

Increased Oxygen Evolution Activity in pH-Universal Electrocatalyst: Urea-Modified NiFeCoCN Medium-Entropy Alloy

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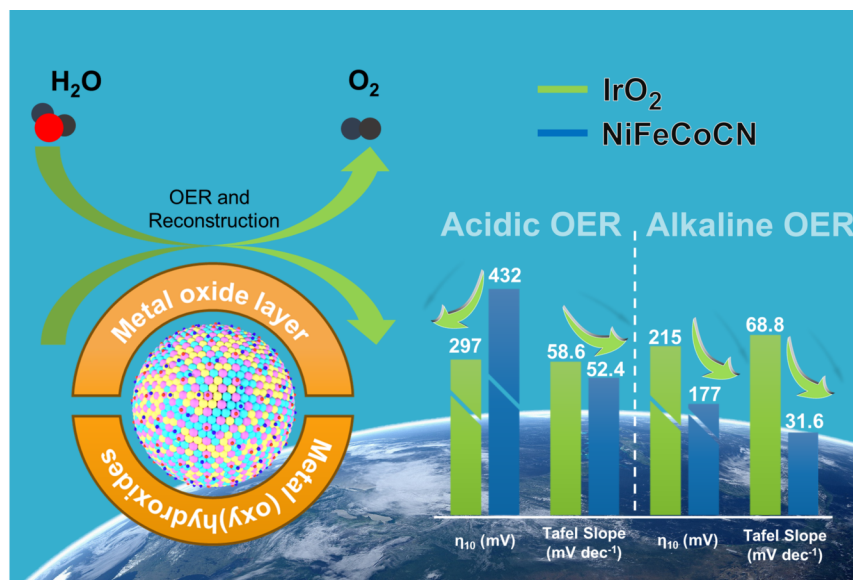
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Abstract

The kinetic process of a slow oxygen evolution reaction (OER) always constrains the efficiency of overall water electrolysis for H₂ production. In particular, nonprecious metal electrodes for the OER have difficulty simultaneously possessing good electrocatalytic activity and long-term stability in pH-universal media. In this work, urea is first used as a pore-forming agent and active C/N source to fabricate a nanoporous NiFeCoCN medium-entropy alloy (MEA) by high-temperature sintering based on the nanoscale Kirkendall effect. The NiFeCoCN MEA achieves an overpotential of 432 mV at a current density of 10 mA cm⁻² and a lower Tafel slope of 52.4 mV dec⁻¹ compared to the IrO₂/Ti electrode (58.6 mV dec⁻¹) in a 0.5 M H₂SO₄ solution. In a 1 M KOH solution, the NiFeCoCN MEA obtains an overpotential of 177 mV for 10 mA cm⁻² and a Tafel slope of 36.1 mV dec⁻¹, which is better than IrO₂/Ni foam. This work proves a novel strategy to design and prepare nanoporous MEA materials with desirable C/N species, which provides promising prospects for the industrial production of H₂ energy.

Graphical abstract

The nanoporous NiFeCoCN medium-entropy alloy achieves outstanding electrochemical activities and long-term durability for durable pH-universal oxygen evolution reaction, which is very competitive among the existing RuO₂-/IrO₂-based and Ni-based electrocatalysts.



Increased Oxygen Evolution Activity in pH-Universal Electrocatalyst: Urea-Modified NiFe-CoCN Medium-Entropy Alloy

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ABSTRACT

The kinetic process of a slow oxygen evolution reaction (OER) always constrains the efficiency of overall water electrolysis for H₂ production. In particular, nonprecious metal electrodes for the OER have difficulty simultaneously possessing excellent electrocatalytic activity and stability in pH-universal media. In this work, urea is first used as a pore-forming agent and active C/N source to fabricate a nanoporous NiFeCoCN medium-entropy alloy (MEA) by high-temperature sintering based on the nanoscale Kirkendall effect. The NiFeCoCN MEA achieves an overpotential of 432 mV at a current density of 10 mA cm⁻² and a lower Tafel slope of 52.4 mV dec⁻¹ compared to the IrO₂/Ti electrode (58.6 mV dec⁻¹) in a 0.5 M H₂SO₄ solution. In a 1 M KOH solution, the NiFeCoCN MEA obtains an overpotential of 177 mV for 10 mA cm⁻² and a Tafel slope of 36.1 mV dec⁻¹, which is better than IrO₂/Ni foam. This work proves a novel strategy to design and prepare nanoporous MEA materials with desirable C/N species, which provides promising prospects for the industrial production of H₂ energy.

