International Journal of ELECTROCHEMICAL SCIENCE www.electrochemsci.org

One-pot hydrothermal synthesis of Fe, W co-doped Ni₃S₂/NiS on Ni foam for bifunctional oxygen evolution and urea oxidation reactions

Lin Zhu, Rui Zhang, Weixin Lv^{*}, Meijie Wei, Wei Wang^{*}

School of Chemistry and Chemical Engineering, Yancheng Institute of Technology, Yancheng 224051, China *E-mail: <u>weixin841230@126.com</u> (W.X. Lv), <u>wangw@ycit.edu.cn</u> (W. Wang).

Received: 14 June 2022 / Accepted: 8 August 2022 / Published: 10 September 2022

Designing highly active electrocatalysts for both the oxygen evolution (OER) and urea oxidation reactions (UOR) is very important for achieving significant reductions in the energy consumption for water electrolysis or wastewater treatment. Porous clusters of Fe, W co-doped nickel sulfide catalysts were directly grown on nickel foam (NF) by one-step hydrothermal method. The obtained FeW-Ni₃S₂/NiS@NF showed excellent catalytic performance toward OER in 1 M KOH, with an overpotential of 236 mV at 50 mA cm⁻² and 251 mV at 100 mA cm⁻², which markedly surpassed the performance of catalyst samples doped with Fe and W alone. In addition, FeW-Ni₃S₂/NiS@NF displayed excellent electrocatalytic performance toward UOR: a potential of only 1.354 V (vs. RHE) was required to drive the reaction at a current density of 100 mA cm⁻². The introduction of Fe and W elements into the catalyst can not only promote the regulation of the morphology of FeW-Ni₃S₂/NiS@NF for exposing more active sites, but also the interaction between the Fe and W salts that significantly increases the OER and UOR performances. This work provides an effective strategy for preparing efficient electrocatalysts.

Keywords: Sulfide; Heteroatom doping; One-pot; Oxygen evolution; Urea oxidation

1. INTRODUCTION

With energy shortage and current levels of environmental pollution, there is an urgent need for environmental protection and supplies of sustainable energy, which makes hydrogen production by water splitting highly relevant. The high energy barrier of anode reaction seriously hinders hydrogen production efficiency [1]. The anodic reaction is generally the oxygen evolution reaction (OER). Noble metal based catalysts display outstanding catalytic performance toward OER, but their large-scale application is limited by high cost and limited resources [2]. In recent years, it has been reported that some other reactions, e.g., urea oxidation reaction (UOR), can replace OER [3-4]. Therefore, the most important objective is to reduce the overpotential of anodic reaction by using inexpensive catalysts.

At present, non-noble metal based catalysts, e.g., those based on nickel, cobalt, iron, and tin, attract considerable interest because of their low cost and the possibility to design and synthesize them by different strategies to improve their catalytic activity toward OER [5-8]. Nickel-based compounds, such as nickel sulfide, have a unique electronic structure and good electrical conductivity. They contain many Ni-S and Ni-Ni bonds, which favor the formation of OER intermediates (OOH*) and the conversion of hydrogen (H*) into H₂, which has become a hot research area [9]. However, the OER catalytic activity of nickel sulfide is still far from that of noble metal catalyst, and doping with heteratoms can be a way to adjust the electronic structure of the catalyst (i.e., nickel sulfide) and effectively improve its OER catalytic activity [10].

Modification by doping can be divided into single-metal doping and bimetal doping [11-13]. For example, Tong et al. prepared Co-doped Ni₃S₂ on nickel foam (NF) by electrodeposition, and the overpotential of this material in OER was only 358 mV at a current density of 50 mA cm⁻² [14]. Zhu et al. synthesized Fe7.2%-Ni₃S₂ nanosheets on a NF by two-step hydrothermal method, the overpotential of this material in OER was only 295 mV at 10 mA cm⁻², and the introduction of Fe significantly improved the OER catalytic activity of Ni₃S₂ [15]. In addition, some studies reported that bimetallic doping of nickel sulfide can further improve the catalytic activity of the catalyst, which is obviously better than single-metal doping. Recently, some Ni₃S₂ catalysts doped with two metals have been reported to show better performance than single-metal doped catalysts [16-18]. Wu et al. reported a bimetal-doped CoCe-Ni₃S₂/NF catalyst synthesized by one-step hydrothermal method, which exhibited higher electrocatalytic activity than single metal-doped Co-Ni₃S₂/NF, Ce-Ni₃S₂/NF or Ni₃S₂/NF: the overpotential in OER was as low as 286 mV at 20 mA cm⁻² [19]. Moreover, Zhang et al. reported one-step hydrothermal reactions leading to the formation of Fe-Mo-S/Ni₃S₂ on Ni foam, the catalyst was effective toward OER, showing a low overpotential of ~300 mV at a current density of 100 mA cm⁻² [20]. Thus, bimetallic doping of nickel sulfide is a promising approach to explore new OER catalysts, because it allows various heteroatoms with different properties to be combined.

