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Article

Direct growth of holey Fe₃O₄-coupled Ni(OH)₂ sheets on nickel foam for the oxygen evolution reaction

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ABSTRACT

The oxygen evolution reaction (OER) is a half-reaction of water electrolysis, and the OER performance of an electrocatalyst is significantly related to its energy conversion efficiency. Due to their high OER activity, transition metal-based nanomaterials have become potential low-cost substitutes for Ir/Ru-based OER electrocatalysts in an alkaline environment. Herein, holey Fe₃O₄-coupled Ni(OH)₂ sheets (Ni(OH)₂-Fe H-STs) were easily achieved by a simple mixed-cyanogel hydrolysis strategy. The two-dimensional (2D) Ni(OH)₂-Fe H-STs with ca. 1 nm thickness have a high specific surface area, abundant unsaturated coordination atoms, and numerous pores, which are highly favorable for electrocatalytic reactions. Meanwhile, the introduction of Fe improves the conductivity and regulates the electronic structure of Ni. Due to their special structural features and synergistic effect between the Fe and Ni atoms, Ni(OH)₂-Fe H-STs with an optimal Ni/Fe ratio show excellent OER activity in a 1 M KOH solution, which significantly exceeds that of the commercial RuO₂ nanoparticle electrocatalyst. Furthermore, Ni(OH)₂-Fe H-STs can be grown on nickel foam (NF), and the resulting material exhibits enhanced OER activity, such as a small overpotential of 200 mV and a small Tafel slope of 56 mV dec⁻¹, than that of Ni(OH)₂-Fe H-STs without NF.

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1. Introduction

Recently, oxygen evolution reaction (OER)-based electrochemical energy conversion systems (such as electrochemical hydrogen production, nitrogen electroreduction, and carbon dioxide electroreduction systems and metal-air batteries) are attracting increasing attention [1–6]. Thus, the achievement of anode catalysts with a high OER performance will undoubtedly elevate the energy conversion efficiency of these systems. Alt-

hough Ru-, Rh-, and Ir-based nanomaterials are highly active and durable OER catalysts [7–11], their low earth-abundance and prohibitively high cost may limit their industrial application. Recently, various transition metal (Mn, Ni, Co, Fe, and Cu)-based nanomaterials (sulfides, hydroxides, oxides, phosphides, and nitrides) have been regarded as highly promising precious metal-alternative OER catalysts in an alkaline environment [12–26]. Among them, Ni(OH)₂-based OER electrocatalysts have attracted wide attention because of their high activ-

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ity and low cost [27–40].

The electroactivity of $\text{Ni}(\text{OH})_2$ -based nanomaterials is significantly related to their morphology and chemical composition due to the area, structural, electronic, and synergistic effects. For instance, Wang et al. [33] synthesized ultrathin $\text{Ni}(\text{OH})_2$ sheets with 1.4 nm thickness, which revealed a higher OER mass activity than thicker $\text{Ni}(\text{OH})_2$ sheets because of their considerable surface area and abundant exposed active atoms on their surface [33]. Bott-Neto et al. [41] synthesized ultra-small spherical $\text{Ni}(\text{OH})_2$ nanoparticles with a size of only 2.4 nm, which revealed excellent electroactivity for the oxidation of methanol, ethanol, and glycerol due to the area effect. Du et al. [40] synthesized CeO_2 nanoparticle-decorated $\text{Ni}(\text{OH})_2$ sheets, which had a higher OER activity than the $\text{Ni}(\text{OH})_2$ sheets. The synergistic effect between the CeO_2 nanoparticles and the $\text{Ni}(\text{OH})_2$ sheets increased the charge transfer rate and the amount of $\text{Ni}^{\text{III/IV}}$ active species in the $\text{Ni}(\text{OH})_2$ sheets, which were responsible for the high OER activity [40]. Huang et al. [42] directly grew $\text{Ni}(\text{OH})_2$ sheets on porous nickel, which displayed a high sensitivity and fast response for glucose sensing. The porous nickel substrate provided a large surface area for the loading of $\text{Ni}(\text{OH})_2$ sheets and accelerated molecular transport. Consequently, this structural effect contributed to the high activity of this material for glucose oxidation [42]. Peng et al. [43] achieved holey $\text{Ni}(\text{OH})_2$ sheets by a sol-gel method, which exhibited a higher activity than pristine $\text{Ni}(\text{OH})_2$ sheets for the OER. The introduction of nanopores not only accelerated mass transport, but also increased the amount of edge-active atoms, which were obviously advantageous for activity enhancement [43].

