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Article

Iron-induced 3D nanoporous iron-cobalt oxyhydroxide on carbon cloth as a highly efficient electrode for oxygen evolution reaction

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ABSTRACT

The development of highly efficient and cost-effective electrode materials for catalyzing the oxygen evolution reaction (OER) is crucial for water splitting technology. The increase in the number of active sites by tuning the morphology and structure and the enhancement of the reactivity of active sites by the incorporation of other components are the two main strategies for the enhancement of their catalytic performance. In this study, by combining these two strategies, a unique three-dimensional nanoporous Fe-Co oxyhydroxide layer coated on the carbon cloth (3D-FeCoOOH/CC) was successfully synthesized by *in situ* electro-oxidation methods, and directly used as a working electrode. The electrode, 3D-FeCoOOH/CC, was obtained by the Fe doping process in (NH₄)₂Fe(SO₄)₂, followed by continuous *in situ* electro-oxidation in alkaline medium of “micro go chess piece” arrays on the carbon cloth (MCPAs/CC). Micro characterizations illustrated that the go pieces of MCPAs/CC were completely converted into a thin conformal coating on the carbon cloth fibers. The electrochemical test results showed that the as-synthesized 3D-FeCoOOH/CC exhibited enhanced activity for OER with a low overpotential of 259 mV, at a current density of 10 mA cm⁻², and a small Tafel slope of 34.9 mV dec⁻¹, as well as superior stability in 1.0 mol L⁻¹ KOH solution. The extensive analysis revealed that the improved electrochemical surface area, conductivity, Fe-Co bimetallic composition, and the unique 3D porous structure together contributed to the enhanced OER activity of 3D-FeCoOOH/CC. Furthermore, the synthetic strategy applied in this study could be extended to fabricate a series of Co-based electrode materials with the dopant of other transition elements.

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1. Introduction

The rapidly increasing demand for sustainable and rene-

ble clean energy sources has attracted considerable interest in promoting the development of energy storage and conversion technologies with low cost, high efficiency and environmental

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benignity [1,2]. Electrochemical water splitting, an efficient and environmentally friendly technology for producing hydrogen fuel and oxygen, is a promising pathway to convert electrical energy into chemical energy. However, the electrolytic efficiency is limited by the oxygen evolution reaction (OER) [3,4]. To date, IrO_2 and RuO_2 are known as the most active OER catalysts; however, some limitations exist such as high cost and relatively poor stability in alkaline medium. Therefore, it is desirable to explore inexpensive, highly efficient and stable OER catalysts based on earth-abundant elements [5–7].

Over the past decades, earth-abundant transition metal catalysts, particularly Co-based catalysts, including metal oxides [8,9], oxyhydroxides [10,11], nitrides [6,12], phosphides [13,14], sulfides [15], selenides [16] and perovskite solids [17], have been extensively synthesized and applied in water splitting. However, well-studied cobalt oxides or (oxy) hydroxides usually suffer from low conductivity and reactivity, in comparison to the corresponding multimetal electrocatalysts doped with other metal such as Fe and Ni [4,11], which results in large overpotentials required to reach the desired current density of 10 mA cm^{-2} during the OER process [5,13]. Therefore, significant efforts have been directed toward improving their catalytic performance [18,19]. Increasing the number and reactivity of active sites are the two main strategies for enhancing their catalytic performance. The first could be achieved by tuning the morphology and structure, such as nanosheet arrays [4,20], ultrathin characteristics [21,22] and porous structure [23–25], to enhance their OER performance. For example, a porous structure is one of the most important requirements because it facilitates the increase in specific surface area, buffering of volume change, and gas release [26,27]. Jiao *et al.* [9] synthesized ordered mesoporous cobalt oxide as a highly efficient oxygen evolution catalyst. The second is the incorporation of other components to optimize the electronic structure, thereby increasing the reactivity of the catalysts [5]. Over the last few years, it has been reported that the incorporation of Fe could significantly increase the performance of Co-based catalysts. Han *et al.* [19] synthesized nanosized porous Fe-CoOOH via etching the CoFeAl-LDH/G in an alkali solution to enhance the activity of Co-based catalysts. These nanosized Fe-CoOOH/G are ultrasensitive and highly effective for OER. Li *et al.* [23] prepared activating CoOOH porous nanosheet arrays by partial Fe substitution for efficient oxygen evolution reaction. Thus, the development of novel catalysts combining these two strategies for OER is of importance.

