Hydroxylated high-entropy alloy as highly efficient catalyst for electrochemical oxygen evolution reaction

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Oxygen evolution reaction (OER), a half reaction involved in electrochemical water splitting, CO₂ reduction, and metal–air batteries, restricts the efficiency of these energy conversion systems due to sluggish reaction kinetics [1,2]. To accelerate OER, highly efficient electrocatalysts are required. However, large-scale applications of the normally used OER catalysts (i.e. RuO₂ and IrO₂) are hampered by their instability and low abundance. It is highly desirable to develop earth-abundant catalysts with low cost, high activity and long-term stability. Co(Ni,Fe) (oxy)hydroxides (Co(Ni)-(O)OH) have emerged as promising OER catalysts in recent years [3]. The catalytic activities of ternary (oxy)hydroxides exceed those of single or binary (oxy)hydroxides due to the charge redistribution and optimized absorbing ability to *OH [4,5]. *In-situ* preparation of multi metals-based (oxy)hydroxides on metals or alloys can afford fast electron transfer, benefit the exposure of catalytic sites and keep the morphological stability in the electrochemical test.

High-entropy alloys (HEAs) possess uniform element distribution and favourable conductivity [6]. Most HEAs contain Co, Fe and Ni metals. Particularly, the addition of corrosion-resistant metals (i.e. Cr and Al) endows HEAs with superior anti-corrosion properties in basic electrolyte. Dai *et al.* [7] optimized the performance of MnFe-CoNi HEA catalyst for OER by constructing metal oxide nanosheets on HEA. Their study shows the interface regulation is an effective strategy to promote the catalytic activity of HEA.

In this study, a highly efficient electrocatalyst for OER was fabricated by introducing abundant OH[−] groups on the CoCrFeNiAl HEA precursor. The Co,Fe,Ni-(O)OH sheets were generated after HF treatment and subsequent

electrochemical activation. The as-obtained HEA-supported Co,Fe,Ni-(O)OH electrocatalyst exhibits an exceptional performance for OER.

Fig. 1a shows the granular morphology of HEA with micron size. The HEA treated by 0.4 mol L^{−1} HF (HF-HEA) presents hierarchical platelets, in good agreement with the morphology of the two-dimensional (2D) metal (oxy)hydroxides (Fig. 1b). The transmission electron microscopy (TEM) image confirms the formation of heterostructure after HF treatment, which consists of HEA core and metal (oxy)hydroxide shell (Fig. 1c) with a thickness of about 150 nm. From the energy dispersive spectrometer (EDS) mappings, the distribution of Co, Cr, Fe, Ni, Al and O is quite uniform (Fig. 1d and e₁–e₆). The selected area electron diffraction (SAED) pattern shows a typical ring structure characteristic for polycrystalline materials and agrees well with the Co₃NiOOH and Co(OH)₂ (Fig. S1).

In the Fourier transform infrared (FTIR) spectrum of HEA (Fig. 2a), only a weak O–H absorption peak from water is observed. For HF-HEA, a broad and strong absorption at 3500 cm^{−1} is attributed to O–H stretching. Absorption peak at 736 cm^{−1} corresponds to the bending and stretching mode of M–O [8]. No obvious signal is observed in the Raman spectrum of HEA (Fig. S2a). For HF-HEA, the peaks of M–OOH (336 cm^{−1}) and M–OH (540 cm^{−1}) appear (Fig. S2b) [9–10]. FTIR and Raman spectra results confirm the hydroxylation of HEA.

SEM-EDS results indicate that the molar ratio of the five elements keeps unchanged after HF treatment (Fig. S3). X-ray photoelectron spectroscopy (XPS) were performed to examine the chemical states of different elements in HEA and HF-HEA. Both HEA and HF-HEA

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Figure 1 Scanning electron microscopy (SEM) images of (a) the CoCrFeNiAl HEA precursor and (b) HF-HEA particles. (c) TEM image, (d) EDS layered image and (e₁–e₆) EDS element mappings of HF-HEA.