According to the abovementioned examples, 2D ultrathin sheets have unique structural characteristics, which can provide a high surface area and substantial surface atoms with a low-coordination number for electrocatalytic reactions. The introduction of heteroatoms may tune the electronic and geometrical structures of nanomaterials, which generally enhances their electroactivity. Moreover, three-dimensional (3D) nickel foam (NF) can prevent the aggregation of the loaded nanomaterials and improve the mass transfer of reactants/products. Inspired by the expected results, herein, we directly synthesized holey Fe_3O_4 -coupled $\text{Ni}(\text{OH})_2$ sheets (denoted as $\text{Ni}(\text{OH})_2$ -Fe H-STs) on the NF substrate (denoted as $\text{Ni}(\text{OH})_2$ -Fe H-STs/NF). Because of large surface area, enough active atoms, synergistic effect between the Fe and Ni atoms, high conductivity, and 3D porous feature of NF, $\text{Ni}(\text{OH})_2$ -Fe H-STs/NF shows an excellent OER performance, including a small overpotential of 200 mV at 10 mA cm^{-2} current density, a small Tafel slope of 56 mV dec^{-1} , and outstanding stability, in KOH solution.

2. Experimental

2.1. Chemicals and reagents

Nickel(II) chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\geq 98.0\%$), iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\geq 98.0\%$), and sodium borohydride (NaBH_4 , 98%) were provided by Sinopharm Chemical Reagent Co., Ltd. Potassium cyanonickelate(II)

($[\text{K}_2\text{Ni}(\text{CN})_4] \cdot x\text{H}_2\text{O}$, 98%) was obtained from Macklin Biochemical Co., Ltd. Potassium hydroxide (KOH, $\geq 95\%$) was purchased from Alfa Aesar.

2.2. Synthesis of $\text{Ni}(\text{OH})_2$ -Fe H-STs

$\text{Ni}(\text{OH})_2$ -Fe H-STs with different Ni/Fe ratios can be easily achieved by a simple mixed-cyanogel hydrolysis strategy. Herein, we chose $\text{Ni}(\text{OH})_2$ -Fe H-STs with a Ni/Fe ratio of 3:1 (denoted as $\text{Ni}(\text{OH})_2$ -Fe H-STs-Ni3Fe1) as a typical example. Typically, the NiCl_2 - $\text{K}_2\text{Ni}(\text{CN})_4$ / FeCl_3 - $\text{K}_2\text{Ni}(\text{CN})_4$ mixed cyanogel was obtained within 15 min by adding 0.374 mmol FeCl_3 , 0.624 mmol NiCl_2 , and 0.5 mmol $\text{K}_2\text{Ni}(\text{CN})_4$ to 4 mL water (Fig. S1). Then, $\text{Ni}(\text{OH})_2$ -Fe H-STs-Ni3Fe1 was obtained by adding 50 mL of 3.5 M NaBH_4 solution to the NiCl_2 - $\text{K}_2\text{Ni}(\text{CN})_4$ / FeCl_3 - $\text{K}_2\text{Ni}(\text{CN})_4$ mixed cyanogel and heating the mixture for 7 h at 70 °C in a water bath. The products were centrifuged and obtained after the reaction followed by drying at 40 °C overnight.

For comparison, other $\text{Ni}(\text{OH})_2$ -Fe H-STs with different Ni/Fe atomic ratios were prepared by adjusting the amount of nickel chloride and iron chloride, which were denoted as $\text{Ni}(\text{OH})_2$ H-STs, $\text{Ni}(\text{OH})_2$ -Fe H-STs-Ni5Fe1, $\text{Ni}(\text{OH})_2$ -Fe H-STs-Ni1Fe1, and $\text{Ni}(\text{OH})_2$ -Fe H-STs-Ni0.5Fe1.

2.3. Synthesis of $\text{Ni}(\text{OH})_2$ -Fe H-STs-Ni3Fe1 on NF ($\text{Ni}(\text{OH})_2$ -Fe H-STs-Ni3Fe1/NF)

The same cyanogel hydrolysis strategy can be applied to directly grow $\text{Ni}(\text{OH})_2$ -Fe H-STs-Ni3Fe1 on NF. Neat NF was immersed in 4 mL NiCl_2 - $\text{K}_2\text{Ni}(\text{CN})_4$ / FeCl_3 - $\text{K}_2\text{Ni}(\text{CN})_4$ mixed cyanogel. After heating this mixture in a water bath at 70 °C for 7 h as abovementioned in Section 2.1, $\text{Ni}(\text{OH})_2$ -Fe H-STs-Ni3Fe1/NF was obtained.