Herein, we have successfully synthesized 3D porous FeCo oxyhydroxide layer coated on the carbon cloth (3D-FeCoOOH/CC) as a highly efficient electrode with a facile and cost-effective electro-oxidation method. The Fe components and unique 3D porous structures were successfully introduced and created after Fe doping and *in situ* electro-oxidation process, which favored the exposure of more active sites, thereby accelerating the diffusion of electrolytes and electronic transfer, as well as effectively buffering the volume change for oxygen release. The electrochemical testing results showed that the as-synthesized 3D-FeCoOOH/CC exhibited a superior OER activity with a relatively low overpotential

of 259 mV at 10 mA cm^{-2} , with a small Tafel slope of 34.9 mV dec^{-1} , and excellent stability in 1.0 mol L^{-1} KOH solution, thereby outperforming commercial IrO_2 catalysts.

2. Experimental

2.1. Chemicals

Carbon cloth (CC) was purchased from Shanghai Hesen Electric Co., Ltd. Cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), hydrochloric acid (HCl), and ethanol were purchased from Aladdin Chemistry Co. Ammonium fluoride (NH_4F), urea, ammonium iron(II) sulfate ($(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$), and potassium hydroxide (KOH) were purchased from Sinopharm Chemical Reagent Co., Ltd. Nafion (5 wt.%) was purchased from Dupont Co. Iridium oxide (IrO_2) was purchased from Makclm Chemistry Co. All chemicals were used as received without any further purification. Distilled water was obtained through the Millipore system.

2.2. Synthesis

2.2.1. Synthesis of “micro go chess piece” arrays on carbon cloth (MCPAs/CC)

Typically, MCPAs/CC is prepared by a modified hydrothermal reaction [28]. A piece of CC ($2 \text{ cm} \times 4 \text{ cm}$) was sonicated in HCl, acetone and deionized water sequentially for 30 min to ensure that the surface of CC was clean. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2.5 mmol), NH_4F (2.5 mmol), and urea (12.5 mmol) were dissolved in a mixture of 40 mL ethylene glycol and 5 mL deionized water under vigorous stirring for 30 min to obtain a uniform solution. Subsequently, the uniform solution and a piece of clean CC were transferred into a 100 mL Teflon-lined stainless-steel autoclave and heated at 120°C for 6 h. After the autoclave naturally cooled down to room temperature, the MCPAs/CC was retrieved, washed with ethanol repeatedly, and dried at 60°C for 4 h.

2.2.2. Synthesis of 3D-FeCoOOH/CC

The 3D-FeCoOOH/CC was fabricated via two steps. First, the Fe doping process was carried out via the *in situ* electro-oxidation of MCPAs/CC in 0.01 mol L^{-1} $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ at a current density of 1.2 mA cm^{-2} for a specific time period. To obtain the optimum catalytic activity, the dopant process time was set at 15, 30 and 45 min. Subsequently, the precursors were cleaned repeatedly using distilled water to remove the excess Fe, followed by direct use as the working electrode in 1.0 mol L^{-1} KOH at an anodic current density of 10.0 mA cm^{-2} for 10 h to obtain 3D-FeCoOOH/CC. Unless specifically noted, the 3D-FeCoOOH/CC mentioned later in this article refers to the sample with an Fe doping time of 30 min.

2.2.3. Synthesis of 3D micro go chess piece like cobalt oxyhydroxide on carbon cloth (3D-CoOOH/CC)

For comparison, the 3D-CoOOH/CC was fabricated using the above-mentioned method with the absence of the Fe doping process.

