysts; d) Current density *vs.* scan rate plots; LSV curves using the current density normalized e) by ECSA and f) by BET surface area of *a*-Co and *a*-Co₂Fe.

Table 1

Comparison of the electrocatalytic performances of FeCo-based OER catalysts.

CoFe-based Materials	Electrolytes	Substrates	η (mV) for 10 mA cm^{-2}	Tafel slope (mV dec^{-1})	Refs.
Co _{0.5} Fe _{0.5} S _x /N-doped carbon	1 M KOH	GC	410	159	[52]
Fe-doped Co ₉ S ₈	1 M KOH	Ni Foam	270	70	[57]
$Co_{0.5}Fe_{0.5}Se_2$	1 M KOH	Carbon fiber	290	64	[58]
Co _{0.4} Fe _{0.28} P	1 M KOH	GC	270	25.6	[53]
Fe ₃ O ₄ /Co ₉ S ₈ /rGO	1 M KOH	GC	320	54.5	[54]
Co ₂ FeO _x /rGO	1 M KOH	GC	340	31	[59]
Reduced CoFe ₂ O ₄ nanosheets	1 M KOH	GC	320	48	[56]
$Co_2Fe(OH)_x$	1 M KOH	Ni foam	300	83	[55]
Co ₃ Fe(OH) _x /rGO	0.1 M KOH	GC	325	43	[60]
a-Co ₂ Fe	1 M KOH	GC	290	62	This work

nature of the recollected catalyst. This is consistent with the XRD results for the recollected catalyst. The Co 2p, Fe 2p, and O1s XPS spectra of the recollected catalyst are shown in Fig. 9f–g. The Co 2p spectrum showed bands at 780.5, 782.9, and 796.4eV corresponding to CoOOH [30]. In addition, two satellite peaks were observed at 786.6 and 803.0 eV. The Fe 2p spectrum showed peaks at 711.6 and

724.7 eV corresponding to Fe^{3+} species. The O1s spectrum showed peaks at 529.8 and 531.1 eV corresponding to M-O (lattice oxygen) and M-OH/(lattice –OH) species, respectively. These peaks showed a red-shift as compared to those of the original catalyst. This indicates that the chemical environment of oxygen changed after the OER operation. These results clearly show the phase change and



Fig. 9. Characterization of the *a*-Co₂Fe catalyst after the OER operation. a) XRD pattern, b) SEM image, c) TEM image and d-e) HRTEM images, f) Co 2p, g) Fe 2p, and h) O 1s XPS spectra.

oxidation of the catalyst during the OER.

The $CoFe(OOH)_x$ phase was formed in situ on the surface of the FeCo-based bimetallic electrocatalyst. This phase acted as the catalytic active phase. For bimetallic catalysts, there is no consensus so far about the catalytic centers [20,21]. In FeCo-based bimetallic catalysts, cobalt sites are the active centers for the OER. The presence of iron modulates the electronic structure of cobalt and enhances of activity of bimetallic catalysts. In contrast, some researchers believe that the iron species in FeCo-based bimetallic catalysts are the catalytic active species. The introduction of cobalt species improves the conductivity of the catalyst layer, thus improving the performance of the catalysts [64]. The OER reaction of FeCo-based bimetal catalysts follows a two-site mechanism, according to which both cobalt and iron sites are involved in the catalytic reaction. The μ -oxo bridged Co–Co or Co–Fe units are considered to be the active sites [21]. The OER predominantly occurs at µ-oxo bridged Co-Co sites below a certain overpotential. At higher overpotentials, µ-oxo bridged Fe-Co sites act as the active centers [20]. The Fe sites in FeCo-based bimetal catalysts not only activate the μ -oxo bridged M-O-M intermediates, but also introduce a reaction pathway with altered electrokinetic behavior. Thus, owing to the strong synergistic effect between the Co and Fe sites, the bimetallic catalyst, *a*-Co₂Fe, showed a better catalytic activity than the monometallic counterpart, *a*-Co. The catalysts with small amounts of iron showed a presence of some Co–O–Fe units. Although it can improve the catalyst performance, its number is small. Excess ion would induce the formation of Fe–O–Fe units, which cannot act as efficient active sites. Hence, the catalyst *a*-Co₂Fe with the optimum Co:Fe ratio shows the highest activity among the samples.

The excellent catalytic activity of the a-Co₂Fe sample can be attributed to its amorphous and porous structure, which provides a large number of exposed active sites for the OER. In addition, in the samples prepared in this study, the interior metallic products also increased the conductivity, and hence the catalytic activity of the samples.

The stability of the a-Co₂Fe catalyst was evaluated by obtaining its CV and *i*-*t* curves. Fig. 10a shows the LSV curves of the catalyst



Fig. 10. a) LSV curves of the *a*-Co₂Fe catalyst before and after 3000 CV cycles on a glass carbon electrode; b) Chronopotentiometry curve of the *a*-Co₂Fe catalyst tested on nickel foam at the overpotential for 10 mA cm⁻².

before and after 3000 continuous CV cycles. No significant difference was observed between the curves obtained before and after cycling. This indicates that the catalyst showed excellent catalytic stability. In order to evaluate the potential of this catalyst for water splitting applications, a piece of nickel foam coated with the *a*- Co_2Fe catalyst (mass loading of 0.4 mg cm⁻²) was tested using the *i*t method (Fig. 10b). The catalyst showed a current density of ~14 mA cm⁻² at the overpotential of 300 mV and retained the same current for at least 36 h. This indicates that the *a*-Co₂Fe catalyst showed excellent stability. The long-term stability of the *a*-Co₂Fe catalyst was also evaluated by obtaining its *i*-t curve on a glass carbon electrode (Fig. S4). The *i*-t curve was obtained at an overpotential of 290 mV, which could drive a current density of ~10 mA cm⁻². The current density remained constant during the OER operation. Because of the release of oxygen bubbles, some current fluctuations were observed in the i-t curves (Figs. 10b and S4).

These results demonstrate the excellent stability of the a-Co₂Fe catalyst towards the OER. Hence, the catalysts prepared in this study could be used for water splitting, CO₂/N₂ reduction, and in metal-air battery applications [65].

4. Conclusions

We developed a NaBH₄ based route for the preparation of FeCo alloy products. The obtained FeCo alloys showed an amorphous and porous structure. These alloys were used as earth-abundant electrocatalysts during the OER. The catalyst with the Co:Fe molar ratio of 2:1 showed a low overpotential of 290 mV at a current density of 10 mA cm⁻². The bimetallic catalysts showed better catalytic activity than the monometallic catalyst. The FeCo-based catalysts showed a two-site mechanism for the OER. This study provides a facile route for the preparation of cost-effective and high-efficiency FeCo-based bimetallic OER catalysts.

Declaration of competing interest

The authors declare no competing financial interest.

CRediT authorship contribution statement

Wenjuan Zhu: Formal analysis, Writing - original draft. Guoxing Zhu: Formal analysis, Writing - original draft. Chengli Yao: Formal analysis. Hu Chen: Formal analysis. Jing Hu: Formal analysis. Yi Zhu: Formal analysis. Wenfu Liang: Formal analysis, Investigation.

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Appendix A. Supplementary data

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