2.4. Physical characterization

Energy-dispersive X-ray spectroscopy (EDX), selected area electron diffraction (SAED), and transmission electron microscopy (TEM) were conducted at a voltage of 200 kV using TECNAI G2 F20. Scanning electron microscopy (SEM) was conducted at 15 kV using SU8220. N_2 isotherm adsorption/desorption (N_2 -IAD) was implemented using the ASAP 2020 micropore physisorption analyzer at 77 K. Powder X-ray diffraction (XRD) was carried out using Bruker D8 Advance. X-ray photoelectron spectroscopy (XPS) was conducted using AXIS ULTRA of Kratos Analytical Ltd., and all binding energies were corrected by the C 1s peak at 284.6 eV. Atomic force microscopy (AFM) was conducted using Bruker Dimension ICON in tapping mode.

2.5. Electrochemical measurements

A typical three-electrode system comprising a saturated calomel electrode (reference electrode), carbon rod (counter electrode), and modified glassy carbon electrode or modified NF (working electrode) was used to perform electrochemical

impedance spectroscopy (EIS), linear sweep voltammetry (LSV), cyclic voltammetry, and chronopotentiometry using the CHI-660 instrument at 30 °C. Herein, all potentials were normalized to the reversible hydrogen electrode. LSV curves were manually calibrated to compensate the iR drop of the solution.

By referring to previous studies, we prepared a catalyst-modified working electrode [44]. Under strong ultrasonic vibration conditions, 10 mg electrocatalyst was dispersed in 4 mL water and 1 mL isopropanol to form a uniform solution. Then, 4 μ L ink was placed on the electrode surface, and 4 μ L 0.5 wt% Nafion was placed on the surface of the electrocatalyst-modified working electrode followed by drying at 50 °C. The effective loading of the electrocatalyst was ~ 0.114 mg cm^{-2} .

Ni(OH)₂-Fe H-STs/NF with a loading of 0.8 mg cm^{-2} was directly used as a working electrode. The RuO₂ nanoparticle (Aladdin Industrial Corporation) ink solution was prepared by strong ultrasonication to disperse 10 mg RuO₂ in a mixed solution containing 4 mL water, 50 μ L 5 wt% Nafion, and 1 mL isopropyl alcohol. Then, 400 μ L ink solution was placed on the NF surface and dried at 50 °C.

3. Results and discussion

3.1. Characterization of Ni(OH)₂-Fe H-STs

The chemical composition of Ni(OH)₂-Fe H-STs-Ni₃Fe₁ was investigated by EDX (Fig. 1(A)). The EDX data reveals that Ni(OH)₂-Fe H-STs-Ni₃Fe₁ is composed of three elements: Ni, Fe, and O. The strong O signal suggests that the products may be oxides or hydroxides of nickel and iron. Moreover, the atomic ratio of Ni/Fe is ca 3:1, close to the feed ratio. The crystallographic texture of the products was characterized by XRD (Fig. 1(B)). The diffraction peaks of Ni(OH)₂-Fe H-STs-Ni₃Fe₁ correspond to the characteristic diffraction peaks of Fe₃O₄ (JCPDS 28-0491) and Ni(OH)₂ (JCPDS 22-0444). The surface

components and valence states of Ni(OH)₂-Fe H-STs-Ni₃Fe₁ were analysed by XPS. The Fe 2p XPS spectrum shows the 2p_{3/2} and 2p_{1/2} doublet peaks and relevant weak satellite peaks (Fig. 1(C)). The Fe 2p_{1/2} and Fe 2p_{3/2} peaks at 723.9 and 710.1 eV are attributed to the Fe^{II} species. The Fe 2p_{3/2} and Fe 2p_{1/2} peaks at 725.1 and 712.1 eV correspond to the Fe^{III} species. The Ni 2p XPS spectrum shows the presence of Ni^{II} species, which is represented by a doublet at 852.9 and 870.5 eV and two satellite peaks at 859.3 and 876.9 eV (Fig. 1(D)). Compared with the case of the Ni 2p XPS spectrum of Ni(OH)₂ H-STs without Fe, the binding energy of the Ni 2p peak for Ni(OH)₂-Fe H-STs-Ni₃Fe₁ negatively shifts by ca. 0.3 eV (Fig. S2), indicating partial electron transfer from Fe to Ni.