2.2.4. Preparation of IrO₂ electrode

A suspension was prepared by dispersing IrO₂ powders (5 mg) in a mixture of 0.99 mL ethanol and 0.01 mL 5 wt.% Nafion solution. The mixed solution was sonicated for 20 min to obtain a homogeneous catalyst ink. The dispersion (0.2 mL) was transferred onto a piece of CC (1 cm × 2 cm) using a pipette. The mass loading was controlled at 1.0 mg cm⁻².

2.3. Material characterization

The catalyst loading was measured as 1.25 mg cm⁻² by the traditional gravimetric method. The morphology and structures were analyzed using field emission scanning electron microscopy (SEM; Hitachi S-4800F) and high-resolution transmission electron microscopy (HRTEM; FEI Tecnai G2F30). The powder X-ray diffraction (XRD) patterns were collected on a Bruker D8AVANCE X-ray powder diffraction spectrometer. Nitrogen adsorption-desorption isotherms were measured using a Micromeritics ASAP 2000 system. The valency of the different components of the catalysts was evaluated by X-ray photoelectron spectroscopy (XPS; VG-Multi-lab 2000).

2.4. Electrochemical measurements

All electrochemical measurements were carried out in a standard three-electrode system with a CHI 660E electrochemical analyzer (CH Instruments, Inc., Shanghai) using 1.0 mol L⁻¹ KOH as the electrolyte. The synthesized 3D-FeCoOOH/CC was used as the working electrode, a graphite plate as the counter electrode, and Hg/HgO electrode as the reference electrode. The potentials reported in this study were calibrated to the reversible hydrogen electrode (RHE), using the following equation:

$$E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.098 + 0.0591\text{pH} \quad (1)$$

The electrochemically active surface area (ECSA) was estimated from the electrochemical double-layer capacitance based on a published report [29]. The electrochemical capacitance (C_{dl}) was estimated by cyclic voltammograms measured in a non-Faradaic region from 1.18 V to 1.26 V at various scan rates of 5–25 mV s⁻¹. The ECSA was calculated according to Equation (2) below:

$$\text{ECSA} = C_{\text{dl}}/C_s \quad (2)$$

The general specific capacitance for the metal oxides or oxyhydroxides, $C_s = 0.040 \text{ mF cm}^{-2}$ in 1.0 mol L⁻¹ KOH was employed based on previous reports [29].

3. Results and discussion

3.1. Physical characterizations

The overall synthetic strategy for 3D-FeCoOOH/CC is illustrated in Fig. 1. First, MCPAs/CC was synthesized by a simple hydrothermal reaction and directly used as a working electrode. Second, Fe doping process was carried out via the *in situ* anodic oxidation of MCPAs/CC in 0.01 mol L⁻¹ (NH₄)₂Fe(SO₄)₂ for a fixed period of time, at 1.2 mA cm⁻². The electrode was *in situ* electro-oxidized in 1.0 mol L⁻¹ KOH solution at 10 mA cm⁻²

Fig. 1. Schematic of the synthesis of 3D-FeCoOOH/CC.

for 10 h continuously, to afford 3D-FeCoOOH/CC. To obtain the optimum catalytic activity, the Fe doping process was fixed at different periods and the corresponding catalytic activity is shown in Fig. S1. It is evident that the 3D-FeCoOOH/CC with an Fe doping time 30 min in (NH₄)₂Fe(SO₄)₂ possesses the best OER catalytic activity. As 3D-FeCoOOH/CC exhibited the best activity, in-depth characterizations were performed on it.