Although a substantial progress has been made toward the development of efficient OER catalysts, it is still challenging to prepare highly efficient bimetal-doped Ni₃S₂ catalysts for OER. Fe is a good candidate to use in doping to improve the OER performance of the Ni₃S₂ catalysts [21-24]. Therefore, we expected that an improvement in the performance of Ni₃S₂ catalysts can be achieved by doping them with Fe and another metal via a one-step hydrothermal method that can also significantly alter the electronic structure of Fe doped Ni₃S₂ catalyst. Therefore, in this paper, porous clusters of FeW-Ni₃S₂/NiS@NF catalysts were prepared on nickel foam by one-step hydrothermal method. It was found that the Ni₃S₂/NiS heterostructure doped with Fe and W had a higher specific surface area, a larger number of exposed active sites, enhanced conductivity, and a faster charge transfer rate and reaction kinetics; i.e., doping improved the OER catalytic activity of nickel sulfide. In this work, the FeW-Ni₃S₂/NiS@NF catalyst showed excellent and very stable catalytic performance toward OER, with an overpotential of only 236 mV at 50 mA cm⁻² and 251 mV at 100 mA cm⁻², as well as excellent mechanical stability, which is very important for practical application. In addition to OER, the electrode has excellent UOR performance, and its potential being only 1.354 V (vs. RHE) at 100 mA cm⁻². This

work provides a promising method for the development of efficient, cheap, and stable bifunctional OER and UOR electrocatalysts.

2. EXPERIMENTAL

2.1 Pretreatment of NF

NF with an area of 1×4 cm² was prepared and then ultrasonically cleaned with 3 M HCl, anhydrous ethanol and deionized water for 10 minutes.

2.2 Preparation of FeW-Ni₃S₂/NiS@NF

Firstly, 540 mg (2.0 mmol) FeCl₃·6H₂O, 390 mg (2.2 mmol) Na₂S and 329 mg (1 mmol) Na₂WO₄·2H₂O were dissolved in 50 mL deionized water in a beaker and stirred for 1 min. The solution and two pieces of NF were then placed in an autoclave, and hydrothermally heated at 150 °C for 6 h. After cooling to room temperature, the reacted NF was washed several times with absolute ethanol and deionized water, and then dried at 60 °C for 10 h to obtain the product FeW-Ni₃S₂/NiS@NF. In the same way, adopt 810 mg (3 mmol) FeCl₃·6H₂O and 390 mg (2.2 mmol) Na₂S were used to obtain product FeNi₃S₂@NF and (3 mmol) 989 mg Na₂WO₄·2H₂O and 390 mg (2.2 mmol) Na₂S were used in synthesis of W-Ni₃S₂@NF.

2.3 Preparation of RuO₂@NF

5 mg RuO₂ was added to a solution containing 50 μ L Nafion solution, 200 μ L absolute ethanol, and 200 μ L deionized (the mixed solution), and the resulting mixture was sonicated for 1 h to obtain a well-mixed ink solution. 180 μ L of the ink solution was added dropwise on a 1 cm² piece of NF and dried overnight at room temperature.

2.4 Materials characterization

The X-ray diffraction (XRD) was performed on Japanese science smartlab 9kw X-ray diffractometer with Cu Kα). The morphologies of the samples were investigated via scanning electron microscopy (SEM, Hitachi SU8100) and transmission electron microscopy (TEM, JEM2100F). X-ray photoelectron spectroscopy (XPS) was carried out using ESCALAB 250Xi electron spectrometer.

2.5. Electrochemical measurements:

The OER performance of as-prepared electrodes was measured in an alkaline solution (1 M KOH, pH = 13.8) at room temperature using a CHI 760 electrochemical workstation. The electrolyte for

UOR was 1 M KOH and a 0.33 M aqueous urea solution. The three-electrode system consisted of the as-prepared sample, Pt foil, and a Hg/HgO reference electrode. The potential of reversible hydrogen electrode (RHE) is represented by the following formula: $E(vs RHE) = E(vs Hg/HgO) + 0.059 \times pH + 0.098 V$. The polarization curves characterizing the oxygen evolution reaction (OER) were recorded at a scan rate of 1 mV s⁻¹ using linear sweep voltammetry (LSV), and all LSV curves were IR-compensated (90% IR compensation) based on the solution resistance. Overpotential η was calculated as $\eta = E(vs RHE) - 1.23 V$. Tafel slope b was calculated from the equation $\eta = blogj + a$ (where η is the overpotential and j is the current density). Electrochemical impedance spectroscopy (EIS) was obtained in the frequency range from 0.05 to 1000000 Hz. Electrochemical double-layer capacitance (C_{dl}) was calculated from the cyclic voltammetry curves recorded within a range where no Faradaic processes occurred. The stability of the catalyst in OER at constant potential for 24 h was tested by chronoamperometry.