KEYWORDS: Oxygen evolution reaction; Medium-entropy alloy; Urea; Electrocatalytic activity; Stability

INTRODUCTION

Hydrogen energy is an important component of the future energy system, and it is an important carrier to achieve green and low-carbon development [1, 2]. The oxygen evolution reaction (OER) as an anode reaction during water decomposition is a four-electron transfer process, which requires a higher overpotential than the hydrogen evolution reaction (HER) in a two-electron transfer process [3, 4]. This phenomenon severely limits the efficiency of electrolyzed water to hydrogen. In industrial applications, the IrO_2 electrocatalyst has good electrocatalytic activity and stability, especially in acidic solution [5, 6], but the scarcity of iridium and extremely high cost make it difficult to apply on a large scale in the industry of H_2 production [7, 8]. Since the anode in the proton exchange membrane (PEM) water electrolytic cell is performed in a strongly acidic environment, the anodic electrocatalyst is usually defined as IrO_2 [9, 10]. Moreover, the current electrocatalysts for the alkalious OER must further decrease the overpotential and increase the Faraday efficiency. Therefore, research on nonprecious metal-based electrocatalysts with high activity performance and long-term stability for pH-universal OER is significant [11-14].

High-entropy alloys (HEAs) can be used as OER electrocatalysts because of the synergistic effect among different elements in the solid solution. However, HEAs requires all atoms to exist in similar proportions to ensure an entropy of 1.5 R or higher, which has fundamental limitations in optimizing the composition of electrocatalysts [15-18]. Medium-entropy alloys (MEAs) are composed of three or four main elements, and their entropy is smaller than that of HEAs but higher than that of traditional alloys. Compared with HEAs, MEAs are easier to control the composition of the alloy to maximize catalytic activity while keeping the long-term stability, and due to the lattice distortion and synergy effects, MEAs also has excellent electrocatalytic activity [15, 19]. Meanwhile, the single phase and low free enthalpy of MEAs contribute to excellent corrosion resistance [20]. However, the application of MEAs in the field of OER electrocatalysis has rarely been reported. Han et al. prepared three-dimensional porous medium-entropy alloy aerogels (MEAAs) of $\text{Ni}_{50}\text{Co}_{15}\text{Fe}_{30}\text{Cu}_5$ by using a self-propagating sintering method, which simultaneously achieved excellent methanol oxygen reaction (MOR) and HER electrocatalytic properties [21].

Compounds of Ni, Fe and Co have higher catalytic activity than Ir in OER, which is due to they are the first-row transition metals in the periodic table, have lower crystal field stabilization energy and smaller d orbitals than Ir [22-24]. The bulk Ni in the elemental Ni-based oxide for the OER is considered the active centre of the OER, and oxygen is released through the NiOO^- precursor. The incorporation of Fe in electrocatalysts usually enables the OER to occur at lower overpotentials because new highly active sites are generated on the surface [25, 26]. The incorporation of Co in electrocatalysts can improve the conductivity of the surface (oxy)hydroxide layer based on the synergistic effect of multiple metal species and further promoting proton migration and charge transportation on the catalyst surface [27, 28]. Recently, studies have shown that the electrocatalyst with C and N elements produces higher OER activity than the pristine one by adjusting the binding energies of the adsorbed/desorbed intermediate ($^*\text{O}$, $^*\text{OH}$ and $^*\text{OOH}$) on the active sites [29-32]. For example, our previous work proves that C/N/S doping in Ni-based alloy electrodes improved the OER activity via the nitrocarburizing and sulfonitrocarburizing technology [33].