The morphologies of MCPAs/CC and 3D-FeCoOOH/CC were investigated using SEM. Fig. 2a shows the low-magnification SEM image of MCPAs/CC. It is clearly observed that numerous micro go pieces (~ 1.3 μm) are coated on the carbon fiber. The high-magnification SEM images in Figs. 2b and 2c show that every micro go piece is composed of a large number of uniformly intertwined nanorods. The corresponding energy-dispersive X-ray spectroscopy (EDS) spectrum in Fig. S2 demonstrates that it contains C, O, F and Co. For 3D-FeCoOOH/CC, the low- and high-magnification SEM images in Figs. 2d and 2e show that the carbon fiber is coated with a uniform layer, which comprises of numerous small nanoparticles (~ 10 nm). The corresponding EDS spectrum in Fig. S3 shows the presence of C, O, Fe and Co elements (Fe:Co molar ratio of 0.034:1), indicating the dopant of Fe element and the complete removal of F. Besides, the SEM images and the corresponding EDS spectra of 3D-FeCoOOH/CC with the Fe dopant times of 15 and 45 min are shown in Figs. S4–S7. The SEM results demonstrate that 3D-FeCoOOH/CC has a unique 3D porous structure, and that the doped Fe atoms play a key role in

Fig. 2. SEM images of MCPAs/CC (a–c), 3D-FeCoOOH/CC (d–f), and 3D-CoOOH/CC (g–i) at various magnifications.

tailoring and converting MCPAs/CC into 3D-FeCoOOH/CC [19]. Electrochemical tests indicate that the 3D-FeCoOOH/CC obtained with an Fe doping time of 30 min exhibits the best catalytic activity, indicating a suitable Fe:Co ratio for OER. For comparison, 3D-CoOOH/CC was synthesized exclusively by the electro-oxidation in 1.0 mol L⁻¹ KOH without the Fe doping process. The low-magnification SEM image in Fig. 2g shows that 3D-CoOOH/CC still exhibits a micro go piece morphology without obvious changes, whereas the high-magnification SEM images in Figs. 2h and 2i demonstrate that the nanorods are completely transformed into small nanoparticles (~ 10 nm), similar to the morphology of 3D-FeCoOOH/CC.

The nanostructure of the 3D-FeCoOOH layer scraped from carbon fiber was investigated by transmission electron microscopy (TEM). As shown in Fig. 3a, the 3D-FeCoOOH layer has a porous structure. HRTEM and selected area electron diffraction (SAED) analyses were performed to further study the morphology and crystallographic properties. The HRTEM image in Fig. 3b and the inset corresponding to the SAED pattern both indicate that 3D-FeCoOOH/CC exhibits a polycrystalline structure. The first, third and fourth diffraction rings close to the central diffraction spot in the SAED pattern correspond to the crystallographic planes of CoOOH (110), CoOOH (021) and CoOOH (140), respectively. Meanwhile, the second diffraction ring corresponds to the crystallographic plane of FeOOH (310), suggesting that FeOOH and a main CoOOH phase exist. High angle annular dark field scanning TEM (HAADF-STEM) images and the corresponding elemental mappings shown in Figs. 3c–f indicate that Co (red), O (blue) and Fe (yellow) are distributed uniformly. The formation of a porous structure was further defined using Brunauer-Emmett-Teller (BET) gas sorptometry measurements, and the corresponding results are shown in Fig. S8. The shapes of the hysteresis loops of 3D-CoOOH/CC and 3D-FeCoOOH/CC were both identified as type H3 according to the International Union of Pure and Applied Chemistry (IUPAC) classification [4], indicating the formation of porous structures.

Fig. 3. (a) TEM image and (b) HRTEM image of 3D-FeCoOOH layer (inset: SAED pattern of 3D-FeCoOOH/CC); (c) Overlay of the HAADF-STEM image and elemental mappings; (d–f) elemental mappings of Co, O, and Fe of the 3D-FeCoOOH layer, respectively.

This result was consistent with the SEM data. Additionally, according to the BET analysis, the total specific surface areas of MCPAs/CC and 3D-CoOOH/CC are 23.59 m² g⁻¹ and 25.80 m² g⁻¹, respectively. When Fe was introduced into 3D-CoOOH/CC, the specific surface area of 3D-FeCoOOH/CC further increased to 27.24 m² g⁻¹, which was facilitated the exposure of more active sites.