3. RESULTS AND DISCUSSION

Figure 1. SEM images of (a) $Ni_3S_2@NF$, (b) W- $Ni_3S_2@NF$, (c) Fe- $Ni_3S_2@NF$, and (d) FeW- $Ni_3S_2/NiS@NF$.

Scanning electron microscopy (SEM) images of each of the prepared catalysts are shown in Fig. 1a-d. The surface of $Ni_3S_2@NF$ electrode is rough, which indicates that the surface morphology of NF has changed as a result of vulcanization (Fig. 1a). The W-Ni_3S_2@NF surface consists of a porous grid structure (Fig. 1b). In comparison with the materials subjected to vulcanization only, the surface of W-

doped materials has no visible cracks. The Fe-Ni₃S₂@NF surface (Fig. 1c) consists of disordered nanorods, and the doping with Fe significantly changed the catalyst morphology. Although this structure facilitates detachment of gas bubbles during the reaction, it also lets the active components of the catalyst to escape, affecting the stability of the catalyst. The FeW-Ni₃S₂/NiS@NF surface (Fig. 1d) has a unique porous structure. In comparison with the other two single-metal doped catalysts, this morphology provides a larger specific surface area, exposes more active sites, and provides channels for the diffusion of bubbles in the reaction. The SEM results indicated that the heteroatom doping enables engineering of the catalyst surface morphology.



Figure 2. (a) XRD pattern of Ni₃S₂@NF, W-Ni₃S₂@NF, Fe-Ni₃S₂@NF and FeW-Ni₃S₂/NiS@NF, (b) TEM, (c) HRTEM, and (d) SAED images of FeW-Ni₃S₂/NiS@NF.

XRD patterns (Fig. 2a) of Ni₃S₂@NF, W-Ni₃S₂@NF, Fe-Ni₃S₂@NF and FeW-Ni₃S₂/NiS@NF showed that in addition to three main diffraction peaks of NF. For FeW-Ni₃S₂/NiS@NF, there are several other small but detectable peaks which correspond to NiS (PDF#12-0041) and Ni₃S₂ (PDF#44-1418). This means that the main structure of the sample is NiS and Ni₃S₂. The structure of Fe-Ni₃S₂@NF catalyst, W-Ni₃S₂@NF catalyst and Ni₃S₂@NF catalyst consists mainly Ni₃S₂. The mixed-phase character of FeW-Ni₃S₂/NiS@NF structure, which consists of NiS and Ni₃S₂ phases, could be the result of simultaneous presence of Fe and W. The FeW-Ni₃S₂/NiS@NF catalyst in the powered form was used in TEM studies. The TEM diagram in Fig. 2b shows that the catalyst structure is made up of many

nanosheets, which is consistent with the SEM results. In the HRTEM figure in Fig. 2d, the crystal plane spacing takes values of 0.22, 0.27 and 0.29 nm, which correspond to the (211), (300) and (101) planes of Ni₃S₂, respectively. The other lattice fringes with a spacing of 0.20, 0.22 and 0.23 nm correspond to the (202), (211) and (021) planes of NiS, respectively. It can be observed that the lattice fringes are clear and the crystallinity is good, which also indicates that the main structure of the sample is NiS and Ni₃S₂. Diffraction rings in the SAED pattern in Fig. 2c are in line with the XRD results, which further proves that the catalyst is composed of NiS and Ni₃S₂. XRD, HRTEM and SAED results confirmed that the FeW-Ni₃S₂/NiS@NF catalyst consisted mainly of NiS and Ni₃S₂, and formed a unique Ni₃S₂/NiS heterostructure.



Figure 3. (a) LSV curves, (b) corresponding Tafel slopes, and (c) linear fittings of the capacitive current densities at different scan rates, (d) EIS curves during OER processes.

The OER activity of the catalyst was studied in 1 M KOH solution. Fig. 3a shows LSV curves for each catalyst. Among the several catalysts tested, the FeW-Ni₃S₂/NiS@NF catalyst had the smallest overpotential at the same current density, which was 236 mV at 50 mA cm⁻² and 251 mV at 100 mA cm⁻². Other catalysts require a higher overpotential to achieve the same current density, the overpotentials of Fe-Ni₃S₂@NF, W-Ni₃S₂@NF, Ni₃S₂@NF, and the precious metal RuO₂@NF are 279 mV, 309 mV, 367 mV and 306 mV, respectively, at the current density of 50 mA cm⁻². The results show that the addition of Fe or W can effectively reduce the overpotential of nickel sulfide, but the effect is more

pronounced when both Fe and W were added, and the difference in overpotential between the codoped catalyst and Ni_3S_2 was 131 mV at a current density of 50 mA cm⁻². The excellent OER performance of FeW-Ni_3S_2/NiS@NF may be due to the fact that the catalytic material offers a larger number of active sites as a result of the simultaneous addition of W and Fe. The synergistic effect between Fe and W can optimize the electronic structure and increase the number of defect sites, thus improving the catalytic performance [25]. In addition, the performance of FeW-Ni_3S_2/NiS@NF toward OER surpasses previously reported electrocatalysts (Table 1).