In this work, urea ($\text{CH}_4\text{N}_2\text{O}$) with theoretical carbon and nitrogen contents of 20 at.% and 46 at.%, respectively [34, 35], is employed as a pore-forming agent and active C/N source to fabricate a nanoporous NiFeCoCN medium-entropy alloy (MEA) based on the nanoscale Kirkendall effect via high-temperature sintering. The NiFeCoCN MEA exhibits excellent electrocatalytic activity and long-term stability in pH-universal media.

EXPERIMENTAL SECTION

Preparation of bulk NiFeCoCN MEA

Iron (12.7 μm , > 99.5%), cobalt (13.7 μm , > 99.5%) and nickel (17.2 μm , > 99.7%) powders and urea (molecular biology grade, [?] 99.5%) were purchased from Search Bureau Chemicals (Shanghai, China). First, Ni, Fe and Co powders were weighed with an atomic percent of 56 at.%, 33 at.%, 11 at.%, then, uniformly ground urea powders were added in different mass percentages (0-30 wt.%). For comparison, pure Ni, pure Fe, pure Co, NiFe, NiCo, FeCo, NiFeCo, NiFeCoCN, NiFeCoCN-1 and NiFeCoCN-2 were fabricated,

and all as-prepared samples were described in Table S1. According to the Linear Sweep Voltammetry (LSV) data of all as-prepared samples (see Figure S1), the optimal composition of NiFeCoCN was identified for the preparation of nanoporous compound electrodes. A planetary ball mill (Nanjing University Instrument Factory XQM-2A) was used to mix all metal and urea at a rotational speed of 260 r/min for 6 hours, and ball grinding beads were not placed in the ball grinding tank to avoid element pollution. The mixed powder was pressed into a cylindrical compact of $\phi 12 \text{ mm} \times 6 \text{ mm}$ under 580 MPa. The tube furnace (Hefei Kejing Materials Technology Corp., OTF-1200X) was employed to sinter the cylindrical compact at a high temperature of 900 degC for 1 hour. Argon gas was poured into evacuate the air in the tube for 20 minutes before sintering. The entire sintering process was performed in a high-purity argon atmosphere.

Materials characterizations

The phase analysis of the as-prepared samples was performed using XRD (Bruker D8 ADVANCE). The surface morphology, microstructure and element distribution of the electrode were determined by FESEM (FEI Nova Nano SEM450). Transmission electron microscopy (TEM) attached with an energy dispersive X-ray spectrometer (EDS), high-resolution TEM (HRTEM, FEI Talos F200X) equipped with selected area electron diffraction (SAED) were used to verify the crystal structure and element distribution. XPS (KRATOS ANALYTICAL LTD Axis Ultra DLD) was used to further determine the change in element valence state before and after the electrochemical ageing of the electrode. To determine the specific surface area and average pore size, BET (Micromeritics ASAP 2460) was tested by using N_2 as the adsorbed gas. An infrared C-S analyzer (LECO CS-844) and O-N-H joint analyzer (LECO ONH-836) were used to quantify the contents of C and N in the sample, respectively.

Electrochemical measurements

Using a standard three-electrode system at an electrochemical workstation (CHI-660C, Shanghai CHI Instruments, Inc.) to finished all electrochemical tests in this work and electrolyte is 0.5 M H_2SO_4 and 1.0 M KOH. The as-prepared samples were connected with copper wires and subsequently sealed to become working electrodes (1 cm^2). A platinum sheet and a graphite rod were used as auxiliary electrodes in the acidic solution and alkaline solution, respectively. Two calibrated saturated calomel electrodes (SCEs) were used as reference electrodes under different solutions of 1 M KOH [33] and 0.5 M H_2SO_4 [36], respectively. The polarization curve of the OER was determined by linear sweep voltammetry (LSV) with a scan rate of 1 mV s^{-1} . Tafel slopes with iR_s correction were obtained by the LSV curves, where R_s is the solution resistance obtained by EIS. Electrochemical impedance spectroscopy (EIS) was measured at 0.01 Hz-100 kHz with an amplitude of 5 mV. The ECSA was obtained by CV measurements of the C_{dl} capacitance at non-Faradaic potentials and different scan rates of 10-100 mV s^{-1} in a 1 M KOH solution, 100 to 1000 mV s^{-1} in a 0.5 M H_2SO_4 solution. Electrode stability was measured at a constant step current density of 10, 50, 100 and 200 mA cm^{-2} . Long-term stability for 28 hours was achieved using a two-electrode cell at a current density of 100 mA cm^{-2} in 0.5 M H_2SO_4 solution. Faraday efficiency formula placed in supplementary materials.