The XRD patterns of the as-synthesized electrodes and CC are shown in Fig. S9. Fig. S9a shows two obvious diffraction peaks for 3D-FeCoOOH/CC at 26.4° and 54.5°, which could be attributed to the (002) and (004) planes of CC. From the magnification in Fig. S9b, notably, no obvious diffraction peak for 3D-FeCoOOH/CC was observed. Fourier transform infrared spectroscopy (FT-IR) analysis was further performed to explore the chemical composition of 3D-FeCoOOH/CC. It can be concluded from Fig. S10 that MCPAs/CC is most likely composed of fluorinated ethylene glycol alkoxide, and that the obtained products after the two-step electrochemical oxidation process are mainly metal oxyhydroxides [35].

High-resolution XPS was carried out to determine the valency of different components. The XPS survey of MCPAs/CC presented in Fig. S11 shows the presence of C, O, F and Co elements, while 3D-FeCoOOH/CC shows the presence of C, O, Fe and Co elements. The Co 2p high-resolution XPS spectrum of MCPAs/CC is shown in Fig. S12. The binding energies of Co 2p_{1/2} and Co 2p_{3/2} are located at 807.8 and 791.9 eV, respectively, revealing the Co²⁺ oxidation state. Fig. 4a shows the comparison of the Co 2p high-resolution XPS spectra for 3D-CoOOH/CC and 3D-FeCoOOH/CC. For 3D-CoOOH/CC, the two peaks with binding energies of 780.5 and 795.7 eV correspond to the typical Co 2p_{3/2} and Co 2p_{1/2} orbitals, while for 3D-FeCoOOH/CC, these could be attributed to 780.9 and 796.1 eV. This result indicates that Co is present in the trivalent oxidation state [19,32]. As expected, the high-resolution Co 2p spectra of 3D-FeCoOOH/CC exhibits a 0.4 eV shift to a higher binding energy compared with the trend exhibited for 3D-CoOOH/CC, indicating a modulated electronic structure of the Co atoms and a strong electronic interaction between Co and Fe atoms [19]. Moreover, the enhanced Co satellite peak of 3D-FeCoOOH/CC at ~ 785 eV indicates the rearrangements of Co 3d electron population owing to the degeneracy breaking of Co ions, which is consistent with the reports in the literature [36]. Additionally, the rearrangements of the Co 3d electron population caused an increase in the electron density of the Co atoms, which facilitated the enhancement of catalytic activity [23,37]. Fig. 4b shows the high-resolution XPS spectrum for Fe 2p of 3D-FeCoOOH/CC. The spectrum displays two major peaks at binding energies of 725.0 eV and 712.5 eV, revealing the characteristics of Fe³⁺ [19,31]. Furthermore, it has been reported that the adsorption energy of OH is considerably strong for FeOOH, whereas it is too weak on CoOOH [5]. The incorporation of Fe could modulate the adsorption energy of OH on the catalysts. As shown in Fig. S13, the high-resolution O 1s spectrum can be clearly defined into four characteristic peaks of oxygen atoms (O1–O4) at binding energies of 530.2, 531.5, 532.2 and 533.0 eV, corresponding to a typical O from O²⁻ (O1), O from the OH⁻ (O2), hydroxyl groups or surface-adsorbed

Fig. 4. (a) Co 2p high-resolution XPS spectra of 3D-CoOOH/CC and 3D-FeCoOOH/CC; (b) Fe 2p high-resolution XPS spectrum of 3D-FeCoOOH/CC.

oxygen (O3) and surface-adsorbed water molecules (O4), respectively [18,33,34]. Based on the analyses of FT-IR and XPS results, it can be concluded that the formed product should be Fe-Co oxyhydroxide.