Tafel curves were obtained from polarization curves of each catalyst to evaluate OER kinetics (Fig. 3b). The Tafel slope of FeW-Ni₃S₂/NiS@NF catalyst (59.72 mV dec⁻¹) was smaller and showed faster OER kinetics. Compared with Fe-Ni₃S₂@NF catalyst (66.03 mV dec⁻¹), W-Ni₃S₂@NF catalyst (47.47 mV dec⁻¹) and Ni₃S₂@NF catalyst (79.48 mV dec⁻¹), the doping of Fe and W elements can accelerate the OER reaction kinetics [34]. Specific capacitance C_{dl} was obtained from linear fitting of the CV data, and the electrochemical active area (ECSA) of each catalyst was compared (Fig. 3c). The maximum C_{dl} value for FeW-Ni₃S₂/NiS@NF catalyst was 115.54 mF cm⁻², and the C_{dl} value for Fe-Ni₃S₂@NF, W-Ni₃S₂@NF and Ni₃S₂@NF were 52.75 mF cm⁻², 53.64 mF cm⁻² and 62.22 mF cm⁻², respectively. The results showed that with the addition of Fe and W the active area of catalysts and the number of (exposed) active sites increased, thus improving their OER performance, which is also consistent with the SEM observations [35]. The electron transfer rate of each catalyst was determined from impedance measurements (Fig. 3d). The FeW-Ni₃S₂/NiS@NF catalyst, compared to Fe-Ni₃S₂@NF catalyst, W-Ni₃S₂@NF catalyst and Ni₃S₂@NF catalyst, was characterized by a smallest arc diameter, indicating that the addition of Fe and W reduces the charge transfer resistance and increases the electron transfer rate. These results indicate that the FeW-Ni₃S₂/NiS@NF catalyst, a Ni₃S₂/NiS heterostructure doped with both Fe and W, has a larger electrochemical active area, a smaller charge transfer resistance to OER, and a faster reaction kinetics than other single-doped samples, which is suggestive of its excellent OER activity.

Catalysts	OER (50 mA cm ⁻²)	OER (100 mA cm ⁻²)	Ref.
Mo W S 20Ni S	250 mV	205 mV	[16]
$100 - w - 5 - 2 @ 101_3 S_2$ CoNi2S4/Ni2S2@NF	335 mV	595 III V 435 mV	[10]
Co ₉ S ₈ -Ni ₃ S ₂ HNTs/Ni	281 mV	341 mV	[20]
Ni-Fe-P-Ni ₃ S ₂ /NF	255 mV	268 mV	[28]
CoS _x /Ni ₃ S ₂ @NF	345 mV	370 mV	[29]
V-Ni ₃ S ₂ @NiO/NF	285 mV	310 mV	[30]
FeS/Ni ₃ S ₂ @NF	284 mV	410 mV	[31]
Ni ₃ S ₂ @FeNi ₂ S ₄ @NF	306 mV	379 mV	[32]
Fe, Ce-Ni _x S _y	227 mV	250 mV	[33]
FeW-Ni ₃ S ₂ /NiS@NF	236 mV	251 mV	This work

 Table 1. Comparison of OER performance of FeW-Ni₃S₂/NiS@NF catalyst with recently reported transition metal-based catalysts.



Figure 4. (a) chronoamperometry curve of FeW-Ni₃S₂/NiS@NF during OER processes, (b) LSV curves of FeW-Ni₃S₂/NiS@NF before and after 24 h OER, and (c) photo of the FeMo-Ni₃S₂/NiS@NF electrode after bending, (d) tensile force test curve curves of catalyst prepared.

Stability testing is important for evaluating potential practical value of a catalyst. A chronoamperometry curve shown in Fig. 4a represents the performance of FeW-Ni₃S₂/NiS@NF catalyst in OER. At the potential corresponding to the current density of 50 mA cm⁻², the OER catalytic activity of the catalyst did not actually decrease but improved within 24 h. It can be seen from Fig. 4b that after the stability test of OER catalyst, the overpotential required driving a current density of 50 mA cm⁻² decreased by 9 mV. Fig. 4c shows the picture of the bent FeW-Ni₃S₂/NiS@NF catalyst, which demonstrates its good mechanical stability. The tensile force test results in also showed that the fracture tensile force for FeW-Ni₃S₂/NiS@NF is 5.82 N (Fig. 4d), and for Fe-Ni₃S₂@NF, W-Ni₃S₂@NF, Ni₃S₂@NF and NF this indicator was 3.27 N, 6.02 N, 4.39 N and 8.03 N, respectively, which further proves good mechanical stability of the FeW-Ni₃S₂/NiS@NF catalyst.