Figure 2 (a) FTIR spectra of HEA precursor and HF-HEA. High-resolution XPS spectra of (b) Co 2p, (c) Ni 2p, (d) Fe 2p, (e) O 1s of HEA and HF-HEA. (f) XRD patterns of HEA and HF-HEA.

contain Co, Cr, Fe, Ni and Al elements (Fig. S4a). The molar ratio of Co/Cr/Fe/Ni/Al is changed from 1.0/1.0/1.1/1.1/1.2 to 3.0/1.0/3.5/3.2/ 3.4. The data of Al and Cr

contents are slightly different from the results of EDS, which is probably due to the difference of the detection methods. According to the high-resolution XPS spectra of

Co 2p, Ni 2p and Fe 2p of HEA (Fig. 2b–d), the peaks of metals and metal oxides coexist [11–13]. The binding energies of Co 2p, Fe 2p and Ni 2p are a little higher than those of the reported papers, which is possibly due to the charge transfer between Co/Fe/Ni and Cr/Al. For HF-HEA, the signals of Co⁰, Fe⁰ and Ni⁰ disappear. The peak located at 783.29 eV in Fig. 2b can be deconvoluted into two peaks at 784.19 and 781.99 eV, which are associated with Co²⁺ and Co³⁺ of Co(OH)_x/CoOOH [14]. The peaks at 856.89 and 859.09 eV in Fig. 2c are derived from Ni²⁺ and Ni³⁺ of Ni(OH)_x/NiOOH [14]. The Fe 2p spectrum in Fig. 2d displays two peaks at 714.78 and 711.58 eV, indicating that Fe species are present as Fe³⁺ and Fe²⁺ in Fe(OH)_x/FeOOH [15]. From Fig. S4b, c, Cr, Cr oxide and Al oxide coexist on HEA. The Al and Cr species in HF-HEA are in the form of Al(OH)₃/AlOOH, Cr(OH)₃/CrOOH and Al_{N_{tv}}O_x/Cr_{N_{tv}}O_x [16–19]. The deconvoluted O 1s spectra of HEA consist of four peaks at 529.48, 530.38, 531.18 and 531.88 eV, which are ascribed to lattice oxygen of metal oxides (O₁), hydroxy oxygen (O₂), defect oxygen (O₃) and adsorbed OH[−] (O₄), respectively [20–22] (Fig. 2e). After HF treatment, the peak of the adsorbed H₂O at 533.47 eV appears (O₅). The ratio of metal(OH)_x/metal-OOH is 3.4, indicating metal(OH)_x dominates on HF-HEA. The X-band electron paramagnetic resonance spectroscopy (EPR) proves that HF-HEA contains O defects (Fig. S5). EPR signal appears when *g*-value is around 2.0, which originates from the unpaired electrons trapped at oxygen vacancies. These O defects can promote the adsorption of reaction intermediates on the catalyst and lower the energy barrier from OH* to O*, leading to faster OER kinetics [23].

X-ray diffraction (XRD) pattern of HEA in Fig. 2f suggests a single phase with face-centred cubic structure. While for HF-HEA, the diffraction peaks are assigned to isostructural Co(OH)₂ (PDF#45-0031), Co₃NiOOH (PDF#29-0491) and HEA. Relative to the standard data of 2θ=18.83° for Co(OH)₂ and 19.45° for Co₃NiOOH, the reflections shift to larger values by 0.12° and 0.26°, respectively (Fig. S6). Low-content Al_{N_{tv}}O_x/Cr_{N_{tv}}O_x could not be detected by XRD. No unary Ni, Fe, Co, Cr and Al based (oxy)hydroxides are generated. However, XPS results indicate the generation of Co,Cr,Fe,Ni,Al-based (oxy)hydroxides. Moreover, the element distribution is uniform. Therefore, it is possible that Fe, Cr and Al ions substitute partial Co or Ni ions in the lattice sites of Co(OH)₂ and Co₃NiOOH matrixes. Therefore, the species on HEA after HF treatment should be (Co,Cr,Fe,Ni,Al)-OH and (Co,Cr,Fe,Ni,Al)-OOH.