3.2. Evaluation of the OER electrocatalytic activity

The electrochemical properties of the as-synthesized catalysts were evaluated in a standard three-electrode system using 1.0 mol L⁻¹ KOH as the electrolyte. According to the linear sweep voltammetry (LSV) curves in Fig. 5a, 3D-FeCoOOH/CC exhibits the best catalytic activity for OER. The obtained 3D-FeCoOOH/CC shows an onset potential (1.4 V) smaller than those of 3D-CoOOH/CC and IrO₂. The potential required to reach a current density of 10 mA cm⁻² and the current density at an overpotential of 300 mV has been widely investigated to evaluate the catalytic activity for OER [38,39]. It can be seen from Fig. 5b (black columns) that to drive the current density of 10 mA cm⁻², 3D-FeCoOOH/CC requires a minimum overpotential of 259 mV. As illustrated in Fig. 5b (red columns), 3D-FeCoOOH/C exhibits a current density of 137 mA cm⁻², which is much larger than those of 3D-CoOOH and IrO₂. It can be concluded that 3D-FeCoOOH/C exhibits an outstanding OER performance in comparison to the performance for others. Additionally, 3D-FeCoOOH/CC exhibits the highest mass electrocatalytic activity for OER (Fig. S14).

The OER reaction kinetics of FeCoOOH/CC was investigated by the Tafel slope according to the Tafel equation ($\eta = \log j + a$, where a , b , and j are a constant, the Tafel slope, and the current density, respectively) [25,29]. As shown in Fig. 5c, the Tafel slope of 3D-FeCoOOH/CC is only approximately 34.9 mV dec⁻¹, which is lower than those of 3D-CoOOH/CC (59.2 mV dec⁻¹) and IrO₂ (80.0 mV dec⁻¹), indicating the most favorable OER kinetics [39]. To compare the catalytic activity of 3D-FeCoOOH/CC with those for the reported Co-based electrocatalysts and other state-of-the-art electrocatalysts, the overpotential at 10 mA cm⁻² and the corresponding Tafel slope are listed in Table S3. It is clearly observed that the as-synthesized 3D-FeCoOOH/CC exhibits superior catalytic activity compared to those of the reported electrocatalysts.

In addition to the catalytic activity, stability is of importance as it is required for commercial applications [2]. The multi-current step chronopotentiometric curve of 3D-FeCoOOH/CC in Fig. 5d shows that the potential rapidly stabilizes at 1.53 V

and remains steady for 20 min. An analogous response is observed through the consequent chronopotentiometric processes, which reflects the superior mass transportation property of the 3D-FeCoOOH/CC electrode [20,40]. The long-term stability was further evaluated by chronopotentiometric method at 20 mA cm⁻², and the corresponding curves are shown in Fig. 5e. It is determined that the overpotential of 3D-FeCoOOH/CC shows almost no change after 100 h of testing, while IrO₂ shows noticeable degradations only after 20 h of testing, indicating the superior stability of 3D-FeCoOOH/CC compared to that of IrO₂. After 100 h of testing, the SEM images in Fig. S15 show that the 3D-FeCoOOH/CC retains its porous structure without noticeable changes. This indicates that 3D-FeCoOOH/CC is structurally robust and highly stable, which is favorable for practical application.

To investigate the reasons for the high catalytic activity of 3D-FeCoOOH/CC, the electrochemically active surface area (ECSA) was measured by the double-layer capacitance (C_{dl}) method in 1.0 mol L⁻¹ KOH solution in no-Faradaic current potential range (1.18–1.26 V) [21]. As shown in Figs. S16a and S16b, the current density of 3D-FeCoOOH/CC at 1.22 V is nearly five times that of 3D-CoOOH/CC. The different assembly of these nanoparticles could be the key to this enhancement. They are a part of a thin conformal coating in 3D-CoOOH/CC in contrast to the micro go shape in 3D-CoOOH/CC, where the center of the go pieces might be not accessible. The C_{dl} values of 3D-FeCoOOH/CC and 3D-CoOOH/CC shown in Fig. S16c are 88.5 and 16.3 mF cm⁻², and the corresponding ECSA values are 2212.5 and 407.5 cm², respectively, indicating more exposed active sites. The higher ECSA of 3D-FeCoOOH/CC further confirms the compositional and structural advantages in terms of the exposure of catalytic active sites [41].