Figure 5. EDS spectrum of FeW-Ni₃S₂/NiS@NF (a) before OER, and (b) after 24 h of OER.

Table 2. Comparison of atomic percentage of each element in as-prepared electrodes in EDS results.

Catalysts	Fe (At %)	W (At %)
FeW-Ni ₃ S ₂ /NiS@NF-Intial	17.18	13.42
FeW-Ni ₃ S ₂ /NiS@NF-After OER	6.41	2.04
Fe-Ni ₃ S ₂ @NF	0.63	-
W-Ni ₃ S ₂ @NF	-	0.39

Changes in the elemental composition of the FeW-Ni₃S₂/NiS@NF catalyst, before and after OER, were studied from its EDS spectra (Fig. 5a and 5b). As can be seen, the W content decreases significantly after the OER and a fraction of Fe was lost, mainly because the tungstate ions adsorbed on the catalyst surface dissociate into the electrolyte during OER, carrying away a fraction of the Fe and W. However, according to the results of stability test, this phenomenon does not significantly affect the OER performance of the catalyst. Moreover, Fe and W elements can still be detected in the EDS after the stability test, which proves that Fe and W were successfully incorporated into the FeW-Ni₃S₂/NiS@NF catalyst. As can be seen from in Table 2, after OER the Fe content of the FeW-Ni₃S₂/NiS@NF catalyst (6.41 at %) was significantly higher than that of Fe-Ni₃S₂@NF (0.63 at %), and its W content (2.04 at %) was also significantly higher compared to W-Ni₃S₂@NF (0.39 at %), which indicated that the amount of Fe and W added to the catalyst can be increased by simultaneous doping it with the elements Fe and W, which leads to the improvement of OER performance of the catalyst. The study of electrode structure before and after OER reaction showed that the Fe and W contents of the catalyst decreased after the reaction because of the adsorption of Fe and W on the surface of sulfide catalyst by one-step method. The Fe and W species that were not effectively doped were released into the solution during the OER process. The results indicate that the elemental composition of sulfide prepared by one-step method needs to be studied after the OER process.



Figure 6. (a) SEM image of FeW-Ni₃S₂/NiS@NF after 24 h of OER; (b) S 2p XPS spectrum of FeW-Ni₃S₂/NiS@NF before and after 24 h OER; (c) Fe 2p XPS spectrum of FeW-Ni₃S₂/NiS@NF before and after 24 h OER; (d) W 4f XPS spectrum of FeW-Ni₃S₂/NiS@NF before and after 24 h OER;

To evaluate the structural stability more directly, we performed SEM imaging of the stabilized FeW-Ni₃S₂/NiS@NF catalyst (Fig. 6a). It was found that the surface pores of the catalyst enlarged significantly due possibly to the release of tungstate ions previously adsorbed on the surface into the electrolyte, resulting in changes in the surface morphology of the catalyst. XPS was also carried out to detect changes in the catalysts before and after the OER process. Fig. 6b shows the S 2p spectrum of the FeW-Ni₃S₂/NiS@NF sample before and after the 24-h OER test, which proves that the original sample has the S configuration of Ni₃S₂ and NiS [36]. However, after 24-h OER test, its S content of element did not change significantly, which is consistent with the EDS results in Fig. 5. It indicates that the structure of sulfide is relatively stable during the OER process, and the sulfide remains the active component of the catalyst. The Fe 2p spectra of FeW-Ni₃S₂/NiS@NF (Fig. 6c) were similar before and after the 24-h OER test, with the Fe 2p spectra of the FeW-Ni₃S₂/NiS@NF sample before and after the 24-h OER test at 711.7 eV and 724.21 eV, respectively [37]. The W 4f spectra of the FeW-Ni₃S₂/NiS@NF sample before and after the 24-h OER test are shown in Fig. 6d. The two peaks in the W 4f spectrum are W 4f_{7/2} (35.6 eV) and W 4f_{5/2} (37.6 eV) respectively, indicating that W in the FeW-Ni₃S₂/NiS@NF electrode exists as W⁶⁺ [38].

The W content decreased significantly after OER test, which is consistent with the EDS results in Fig. 5, and might be caused by the dissociation of adsorbed tungstate ions on catalyst surface into electrolyte during OER process. Therefore, it can be concluded that Fe and W are still effectively incorporated into nickel sulfide, and synergistic improve the OER performance of FeW-Ni₃S₂/NiS@NF, although Fe and W are partially lost in the long-term OER test. At the same time, the S content did not change significantly, indicating that the sulfide remained the active component of the catalyst during the OER process.



Figure 7. (a) LSV curves of FeW-Ni₃S₂/NiS@NF for the OER and UOR, (b) chronoamperometry curve of FeW-Ni₃S₂/NiS@NF during UOR processes, and the mini-figure shows the UOR polarization curves of FeW-Ni₃S₂/NiS@NF catalyst before and after the replacement of a new electrolyte after the UOR stability test.