The SEM image shows that Ni(OH)₂-Fe H-STs-Ni₃Fe₁ has a flower-like morphology (Fig. 2(A)). The magnified SEM image displays that the nanoflowers are composed of numerous sheets (Fig. 2(B)). The lamellar structure of Ni(OH)₂-Fe H-STs-Ni₃Fe₁ was further confirmed by TEM (Fig. 2(C)). The TEM image clearly shows a lamellar structure with folds. The inset image in Fig. 2(C) shows some black thin lines that can indicate the thickness of the lamellae [45], showing an ultra-thin lamellar structure of ca. 1 nm. AFM characterization further showed that the ultra-thin thickness of the lamellar structure is ca. 1 nm (Fig. 2(D)), similar to the TEM observation. The scanning TEM-EDX (STEM-EDX) mapping images display the presence of Fe, Ni, and O, and their distributions are similar, which further suggest that the products are composed of nickel-iron oxides or hydroxides (Fig. 2(E)). Herein, 2D Ni(OH)₂-Fe sheets can be easily generated from the lamellate skeletons of cyanogel precursor [46–50]. Specifically, the generated Ni and Fe atoms preferentially grow in the direction of the lamellate skeleton of cyanogel precursor, which leads to the formation of sheets. Meanwhile, the Ni²⁺ and Fe³⁺ precursors are uniformly mixed at the atomic level during the generation of

Fig. 1. EDX data (A), XRD patterns (B), and Fe 2p (C) and Ni 2p (D) spectra of Ni(OH)₂-Fe H-STs-Ni₃Fe₁.

Fig. 2. SEM (A), magnified SEM (B), TEM (C), AFM (D), and STEM-EDX (E) mapping images of Ni(OH)₂-Fe H-STs-Ni₃Fe₁.

Fig. 3. HR-TEM image (A), N₂ IAD curve (B), partially magnified HR-TEM image (C), and SAED pattern (D) of Ni(OH)₂-Fe H-STs-Ni3Fe1.

NiCl₂-K₂Ni(CN)₄/FeCl₃-K₂Ni(CN)₄ mixed-cyanogel; this leads to the uniform distribution of Fe and Ni atoms in Ni(OH)₂-Fe H-STs-Ni3Fe1.

Structural features of Ni(OH)₂-Fe H-STs-Ni3Fe1 were further explored by high-resolution TEM (HR-TEM). Nanoholes of about 1 nm are observed in the HR-TEM image (Fig. 3(A)). The N₂ IAD curves display a typical IV hysteresis loop, which confirms the porous characteristic of Ni(OH)₂-Fe H-STs (Fig. 3(B)). The surface area of Ni(OH)₂-Fe H-STs-Ni3Fe1 is measured to be 181.6 m² g⁻¹, and the pore width is 0.96 nm. These pores mainly originate from the natural exfoliation of cyanide ions and chloride ions during cyanogel hydrolysis [47–49]. The presence of these pores increases the mass transfer of reactants as well as the amount of edge-active atoms, which are extremely favorable for electrocatalytic reactions. Clear lattice stripes can be

observed in the magnified HR-TEM image (Fig. 3(C)), which refers to the crystallographic (210) plane of Fe₃O₄ and (103) plane of Ni(OH)₂; this is in agreement with the EDX and XRD results. The SAED pattern of Ni(OH)₂-Fe H-STs-Ni3Fe1 shows obvious diffraction rings corresponding to Ni(OH)₂ and Fe₃O₄, revealing the polycrystalline property (Fig. 3(D)).

3.2. OER performance of Ni(OH)₂-Fe H-STs

As the chemical composition of an electrocatalyst strongly affects its electrocatalytic performance, the effect of Fe content on the OER performance of Ni(OH)₂ should be investigated. For this, four Ni(OH)₂-Fe H-STs with different Ni/Fe atomic ratios, which included Ni(OH)₂ H-STs without Fe, Ni(OH)₂-Fe H-STs-Ni0.5Fe1, Ni(OH)₂-Fe H-STs-Ni1Fe1, and Ni(OH)₂-Fe H-STs-Ni5Fe1, were synthesized by the same cyanogel hydrolysis strategy. EDX (Fig. S3) and SEM (Fig. S4) characterizations confirm their successful synthesis, indicating that via this preparation process, the chemical composition of Ni(OH)₂-Fe H-STs can be conveniently adjusted in a controlled range by simply adjusting the feed ratio.