The electrochemical impedance spectroscopy (EIS) and the corresponding circuit model fitting analysis were further performed (Fig. S16d) at an overpotential of 300 mV. The equivalent circuit of EIS is comprised of a solution resistance (R_s), charge-transfer resistance (R_{ct}), and constant phase element (CPE) [23]. The R_{ct} of 3D-FeCoOOH/CC is 0.797 Ω , which is lower than that of 3D-CoOOH/CC (5.636 Ω), indicating a faster electron transfer in 3D-FeCoOOH/CC. The high conductivity of 3D-FeCoOOH/CC plays a key role in enhancing its OER performance, particularly at low overpotentials [11].

The above experimental results demonstrate that 3D-FeCoOOH/CC exhibits excellent electrocatalytic perfor-

Fig. 5. (a) LSV curves and (c) Tafel plots of 3D-FeCoOOH/CC, 3D-CoOOH/CC, and IrO₂ with IR-correction; (b) Comparison of the overpotentials at a current density of 10 mA cm⁻² and the current density at an overpotential of 300 mV for 3D-FeCoOOH/CC, 3D-CoOOH/CC, and IrO₂, respectively; (d) Chronopotentiometric responses for 3D-FeCoOOH/CC at various current densities (20–200 mA cm⁻² with an increment of 20 mA cm⁻²); (e) Chronopotentiometry curves of 3D-FeCoOOH/CC and IrO₂ at a constant current density of 20 mA cm⁻².

mances for OER. This could be attributed to the following features. First, the increased ECSA, conductivity and mass transportation caused by the incorporation of Fe led to its enhanced OER performance. Second, the strong interaction between Co and doped Fe modulated the electron density and the adsorption energies of OH on the catalysts, leading to the enhanced OER performance. Third, the unique 3D porous structure of 3D-FeCoOOH/CC possessed large surface area and it favored the exposure of more active sites, increase in the contact area of electrolyte and catalyst, and release of generated oxygen. Fourth, the unique 3D porous structure was highly robust and stable, leading to a good long-term stability. Owing to these unique features, the as-synthesized 3D-FeCoOOH/CC electrode exhibited superior electrocatalytic performances for OER.

4. Conclusions

In summary, we have successfully developed an efficient strategy for the assembly of 3D-FeCoOOH/CC. The 3D-FeCoOOH/CC possessed a low overpotential of 259 mV at 10 mA cm⁻² and small Tafel slope of 34.9 mV dec⁻¹ for OER, thereby outperforming Ir- and Ru-based catalysts. The as-synthesized 3D-FeCoOOH/CC also exhibited excellent stabil-

ities after continuous electrolysis in alkaline electrolyte for more than 100 h with negligible activity decay. The 3D-FeCoOOH/CC with excellent OER catalytic activity has excellent potential for application in water splitting. Furthermore, the synthetic strategy is also of significance for the fabrication of a series of Co-based electrode materials with the dopant of other earth-abundant transition elements.

Acknowledgments

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Iron-induced 3D nanoporous iron-cobalt oxyhydroxide on carbon cloth as a highly efficient electrode for oxygen evolution reaction

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“Micro go chess piece” arrays on carbon cloth (MCPAs/CC) were transformed into a three-dimensional nanoporous iron-cobalt oxyhydroxide conformal coating on carbon cloth (3D-FeCoOOH/CC) via electrochemical oxidation. Superior OER performance was exhibited by 3D-FeCoOOH/CC, thereby outperforming IrO₂.