The UOR performance of FeW-Ni₃S₂/NiS@NF was further measured in 1 M KOH and 0.33 M urea. As shown in Fig. 7a, the FeW-Ni₃S₂/NiS@NF catalyst displayed excellent UOR performance, and the potential required to drive the reaction in 1 M KOH at 50 mA cm⁻² and 100 mA cm⁻² was 1.466 V (vs. RHE) and 1.481 V (vs. RHE), respectively. However, in 1 M KOH and 0.33 M urea, the potential the potential required to drive at 50 mA cm⁻² and 100 mA cm⁻² was only 1.344 V (vs. RHE) and 1.354 V (vs. RHE), respectively. Compared with OER, the potential of FeW-Ni₃S₂/NiS@NF catalyst needed to drive the UOR reaction at 50 mA cm⁻² and 100 mA cm⁻² decreased by 0.122 V and 0.127 V, respectively, indicating that the catalyst requires less driving force in UOR and can effectively reduce the extra voltage required for water electrolysis. In addition, the stability of the FeW-Ni₃S₂/NiS@NF catalyst in UOR was measured by chronoamperometry (Fig. 7b). Moreover, FeW-Ni₃S₂/NiS@NF showed superior UOR performance compared with the previously reported electrocatalysts (Table 3). At the potential corresponding to the current density of 50 mA cm⁻², the activity of the catalyst decreased within 15 h and constituted only 85% of the initial current. However, as can be seen from the inset in Fig. 7b, after the UOR stability test, the UOR performance of FeW-Ni₃S₂/NiS@NF in the new electrolyte was significantly better than in the electrolyte used for 15 h. This indicates the decline of the UOR stability test curve, part of the reason is that the UOR catalytic activity of FeW-Ni₃S₂/NiS@NF

decreases, but obviously, as the reaction progresses, the decreasing content of urea in the electrolyte will significantly affect the UOR performance of the catalyst, suggesting that its UOR catalytic activity of the catalyst is relatively stable. In conclusion, the FeW-Ni₃S₂/NiS@NF catalyst also has excellent UOR performance and good stability in UOR.

Catalysts	Electrolyte	UOR (50 mA cm ⁻²)	Ref.
Nic popotubos	1 M KOU and 0.22 M surge	1.27 W (v.e. DHE)	[20]
Facoll@Cacol240	1 M KOH and 0.35 M urea	1.37 V (VS. KHE) 1.265 V (vg. DHE)	[39]
$FeOOH@C0_3O_4-240$	1 M KOH and 0.35 M urea	1.303 V (VS. KHE)	[40]
$AC-Co_2(OH)_3CI-V-0.1$	1 M KOH and 0.33 M urea	1.58 V (vs. RHE)	[41]
NiMoV LDH/NF	1 M KOH and 0.33 M urea	1.36 V (vs. RHE)	[42]
$Ni_2Fe(CN)_6$	1 M KOH and 0.33 M urea	1.34 V (vs. RHE)	[43]
Ni ₂ Fe _{0.5} Co _{0.5} -BP	1 M KOH and 0.33 M urea	1.44 V (vs. RHE)	[44]
CoP@PNC/PCWF	1 M KOH and 0.5 M urea	1.321 V (vs. RHE)	[45]
Ni-DMAP-2/NF	1 M KOH and 0.5 M urea	1.40 V (vs. RHE)	[46]
NCVS-3	1 M KOH and 0.33 M urea	1.43 V (vs. RHE)	[47]
FeW-Ni ₃ S ₂ /NiS@NF	1 M KOH and 0.33 M urea	1.344 V (vs. RHE)	This work

Table 3. Performance of some recently reported electrocatalysts for the UOR

4. CONCLUSIONS

In summary, the FeW-Ni₃S₂/NiS@NF catalyst was successfully synthesized on NF by one-step hydrothermal method. FeW-Ni₃S₂/NiS@NF showed excellent catalytic performance toward OER in 1 M KOH, with an overpotential of 236 mV at 50 mA cm⁻² and only 251 mV at 100 mA cm⁻², w which noticeably surpasses the performance of the catalyst doped with Fe or W alone. The EDS and XPS spectra recorded before and after OER reaction featured prominent Fe and W peaks, indicating that the structure was successfully doped with Fe and W. The introduction of Fe and W elements into the catalyst can not only promote the regulation of the morphology of FeW-Ni₃S₂/NiS@NF for exposing more active sites, but the added Fe and W elements can also interact with each other to increase the doping amount of the two elements in the catalyst, leading to significant improvement in the OER and UOR behavior of FeW-Ni₃S₂/NiS@NF. This work provides an effective strategy for increasing the amount of a doping element in the catalyst and a general approach to prepare efficient bifunctional OER and UOR electrocatalysts.