XPS measurement indicates Co(OH)_x/CoOOH, Ni

(OH)_x/NiOOH and Fe(OH)_x/FeOOH are generated on HF-CoFeNi (Fig. S7). By contrast, HF-HEA shows decreased binding energies of Fe³⁺, Co³⁺ and Ni³⁺ (Table S1), suggesting the stronger ability of transferring electrons of HEA than that of CoFeNi. Additionally, the molar ratio of Ni³⁺/Ni²⁺ on HF-HEA is noticeably higher than that on HF-CoFeNi (Fig. 2c and Fig. S7c), which might be caused by the introduction of Cr/Al ions.

We further performed EPR to reveal the electronic structures of HEA and HF-HEA. The spectra of HEA and HF-HEA show broad signals with *g*=2.2 (Fig. S8), which can be attributed to the high spin Co²⁺, Ni²⁺ and Cr³⁺ sites in octahedral environments [24–26]. The signals at *g*=4.20 are ascribed to Fe³⁺ ions in distorted octahedral field [27]. After HF treatment, the intensities of the two signals are decreased, suggesting the change of the electronic structures and the valence states of Co, Fe, Cr, Ni cations on the surface of HEA in the transition process from metal oxides to metal hydroxides.

The performances of different electrocatalysts were evaluated. The OER polarization curves of HEA precursor, HF-HEA and commercial RuO₂ are shown in Fig. 3a. The OER catalyzed by RuO₂ occurs at 1.40 V and 235 mV of overpotential (*η*) is required to reach a current density of 10 mA cm^{−2} (*j*₁₀). HEA shows an onset potential (*E*_{on}) of 1.492 V and *η* of 360 mV at *j*₁₀. Compared with the HEA precursor, HF-HEA shows a negative shift of *E*_{on} (1.434 V) and *j*₁₀ can be achieved at *η* of 265 mV. The current density of HF-HEA at potential positive than 1.53 V is higher than that of RuO₂. After continuous cyclic voltammetry (CV) operation in the range of 1.2–1.7 V with a scan rate of 100 mV s^{−1} for 1000 cycles, the activity of HF-HEA is further optimized with *E*_{on} of 1.41 V and *η* of 240 mV to reach *j*₁₀ (Fig. 3b). The activated HF-HEA is abbreviated as HF-HEA-a. The activities of RuO₂ and HEA after same operation are worsened due to the instability (Fig. 3b and Fig. S9). After further activation of 1000 cycles of CV, the performance of HF-HEA-a shows no obvious improvement (Fig. S10).

The states of Co, Cr, Fe, Ni, Al and O on HF-HEA-a were examined by XPS (Fig. S11). The molar ratio of Co/Fe/Ni is 1.64:1:1.62. The signals of low-valence Co/Fe ions disappear and the binding energy of Ni³⁺ increases from 859.19 to 861.5 eV, indicating the electrochemical activation can transform Co²⁺, Fe²⁺ and Ni³⁺ to higher-valence ions [28]. The contents of Cr and Al are approaching 0, suggesting the dissolution/leaching of Al and Cr ions. Therefore, the main active component on the surface of HF-HEA-a is Co,Fe,Ni-(O)OH.