The OER activities of Ni(OH)₂-Fe H-STs were characterized by LSV (Fig. 4(A)). The LSV curves show that among all samples, Ni(OH)₂-Fe H-STs-Ni3Fe1 has a lower onset potential and larger current density. The expected current density of solar water-splitting cells with the solar-to-fuel conversion efficiency of 10% is about 10 mA cm⁻² under 1 sun illumination. Therefore, the overpotential at 10 mA cm⁻² ($\eta_{10} = E_{10} - 1.23$ V) is a major parameter to evaluate the performance of a water-splitting device [51]. The η_{10} values of Ni(OH)₂ H-STs, Ni(OH)₂-Fe H-STs-Ni5Fe1, Ni(OH)₂-Fe H-STs-Ni3Fe1, Ni(OH)₂-Fe H-STs-Ni1Fe1, and Ni(OH)₂-Fe H-STs-Ni0.5Fe1 are 356, 255, 220, 276, and 336 mV, respectively (Fig. 4(B)). With the increasing iron content, the OER overpotential at

Fig. 4. (A) LSV polarization curves of Ni(OH)₂-Fe H-STs in 1 M KOH electrolyte at 2 mV s⁻¹; (B) Histogram of η_{10} at Ni(OH)₂-Fe H-STs; (C) Tafel plots of Ni(OH)₂-Fe H-STs for the OER; (D) Nyquist plots in 1 M KOH electrolyte at 1.5 V for Ni(OH)₂-Fe H-STs with different Ni/Fe ratios.

$\text{Ni(OH)}_2\text{-Fe}$ H-STs- Ni_3Fe_1 reaches a minimum value. Upon further increasing the iron content, the OER overpotential at $\text{Ni(OH)}_2\text{-Fe}$ H-STs- Ni_1Fe_1 increases. Electrochemical measurements reveal that the Fe content plays an important role in the OER performance of $\text{Ni(OH)}_2\text{-Fe}$ H-STs. The introduction of iron can not only improve the conductivity of Ni(OH)_2 H-STs [32,52–54] but can also change the electronic structure of Ni(OH)_2 H-STs (Fig. S2). The LSV curves (Fig. 4(A)) show that the nickel oxidation peaks of $\text{Ni(OH)}_2\text{-Fe}$ H-STs undergo a positive shift with the increasing iron content and the higher valence Ni^{IV} active species are formed [55]. However, upon further increasing the iron content, the active sites of nickel on $\text{Ni(OH)}_2\text{-Fe}$ H-STs are blocked by the inactive $\gamma\text{-FeOOH}$ species [56], which decreases the activity of $\text{Ni(OH)}_2\text{-Fe}$ H-STs for the OER.

To gain information about the OER kinetics of $\text{Ni(OH)}_2\text{-Fe}$ H-STs, Tafel plots ($\log j$ vs. η) were recorded (Fig. 4(C)). $\text{Ni(OH)}_2\text{-Fe}$ H-STs- Ni_3Fe_1 shows a minimum Tafel slope (53 mV dec^{-1}), which overmatches those of $\text{Ni(OH)}_2\text{-Fe}$ H-STs- $\text{Ni}_{0.5}\text{Fe}_1$ (87 mV dec^{-1}), $\text{Ni(OH)}_2\text{-Fe}$ H-STs- Ni_1Fe_1 (73 mV dec^{-1}), $\text{Ni(OH)}_2\text{-Fe}$ H-STs- Ni_5Fe_1 (75 mV dec^{-1}), and Ni(OH)_2 H-STs (76 mV dec^{-1}). A Tafel slope between 40 and 120 mV dec^{-1} illustrates that the rate-determining steps on $\text{Ni(OH)}_2\text{-Fe}$ H-STs- Ni_3Fe_1 are dominated by the Krasil'shchikov path involving the adsorption of OH^- and the production of $\ast\text{-O}$ -intermediate [57]. As Tafel slope serves as an estimable index of electron transfer rate for the OER, the present experimental results indicate that the OER at $\text{Ni(OH)}_2\text{-Fe}$ H-STs- Ni_3Fe_1 has fastest reaction kinetics.

The OER charge transfer rate at $\text{Ni(OH)}_2\text{-Fe}$ H-STs was further explored by EIS (Fig. 4(D)). The EIS curves of all samples show a semicircular shape in the high frequency range, and the radius reflects the charge transfer resistance (R_s). $\text{Ni(OH)}_2\text{-Fe}$ H-STs- Ni_3Fe_1 shows a smaller R_s value (6 Ω) than those of $\text{Ni(OH)}_2\text{-Fe}$ H-STs- $\text{Ni}_{0.5}\text{Fe}_1$ (68 Ω), $\text{Ni(OH)}_2\text{-Fe}$ H-STs- Ni_1Fe_1 (35 Ω), $\text{Ni(OH)}_2\text{-Fe}$ H-STs- Ni_5Fe_1 (17 Ω), and Ni(OH)_2 H-STs (390 Ω); this confirms the fast OER kinetics at $\text{Ni(OH)}_2\text{-Fe}$ H-STs- Ni_3Fe_1 .