DFT calculations

The data of density functional theory (DFT) are calculated by Vienna ab initio simulation package (VASP). The generalized gradient approximation (GGA) is used to calculate the exchange correlation energy in the Perdew-Burke-Ernzerhof (PBE) functional framework, and the projector augmented wave (PAW) method is used to describe the electron-ion interaction. The energy cutoff for the plane wave expansions is set to 600 eV, while the energy and force for the convergence threshold are set to 10^{-5} eV and $0.03 \text{ eV \AA}^{-1}$, respectively. A vacuum space of 10 Å is increased to avoid the interaction between periodic images generated during the calculation of the flat plate model. In addition, the dipolar correction was adopted for slab models with the symmetrization switching off. The Brillouin zone was sampled with $2 \times 2 \times 1$ k-points.

Both EDS and XPS data (see Table S2 and Table S3) show that Ni in the as-prepared electrodes will dissolve in 0.5 M H_2SO_4 solution, so the $\gamma\text{-Fe}_2\text{O}_3$ after OER ageing is selected as the main model. Initially, constructing a (110) slab model of $\gamma\text{-Fe}_2\text{O}_3$ consisting of four layers to facilitate comparison. To conform with XPS data, randomly substituted some Fe atoms in the structure with Co and Ni atoms while maintaining

the appropriate ratios of Fe, Co, and Ni atoms. Subsequently, employing the Ovito method in the AtomsK software to amorphize the first layer of the slab, resulting in an amorphous model.

RESULTS AND DISCUSSION

Figure 1a shows the electrode fabrication process of nanoporous NiFeCoCN MEAs with different urea contents. Interconnected nanopores and nanogaps are formed based on the nanoscale Kirkendall effect due to the different diffusion rate of atoms/vacancies between the diffusion couples (e.g., Ni/Co, Ni/Fe and Fe/Co) during the high-temperature sintering process [36, 37]. Urea is first isomerized into isocyanic acid (HNCO) during the heating process via a boiling reaction at 380 °C-400 °C. When the temperature increases to 900 °C, urea volatilizes to form pores, and part of the decomposed active C and N form solid solutions with Ni, Fe and Co [38-40]. Figure 1b shows the X-ray diffraction (XRD) curves of NiFeCoCN. The three peaks of NiFeCoCN at 44.3°, 51.5° and 75.8° correspond to the (111), (200), and (220) facets of the γ -Ni solid solution of the face-centred cubic (FCC) structure, respectively. This consequence is consistent with the MEA composed of NiFeCo elements analysed by XRD in other papers [41, 42]. The diffraction peaks of NiFeCo, NiFeCoCN, NiFeCoCN-1 and NiFeCoCN-2 were basically unchanged (see Figure S2), which indicates the urea content had little effect on the MEA structure. However, compared with the standard PDF card (PDF#04-0850) of pure Ni, the diffraction peaks of the NiFeCoCN exhibit an obvious negative shift, which should be ascribed to the incorporation of Fe, Co, C and N in the γ -Ni solid solution. Hence, nanoporous NiFeCoCN with a single γ -Ni solid solution structure is confirmed in combination with the latter TEM analysis in Figure 1e.