The intrinsic activities of HEA, HF-HEA and HF-HEA-

Figure 3 (a) Polarization curves of HEA, HF-HEA and RuO₂. (b) CV curves of HF-HEA and RuO₂ before and after 1000 CV cycles activation. (c) Tafel slopes of HEA, HF-HEA, HF-HEA-a and RuO₂. (d) Nyquist plots of HEA, HF-HEA and HF-HEA-a.

a were analyzed in terms of Tafel plots (Fig. 3c). The Tafel slope of HF-HEA is 56.8 mV dec⁻¹, smaller than those of HEA (88.1 mV dec⁻¹) and RuO₂ (77.2 mV dec⁻¹). After 1000 cycles of CV, Tafel slope of HF-HEA is reduced to 52.7 mV dec⁻¹. Therefore, the OER catalyzed by HF-HEA-a is controlled by *OH adsorption and O-O formation. The performance of HF-HEA-a is comparable or superior to other HEA electrocatalysts (Table S2). The electrochemical impedance spectroscopy (EIS) data of HEA, HF-HEA and HF-HEA-a are fitted with an equivalent circuit (Fig. 3d). The Nyquist plots unravel that HF-HEA-a exhibits significantly decreased charge-transfer resistance (R_{ct} =15 Ω) in comparison with HF-HEA (27.9 Ω) and HEA (531.5 Ω).

The performance of HF-HEA-a is superior to that of HF-CoFeNi-a (Fig. S12), indicating the key role of Cr and Al in improving the performance of HF-CoFeNi-a. To further explore the influence of Cr and Al on the performance of HF-HEA-a, OER polarization curves and

Tafel slopes of other HF-treated alloys after the same electrochemical activation operation were compared (Fig. S13). The samples are abbreviated as HF-N-a (N: different alloys). Compared with HF-CoCrFeNi-a and HF-CoFeNiAl-a, HF-CoFeNi-a has lower E_{on} , but higher Tafel slope. Compared with the three catalysts, HF-HEA-a presents the optimized catalytic activity with lower E_{on} and smaller Tafel slope, demonstrating the essential role of coexistence of Cr and Al in the formation of highly active electrocatalyst. HF-CoCr_{0.8}FeNiAl_{0.8}-a and HF-CoCr_{1.2}FeNiAl_{1.2}-a with insufficient and excessive Cr and Al show inferior performances to HF-HEA-a with OER currents at 1.51 and 1.52 V and Tafel slopes of 71.77 and 75.96 mV dec⁻¹, respectively. Therefore, HF-HEA-a derived from equimolar CoCrFeNiAl exhibits the optimized performance.

We compared the performances of Fe, Co, Ni metals and CoFeNi alloy after HF treatment and electrochemical activation (Fig. S14). It is discovered that the activity of

HF-CoFeNi-a is superior to the sample of HF-Co-a, HF-Fe-a and HF-Ni-a. The performance of Fe metals is improved after HF treatment, indicating that Fe plays important roles in enhancing the performance of HF-HEA. Previous literatures have proved that the catalytic activities of ternary (oxy)hydroxides exceed those of single or binary (oxy)hydroxides due to the charge redistribution and optimized adsorbing ability to $^*\text{OH}$ [4–6]. The introduction of Fe could improve the performance of CoOOH and NiOOH. For example, Ye *et al.* [29] proved that the incorporation of Fe into CoOOH lattice could obviously induce lower energy levels of the intermediates through density functional theory (DFT) calculations. Trotochaud *et al.* [30] confirmed that Fe exerted a partial-charge transfer activation effect and then promoted the OER of the Ni sample. The role of Fe is different from those of Cr and Al. Cr and Al increase the concentration of Ni^{3+} on HF-HEA and the dissolution/leaching of Cr and Al ions in the electrochemical activation process increases the electrochemically active specific surface area (ECSA) of HF-HEA. Therefore, all the metal elements (Co, Cr, Fe, Ni and Al) are necessary for the highly efficient electrocatalyst.

The high electrochemical performance of HF-HEA-a might also be related to the HEA support. The performances of different metals and alloys as OER catalysts

were detected to estimate the contribution of HEA to OER performance. All the alloys show higher current intensity than metals, as seen from the polarization curves in Fig. S15. The catalytic activities of the alloys follow the sequence of: $\text{CoFeNiAl} > \text{CoCrFeNiAl} > \text{HEA} > \text{CoFeNi} > \text{CoCr}_{0.8}\text{FeNiAl}_{0.8} > \text{CoCrFeNi} > \text{CoCr}_{1.2}\text{FeNiAl}_{1.2}$. The addition of equimolar Al promotes the performance of CoFeNi, while equimolar Cr shows a negative effect. HEA is second only to CoFeNiAl in terms of catalytic performance. Therefore, HF-HEA-a exhibits the best catalytic activity among these catalysts due to the high performance of HEA-derived Co,Fe,Ni-(O)OH and the contribution of HEA.