ACKNOWLEDGMENTS

The work was supported by the National Natural Science Foundation of China [grant numbers 21906142, 22176166, 21876144], Jiangsu Province for the College Graduate Research and Innovation Projects [KYCX21_3146].

References

- 1. Z. Y. Pan, M. Yaseen, P. K. Shen, and Y. Z. Zhan, J. Colloid Interface Sci., 616 (2022) 422.
- Z. H. Li, K. H. Wang, X. Tan, X. Liu, G. X. Wang, G. W. Xie, and L. H. Jiang, *Chem. Eng. J.*, 424 (2021) 130490.
- T. Li, H. C. Fu, X. H. Chen, F. Gu, N. B. Li, and H. Q. Luo, J. Colloid Interface Sci., 618 (2022) 196.
- 4. X. Y. Yang, L. Y. Kang, Z. M. Wei, S. S. Lou, F. C. Lei, P. Hao, J. F. Xie, and B. Tang, *Chem. Eng. J.*, 422 (2021) 130139.
- 5. J. Jian, X. Y. Kou, H. R. Wang, L. M. Chang, L. Zhang, S. Gao, Y. Xu, and H. M. Yuan, ACS Appl. Mater. Interfaces, 13 (2021) 42861.
- X. H. Xu, T. Wang, W. B. Lu, L. J. Dong, H. S. Zhang, and X. Y. Miao, ACS Sustainable Chem. Eng., 9 (2021) 4688.
- R. Zhang, L.Z. Cheng, Z. Wang, F.Y. Kong, Y. Tsegazab, W.X. Lv, W. Wang, *Appl. Surf. Sci.*, 526 (2020) 146753.
- P. W. Menezes, C. Panda, S. Garai, C. Walter, A. Guiet, and M. Driess, *Angew. Chem. Int. Ed.*, 57 (2018) 15237.
- 9. X. Y. Wang, W. Z. Z. Zhang, J. L. Zhang, and Z. C. Wu, ChemElectroChem, 6 (2019) 4550-4559.
- 10. B. Fei, Z. L. Chen, J. X. Liu, H. B. Xu, X. X. Yan, H. L. Qing, M. Chen, and R. B. Wu, *Adv. Energy Mater.*, 10 (2020) 2001963.
- 11. J. Jian, L. Yuan, H. Qi, X. J. Sun, L. Zhang, H. Li, H. M. Yuan, and S. H. Feng, *ACS Appl. Mater. Interfaces*, 10 (2018) 40568.
- 12. L. Xie, R. Tong, W. Zhang, D. J. Wang, T. Liu, Q. Li, X. N. Peng, and X. N. Wang, *Energy Technol.*, 7 (2019) 1801053.
- 13. Y. B. Chen, X. Y. Zhang, J. Q. Qin, and R. P. Liu, Molecular Catalysis, 516 (2021) 111955.
- 14. X. Tong, Y. Li, N. Pang, Y. H. Qu, C. H. Yan, D. Y. Xiong, S. H. Xu, L. W. Wang, and P. K. Chu, *Chem. Eng. J.*, 425 (2021) 130455.
- 15. Y. Zhu, H. D. Yang, K. Lan, K. Iqbal, Y. Liu, P. Ma, Z. M. Zhao, S. Luo, Y. T. Luo, and J. T. Ma, *Nanoscale*, 11 (2019) 2355.
- 16. M. Y. Zheng, J. Du, B. P. Hou, and C. L. Xu, ACS Appl Mater Interfaces, 9 (2017) 26066.
- 17. L. X. Zhao, H. Y. Ge, G. H. Zhang, F. B. Wang, and G. D. Li, *Electrochim. Acta*, 387 (2021) 138538.
- 18. P. Hu, Z. Y. Jia, H. B. Che, W. Y. Zhou, N. Liu, F. Li, and J. S. Wang, *J. Power Sources*, 416 (2019) 95.
- 19. X. X. Wu, T. Zhang, J. X. Wei, P. F. Feng, X. B. Yan, and Y. Tang, Nano Res., 13 (2020) 2130.
- 20. Y. Zhang, H. R. Guo, X. P. Li, J. Du, W. L. Ren, and R. Song, Chem. Eng. J., 404 (2021) 126483.
- 21. D. Lim, E. Oh, C. Lim, S. E. Shim, and S. H. Baeck, *Electrochim. Acta*, 361 (2020) 13708.
- 22. M. Wang, L. Zhang, J. L. Pan, M. R. Huang, and H. W. Zhu, Nano Res., 14 (2021) 4740.
- 23. N. Xie, D. D. Ma, X. T. Wu, and Q. L. Zhu, Nanoscale, 13 (2021) 1807.
- 24. W. X. Zhang, Q. Jia, H. Liang, L. Cui, D. Wei, and J. Q. Liu, Chem. Eng. J., 396 (2020) 125315.
- 25. Y. Zhao, J. H. You, L. Wang, W. T. Bao, and R. Y. Yao, Int. J. Hydrogen Energy, 46 (2021) 39146.
- 26. W. J. Dai, K. Ren, Y. A. Zhu, Y. Pan, J. Yu, and T. Lu, J. Alloys Compd., 844 (2020) 156252.
- 27. J. W. Li, P. M. Xu, R. F. Zhou, R. C. Li, L. J. Qiu, S. P. Jiang, and D. S. Yuan, *Electrochim. Acta*, 299 (2019) 152.
- 28. Z. H. Li, K. H. Wang, X. Tan, X. Liu, G. X. Wang, G. W. Xie, and L. H. Jiang, *Chem. Eng. J.*, 424 (2021) 130490.
- 29. S. Shit, S. Chhetri, W. Jang, N. C. Murmu, H. Koo, P. Samanta, and T. Kuila, *ACS Appl. Mater. Interfaces*, 10 (2018) 27712.
- 30. Q. Liu, J. F. Huang, L. Y. Cao, K. Kajiyoshi, K. Li, Y. Q. Feng, C. L. Fu, L. J. Kou, and L. L. Feng, ACS Sustainable Chem. Eng., 8 (2020) 6222.