Figures 1c and d show the FESEM images of NiFeCoCN. As shown in the figures, NiFeCoCN has an interconnected porous structure with a nanosheet morphology of approximately 10-20 nm (see Figure S3). Figure S4 and Table S4 show that NiFeCoCN has a BET surface area of 0.63 m² g⁻¹ with an average pore diameter of 10.21 nm. This result indicates that urea plays a critical role in the formation of nanoporous structures of NiFeCoCN and favourably forms abundant active sites for OER. As shown in Figure 1e, the 0.211 nm and 0.182 nm interplanar spacings of NiFeCoCN correspond to the (111) and (200) facets of the γ -Ni solid solution, respectively. The selective diffraction pattern (SAED) also shows the (111), (200), and (220) facets of the γ -Ni solid solution, which is consistent with the XRD analysis. Figure 1f is the HRTEM taken from Figure 1e and clearly shows that the crystal lattice has many defects. Figure 1g is obtained by performing an inverse fast fourier transformation (IFFT) on Figure 1f. As shown in the figure, the dislocations can also demonstrate lattice distortion occurred in NiFeCoCN. The high-angle annular dark-field scanning-transmission electron microscopy (HAADF-STEM) and energy dispersive X-ray (EDX) elemental mappings in Figures 1h-n show that Fe, Co, Ni and C, N, O atoms are uniformly dispersed in the nanoporous NiFeCoCN bulk. The atomic percentages of C and N in NiFeCoCN are 1.1 at.% and 0.25 at.%, respectively (see Table S5). These results prove the incorporation of C/N in the NiFeCoCN bulk and show that urea can be used as a C/N source. Based on the above analysis, NiFeCoCN is indeed a MEA with the nonmetallic incorporation of C/N.