Fig. 5. SEM images of the NF substrate (A) and $\text{Ni(OH)}_2\text{-Fe}$ H-STs- $\text{Ni}_3\text{Fe}_1/\text{NF}$ (B); (C) SEM-EDX-mapping images of $\text{Ni(OH)}_2\text{-Fe}$ H-STs- $\text{Ni}_3\text{Fe}_1/\text{NF}$; (D) partially magnified SEM image of $\text{Ni(OH)}_2\text{-Fe}$ H-STs- $\text{Ni}_3\text{Fe}_1/\text{NF}$.

3.3. The OER performance of $\text{Ni(OH)}_2\text{-Fe}$ H-STs- $\text{Ni}_3\text{Fe}_1/\text{NF}$

As $\text{Ni(OH)}_2\text{-Fe}$ H-STs- Ni_3Fe_1 has a high OER activity, we applied the same cyanogel hydrolysis strategy to directly grow $\text{Ni(OH)}_2\text{-Fe}$ H-STs- Ni_3Fe_1 on NF. Compared to the smooth surface of NF (Fig. 5(A)), the surface of $\text{Ni(OH)}_2\text{-Fe}$ H-STs- $\text{Ni}_3\text{Fe}_1/\text{NF}$ is rough (Fig. 5(B)); this provides an initial evidence about the successful combination of $\text{Ni(OH)}_2\text{-Fe}$ H-STs- Ni_3Fe_1 and NF. EDX-mapping images show the uniform distribution of Ni, Fe, and O elements, further proving the successful growth of $\text{Ni(OH)}_2\text{-Fe}$ H-STs- Ni_3Fe_1 on NF (Fig. 5(C)). The magnified SEM images show that $\text{Ni(OH)}_2\text{-Fe}$ H-STs- Ni_3Fe_1 maintains its sheet morphology even after its growth on NF, very similar to the case of $\text{Ni(OH)}_2\text{-Fe}$ H-STs- Ni_3Fe_1 without NF (Fig. 5(D)). Generally, the in-situ growth of electrocatalysts on a conductive substrate can make them bond without the use of a binder; this accelerates the mass/electron transfer during electrocatalysis [58]. As NF has excellent conductivity, the direct growth of $\text{Ni(OH)}_2\text{-Fe}$ H-STs- Ni_3Fe_1 on NF undoubtedly facilitates mass/electron transfer. Meanwhile, open microporous 3D structures can accelerate the mass transfer of reactants and products. Thus, $\text{Ni(OH)}_2\text{-Fe}$ H-STs- $\text{Ni}_3\text{Fe}_1/\text{NF}$ is expected to possess an enhanced OER activity as compared to that of $\text{Ni(OH)}_2\text{-Fe}$ H-STs- Ni_3Fe_1 without NF.

To investigate the possibility of practical applications of $\text{Ni(OH)}_2\text{-Fe}$ H-STs- $\text{Ni}_3\text{Fe}_1/\text{NF}$, we compared its OER performance with that of commercial RuO_2 nanoparticles on NF (denoted as RuO_2/NF) under the same conditions. LSV measurements clearly show that $\text{Ni(OH)}_2\text{-Fe}$ H-STs- $\text{Ni}_3\text{Fe}_1/\text{NF}$ has better activity, such as a lower onset oxidation potential and higher oxidation current, than commercial RuO_2/NF for the OER (Fig. 6(A)). At 10 and 60 mA cm^{-2} , the η_{10} and η_{60} values of $\text{Ni(OH)}_2\text{-Fe}$ H-STs- $\text{Ni}_3\text{Fe}_1/\text{NF}$ are 200 mV and 250 mV, respectively, significantly lower than those of RuO_2/NF ($\eta_{10} = 280$ mV and $\eta_{60} = 340$ mV) (Fig. 6(B)). In particular, the η_{10} value of

Fig. 6. (A) LSV polarization curves of $\text{Ni(OH)}_2\text{-Fe}$ H-STs- $\text{Ni}_3\text{Fe}_1/\text{NF}$ and RuO_2/NF in 1 M KOH electrolyte at 2 mV s^{-1} ; (B) the OER overpotentials at 10 and 60 mA cm^{-2} for $\text{Ni(OH)}_2\text{-Fe}$ H-STs- $\text{Ni}_3\text{Fe}_1/\text{NF}$ and RuO_2/NF ; (C) Tafel plots for $\text{Ni(OH)}_2\text{-Fe}$ H-STs- $\text{Ni}_3\text{Fe}_1/\text{NF}$ and RuO_2/NF ; (D) Chronopotentiometric curves of $\text{Ni(OH)}_2\text{-Fe}$ H-STs- $\text{Ni}_3\text{Fe}_1/\text{NF}$ and RuO_2/NF in 1 M KOH electrolyte at 10 mA cm^{-2} .