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铁诱导生长在碳布上三维纳米多孔铁钴羟基氧化物作为高效电催化析氧反应电极

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摘要: 开发高效、廉价的电极材料应用于电催化析氧反应(OER)在水分解技术中起着至关重要的作用. 提高催化剂催化活性的策略主要有两种, 一是通过调整催化剂形貌和结构来增加催化活性位点数量, 二是通过掺入其它组分来增强催化活性位点的反应活性. 本工作结合这两种策略, 通过原位电氧化方法成功合成了生长在碳布上具有独特三维结构的纳米多孔铁钴羟基氧化物(3D-FeCoOOH/CC), 合成的电极材料直接用作电催化析氧反应的工作电极. 以生长在碳布上的“微型棋子”阵列(MCPAs/CC)作为前驱体, 先后通过在 $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ 溶液中进行Fe掺杂工艺和在碱性介质中原位电化学氧化制备了3D-FeCoOOH/CC. 微观表征表明, MCPAs/CC上的“微型棋子”阵列完全转化为一层薄形涂层包覆在碳布纤维上. 电化学测试结果表明, 合成的3D-FeCoOOH/CC在 1.0 mol L^{-1} KOH溶液中表现出优异的OER催化活性, 在电流密度为 10 mA cm^{-2} 时所需的过电势仅为259 mV, 塔菲尔斜率为 34.9 mV dec^{-1} , 并且具有优异的稳定性. 详细的表征表明, 电化学表面积的增加、电导率的增高、FeCo双金属组成和独特的3D多孔结构共同使得3D-FeCoOOH/CC的催化OER活性增强. 此外, 本实验所应用的合成策略可以扩展到制备一系列其他过渡元素掺杂的Co基电极材料.

利用选区电子衍射、红外光谱和XPS等技术证明了双金属羟基氧化物的合成. 从扫描电子显微镜图和透射电子显微镜图可以看出, 本实验所合成的3D-FeCoOOH/CC具有多孔结构, 相应的元素分布图表明Fe和Co元素在催化剂中均匀分布. N_2 吸脱附测试进一步证明了多孔结构的生成. XPS测试结果表明, 前驱体中Co元素为+2价, 3D-CoOOH/CC中的Co元素为+3价, Co 2p电子结合能分别为780.5和795.7 eV, 当将Fe引入其中时, 3D-FeCoOOH/CC中的Co元素也为+3价, 但Co 2p电子结合能变为780.9和796.1 eV. 相比于3D-CoOOH/CC, 3D-FeCoOOH/CC中Co元素的电子结合能增加了0.4 eV, 这表明Fe的引入调节了Co原子的电子结构, 并且Fe原子和Co原子之间存在强烈的相互作用. 3D-FeCoOOH/CC在 $\sim 785 \text{ eV}$ 处增强的Co的伴随峰表明Co原子的简并轨道被破坏引起Co 3d电子群重排, 而Co 3d电子群的重排导致Co原子电子密度增加, 有利于催化活性的增强. 此外Fe元素的加入可以调节OH在催化剂上的吸附, 从而增强催化活性.

3D-FeCoOOH/CC表现出优异的电催化析氧性能, 可以归因于以下几方面: 首先, Fe元素掺入提高电极材料的电化学活性面积(ECSA)、电导率和质量传递; 其次, Co与掺杂Fe之间的强烈相互作用调节了电子密度和OH在催化剂表面吸附; 第三, 3D-FeCoOOH/CC独特的3D多孔结构具有较大的表面积, 有利于催化活性位点的暴露、电解质与催化剂的接触和产生氧气的释放; 第四, 独特的3D多孔电极材料具有良好的结构稳定性, 从而使3D-FeCoOOH/CC具有更好的稳定性. 得益于上述优势, 本实验所合成的3D-FeCoOOH/CC电极表现出优异的电催化析氧性能.

关键词: 3D纳米多孔铁钴羟基氧化物; 微型棋子阵列; 电极材料; 电氧化; 氧析出反应

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