The ECSA was estimated. The double-layer capacitance (C_{dl}) could well assess the ECSA [31]. The C_{dl} of HF-HEA-a (0.576 mF cm^{-2}) is higher than that of HF-CoFeNi-a ($0.0476 \text{ mF cm}^{-2}$), which means that Cr and Al can increase the ECSA of HF-CoFeNi-a (Fig. 4a and Figs S16, S17). The double-layer capacitances are 0.306 and 0.503 mF cm^{-2} for HEA and HF-HEA, respectively (Fig. 4a). The current densities were normalized to ECSA to compare the intrinsic activities of HEA, HF-HEA and HF-HEA-a (Fig. S18). Hydroxylation can enhance the intrinsic activity of HEA. The activity of HF-HEA-a surpasses that of HF-HEA, which means electrochemical activation not only increases ECSA, but enhances the

Figure 4 (a) C_{dl} of HEA, HF-HEA and HF-HEA-a. (b) Current density *versus* time curve of HF-HEA-a at 1.47 V for OER. (c, d) TEM images of HF-HEA-a after stability test.

catalytic ability of single catalytic site.

The current density of 10 mA cm^{-2} can be maintained for 11 h, indicating high stability of HF-HEA-a (Fig. 4b). After stability test, the morphology of the catalyst remains unchanged (Fig. 4c, d). The lattice fringe with spacing of 0.24 nm corresponds to the (101) facet of Co_2NiOOH . In view of the doping of Fe ions to Co_2NiOOH , approximate molar ratio and the similar radii of Fe, Co and Ni ions, the main component of the 2D shell is identified as $\text{Co}_2\text{FeNi-OOH}$. No lattice fringes of $\text{Co}_2\text{FeNi-OH}$ are observed due to the reconstruction of $\text{Co}_2\text{FeNi-OH}$ to $\text{Co}_2\text{FeNi-OOH}$ in the electrocatalysis process [32,33].

To sum up, there are several reasons for the superior performance of HF-HEA-a. First, HEA accelerates the charge transfer. Second, *in situ* generated metal (oxy) hydroxides sheets reduce the interface resistance of metal (oxy)hydroxides/HEA heterostructure. Third, oxygen defects on HF-HEA can promote the adsorption of reaction intermediates. Last, Cr and Al increase the concentration of Ni^{3+} on HF-HEA and the dissolution/leaching of Cr and Al ions in the electrochemical activation process increases the ECSA of HF-HEA.

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Supplementary information Experimental details and supporting data are available in the online version of the paper.

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羟基化高熵合金用作电化学析氧反应高效催化剂

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摘要 高熵合金(HEA)不仅是有潜力的电化学析氧反应的催化剂,也可以用作电催化剂的载体. 本文采用HF处理高熵合金使其羟基化(HF-HEA),然后再进行原位电化学活化,从而得到一种新型高效的CoCrFeNiAl HEA负载的Co,Fe,Ni-(O)OH电催化剂. 该电催化剂仅用240 mV超电势就可产生10 mA cm⁻²的电流密度, Tafel斜率为52.7 mV dec⁻¹. 本研究发现Cr和Al促进了HEA/Co,Fe,Ni-(O)OH的电化学活性. Cr和Al不仅增加了HF-HEA表面Ni(OH)_x/NiOOH的Ni³⁺/Ni²⁺摩尔比例,而且在电化学活化过程中Cr³⁺和Al³⁺的溶出增加了HF-HEA的电化学活性表面积.