- 31. H. Li, S. L. Yang, W. Wei, M. M. Zhang, Z. F. Jiang, Z. X. Yan, and J. M. Xie, *J. Colloid Interface Sci.*, 608 (2022) 536.
- 32. Y. Y. Yang, H. X. Meng, C. Kong, S. H. Yan, W. X. Ma, H. Zhu, F. Q. Ma, C. J. Wang, and Z. A. Hu, *J. Colloid Interface Sci.*, 599 (2021) 300.
- 33. X. Y. Zhang, Y. L. Qiu, Q. Li, X. Q. Ji, and J. Q. Liu, J. Power Sources, 522 (2022) 231004.
- 34. J. He, X. Zhou, P. Xu, and J. M. Sun, Nano Energy, 80 (2021) 105540.
- 35. X. Y. Zhang, Y. Han, W. W. Cai, D. Zhang, Z. C. Wang, H. D. Li, Y. Y. Sun, Y. Y. Zhang, J. P. Lai, and L. Wang, *Adv. Mater. Interfaces* 9 (2022) 2102154.
- 36. P. Mukherjee, K. Sathiyan, A. K. Vijay, R. Bar-Ziv, and T. Zidki, *Isr. J. Chem.*, 62 (2021) e202100110.
- 37. X. X. Wang, Y. Yang, L. C. Diao, Y. Tang, F. He, E. Z. Liu, C. N. He, C. S. Shi, J. J. Li, J. W. Sha, S. H. Ji, P. Zhang, L. Y. Ma, and N. Q. Zhao, *ACS Appl. Mater. Interfaces*, 10 (2018) 35145.
- 38. H. H. Wang, T. Liu, K. Bao, J. Cao, J. C. Feng, and J. L. Qi, J. Colloid Interface Sci., 562 (2020) 363.
- 39. M. X. Zhong, W. M. Li, C. Wang, and X. F. Lu, Appl. Surf. Sci., 575 (2022) 151708.
- 40. Q. Zhang, M. S. Sun, M. Q. Yao, J. Zhu, S. D. Yang, L. Chen, B. L. Sun, J. C. Zhang, W. C. Hu, and P. Zhao, *J. Colloid Interface Sci.*, 623 (2022) 617.
- 41. B. J. Zhang, C. T. Pan, H. J. Liu, X. S. Wu, H. L. Jiang, L. Yang, Z. M. Qi, G. Li, L. Shan, Y. X. Lin, L. Song, and Y. Jiang, *Chem. Eng. J.*, 439 (2022) 135768.
- 42. Z. L. Wang, W. J. Liu, J. Bao, Y. H. Song, X. J. She, Y. J. Hua, G. A. Lv, J. J. Yuan, H. M. Li, and H. Xu, *Chem. Eng. J.*, 430 (2022) 133100.
- 43. Y. T. Sun, and S. Chen, Sci. China-Chem., 65 (2022) 199.
- 44. T. Mushiana, M. Khan, M. I. Abdullah, N. Zhang, and M. M. Ma, Nano Research, 15 (2022) 5014.
- 45. J. F. Kang, F. Yang, C. Sheng, H. Xu, J. Y. Wang, Y. Qing, Y. Q. Wu, and X. H. Lu, *Small*, 18 (2022) 2200950.
- 46. H. Jiang, S. Y. Bu, Q. L. Gao, J. Long, P. F. Wang, C.-S. Lee, and W. J. Zhang, *Mater. Today Energy*, 27 (2022) 101024.
- 47. Z. J. Ji, Y. J. Song, S. H. Zhao, Y. Li, J. Liu, and W. Hu, Acs Catal., 12 (2022) 569.

© 2022 The Authors. Published by ESG (<u>www.electrochemsci.org</u>). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (http://creativecommons.org/licenses/by/4.0/).