Table 1

OER performance of NiFe-based nanomaterials in KOH.

Electrocatalysts	Electrolyte	η at i_{10}	Ref. (year)
Fe@Ni HNSs	1 M KOH	220	This work
Iron-doped Ni ₃ S ₂ sheets	1 M KOH	295	[59] 2019
Ni ₂ Fe ₁ nanometer pearl necklaces	1 M KOH	240	[60] 2019
NiFe-co-doped polymeric carbon nitride	1 M KOH	310	[61] 2019
NiFe/MoS ₂ sheets	1 M KOH	260	[62] 2019
Ni-Fe-P/NF	1 M KOH	229	[63] 2019
Fe-doped NiCo-LDH	1 M KOH	285	[64] 2019
F-NiFe LDH	1 M KOH	225	[29] 2019
NiCoFe alloy nanoparticles	1 M KOH	320	[65] 2019
NiCoFeB nanochains	1 M KOH	284	[62] 2019
CoFe ₂ O ₄ sheets	1 M KOH	275	[66] 2019
Fe-Ni-Mo nitride porous nanotubes	1 M KOH	228	[67] 2018
Ni _{0.83} Fe _{0.17} (OH) ₂ sheets	1 M KOH	245	[32] 2018
Ni _{0.67} Fe _{0.33} /C sheets	1 M KOH	325	[68] 2018
N-CoFe LDHs	1 M KOH	233	[69] 2018
Vacancies Ni-NiFe LDHs	1 M KOH	245 229	[70] 2018
Fe-doped Ni(OH) ₂ sheets	1 M KOH	271	[71] 2018
Ni-Co-Fe hydroxides/N-doped carbon nanoplates	0.1 M KOH	250	[72] 2018
Fe-Co-P alloy nanospheres	1 M KOH	252	[73] 2018
Bimetallic Ni-Fe phosphide nanocomposites	1 M KOH	233	[74] 2018
Fe/Ni/CoMn-MIL-53 nanostructures	1 M KOH	236	[75] 2018
Ni-Fe-O nanowires	1 M KOH	224	[76] 2018
Mo-doped Ni-Fe oxide nanowires	1 M KOH	231	[77] 2018
Ni-Co-Fe hollow multivoid nanocuboids	0.1 M KOH	320	[78] 2018

Ni(OH)₂-Fe H-STs-Ni₃Fe₁/NF is lower than that of most of the reported NiFe-based electrocatalysts (Table 1), also indicating its high activity. A comparative experiment was performed to exclude the contribution of NF (Fig. S5). Tafel plots show that the OER at Ni(OH)₂-Fe H-STs-Ni₃Fe₁/NF has a smaller Tafel slope than that at RuO₂/NF (56 vs. 111 mV dec⁻¹, respectively), revealing improved OER kinetics at Ni(OH)₂-Fe H-STs-Ni₃Fe₁/NF (Fig. 6(C)). The durability of Ni(OH)₂-Fe H-STs-Ni₃Fe₁/NF and RuO₂/NF was investigated by chronopotentiometry measurements (Fig. 6(D)). After 15 h, the potential of Ni(OH)₂-Fe H-STs-Ni₃Fe₁/NF only increases by 30 mV, and its voltage at 10 mA cm⁻² is still less than that of RuO₂/NF, further indicating good durability and high activity of

Ni(OH)₂-Fe H-STs-Ni₃Fe₁/NF. After stability test, the EDX and SEM characterizations show that the composition and morphology of Ni(OH)₂-Fe H-STs-Ni₃Fe₁/NF are basically maintained (Fig. S6). Possibly, the lamellar nanostructures can inhibit Ostwald ripening and support each other in three dimensions to prevent aggregation, which greatly improve the stability.

4. Conclusions

Herein, we developed a simple mixed-cyanogel hydrolysis strategy to successfully synthesize Ni(OH)₂-Fe H-STs. The lamellate skeletons and the solid property of cyanogel precursor contributed to the formation of a holey and ultrathin 2D structure of Ni(OH)₂-Fe H-STs. All electrochemical results demonstrate that Ni(OH)₂-Fe H-STs-Ni₃Fe₁/NF with the optimal Ni/Fe ratio of 3:1 has excellent OER activity in an alkaline environment, which also exceeds that of most of the reported NiFe-based OER electrocatalysts. Due to the ultrathin 2D structure of Ni(OH)₂-Fe H-STs-Ni₃Fe₁, most of the metal atoms are exposed to the surface of sheets; this maximizes the atomic utilization. Simultaneously, the ultra-thin surface is filled with low-coordination-number central atoms with high activity, which can serve as highly active reaction sites for the OER. The pores on the sheets efficiently increase the amount of edge-active atoms with high activity and accelerate mass transfer. Meanwhile, the introduction of iron improves the conductivity of Ni(OH)₂ H-STs and promotes the generation of valence Ni^{IV} active species. The introduction of NF with 3D morphology further improves the conductivity and accelerates mass transfer. All these factors contribute to the high OER activity of Ni(OH)₂-Fe H-STs-Ni₃Fe₁/NF.

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Graphical Abstract

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Direct growth of holey Fe₃O₄-coupled Ni(OH)₂ sheets on nickel foam for the oxygen evolution reaction

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Herein, ultrathin holey Fe₃O₄-coupled Ni(OH)₂ sheets (Ni(OH)₂-Fe H-STs) were easily synthesized, which showed outstanding activity for the OER due to special structural features and synergistic effect between the Fe and Ni atom.

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多孔Fe₃O₄修饰的Ni(OH)₂纳米片的制备及其析氧性能研究

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摘要: 近年来, 基于析氧反应(OER)的电化学能量转换体系(如电化学制氢、金属空气电池、氮气电还原和二氧化碳电还原)日益受到人们的关注. 各种过渡金属基(Mn, Ni, Co, Fe, Cu等)纳米材料(硫化物、氢氧化物、氧化物、磷化物和氮化物等)被认为是潜在的、可以代替贵金属的碱性OER催化剂. 其中, 高活性和低成本的Ni(OH)₂基电催化剂被广泛关注. 由于面积效应、结构效应、电子效应和协同效应等因素, Ni(OH)₂基纳米材料的电化学活性与其形貌和化学成分密切相关. 引入纳米尺寸的孔, 不仅加快了传质, 而且增加了边缘活性原子的数量, 因而有利于活性的增强. 超薄二维(2D)纳米片因具有独特的结构特征, 可以为电催化反应提供充足的反应位点和低配位数的表面活性原子. 杂原子的引入可以调节纳米材料的电子结构和几何结构以提高它们的电催化活性. 本文提出了一种简单的混合氰胶水解策略, 成功合成了Fe掺杂的Ni(OH)₂纳米片(Ni(OH)₂-Fe H-STs). 氰胶前驱体骨架结构有助于形成超薄多孔的2D结构, 而且, 通过调节前驱体的浓度就可以获得一定镍铁原子比的产物. 不同Fe含量的Ni(OH)₂纳米片的OER活性测试结果表明, Ni/Fe比为3:1的Ni(OH)₂-Fe H-STs-Ni₃Fe₁在碱性环境中具有最佳的OER活性. 由于Ni(OH)₂-Fe H-STs-Ni₃Fe₁的超薄2D结构使大多数金属原子暴露在表面, 使原子利用率最大化. 同时, 超薄表面上高活性的低配位数的中心原子, 可以作为催化OER的高活性中心. 薄片上的孔隙有效地增加了高活性边缘原子的数量并且能够加速反应物和生成物的传质. XPS测试结果表明, Fe的引入显著改变了Ni的电子结构, 提高了Ni(OH)₂ H-STs的导电性, 从而促进了电化学过程中Ni^{IV}活性物种的产生, 进而改变其OER本征活性. 三维镍泡沫(NF)可以防止负载纳米材料的聚集, 提高转移反应物/产物的传质速率. 因此, 本文将Fe掺杂的Ni(OH)₂纳米片直接生长在NF基底(简称为Ni(OH)₂-Fe H-STs/NF). 结果表明, NF基底的引入进一步提升导电性和增加传质. 综上所述, 由于具有高比表面积、丰富的活性原子、Fe/Ni原子之间的协同效应以及NF基底的高导电性和三维多孔特性, 通过氰胶水解法获得的Ni(OH)₂-Fe H-STs/NF在KOH溶液中表现出优异的OER活性, 在10 mA cm⁻²电流密度下过电位仅为200 mV, Tafel斜率为56 mV dec⁻¹, 并且材料具有良好的稳定性.

关键词: 析氧反应; 过渡金属纳米材料; 多孔二维材料; 异原子掺杂; 电催化

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