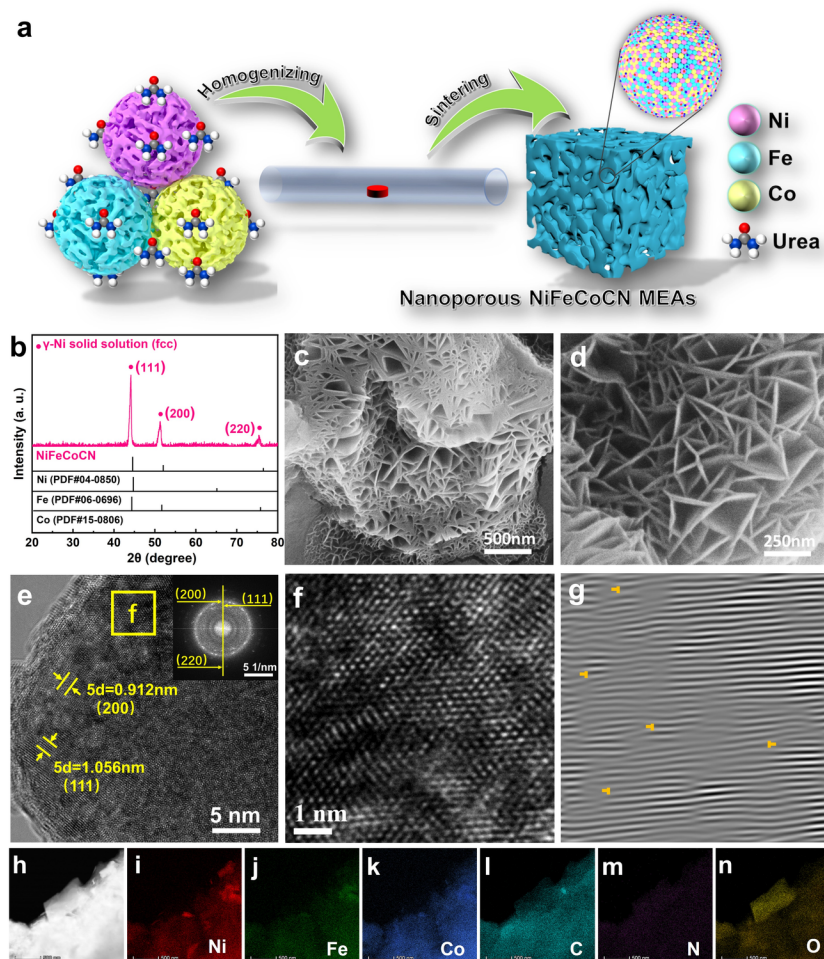


Figure 1 (a) Preparation process of Nanoporous NiFeCoCN MEAs. (b) XRD patterns of NiFeCoCN (c, d) FESEM images of the NiFeCoCN at different magnifications. (e) HRTEM and SAED images of the NiFeCoCN before ageing. (f) Part of the HRTEM images in e. (g) IFFT images of f. (h) HAADF-STEM images of the NiFeCoCN before ageing. (i) Ni, (j) Fe, (k) Co, (l) C, (m) N and (n) O elemental mapping from EDX in the unaged NiFeCoCN.

To explore the real intrinsic nature of the acidic OER, the NiFeCoCN electrode for XPS measurement was subjected to an ageing of 5000 seconds at a current density of 100 mA cm^{-2} in a $0.5 \text{ M H}_2\text{SO}_4$ solution. Figure 2 displays the XPS spectra of the NiFeCoCN electrode before and after electrochemical ageing. The XPS full spectra of NiFeCoCN before and after electrochemical ageing confirm the Ni, Fe, Co, C, N and O elements exist on the outer surfaces (Figure S5 and Table S3). The Ni 2p spectrum of the unaged sample in Figure 2a displays the two main peaks of Ni 2p_{3/2} at 852.1 eV and Ni 2p_{1/2} at 859.3 eV correspond to Ni^{0+} , Ni 2p_{3/2} at 854.6 eV and Ni 2p_{1/2} at 873.1 eV correspond to Ni^{2+} . After electrochemical ageing, the peaks of Ni 2p_{3/2} at 856.3 eV and Ni 2p_{1/2} at 874.1 eV correspond to Ni^{2+} , and the peaks of Ni^{0+} disappear [43-45]. The Fe 2p spectrum of the unaged sample in Figure 2b displays the two main peaks of Fe 2p_{3/2} at 706.7 eV and Fe 2p_{1/2} at 719.5 eV correspond to Fe^{0+} , Fe 2p_{3/2} at 709.7 eV and Fe 2p_{1/2} at 724.3 eV correspond to Fe^{2+} . After electrochemical ageing, the peaks of Fe 2p_{3/2} at 711.1 eV and Fe 2p_{1/2} at 724.8 eV correspond to Fe^{3+} and the peaks of Fe^{0+} disappear [45-47]. The Co 2p spectrum of the unaged sample in Figure 2c displays the two main peaks of Co 2p_{3/2} at 780.3 eV and Co 2p_{1/2} at 795.5 eV correspond to Co^{2+} , the peak of Co 2p_{3/2} at 777.5 eV correspond to Co^{0+} . After electrochemical ageing, the peaks of Co 2p_{3/2} at 781.8

eV and Co 2p_{1/2} at 798.2 eV correspond to Co³⁺, Co 2p_{3/2} at 786.2 eV can correspond to Co²⁺ and the peaks of Co⁰⁺ disappear [48, 49]. In Figure 2d, the O 2p spectra of the unaged sample located at 532.9 eV, 531.3 eV, and 529.4 eV correspond to adsorbed water, absorbed oxygen and lattice oxygen, respectively [44, 48, 50]. After electrochemical ageing, the binding energy of the absorbed oxygen peak is positively shifted by approximately 0.4 eV. Obviously, the binding energy of metals and low-valence metal oxides (e.g., Ni, Fe, Co, NiO, FeO, CoO) is positively transferred to a higher binding energy to form high-valence metal oxides (e.g., NiO, Fe₂O₃, Co₃O₄), which indicates the NiFeCoCN has surface reconstruction during the initial OER process in a 0.5 M H₂SO₄ solution. The C 1s spectrum of the unaged sample in Figure 2e shows peaks at 284.6 eV, 286.1 eV, 284.6 eV, and 282.0 eV, which correspond to C-C, C-N, C-O and NiC_x, respectively [40]. However, the NiC_x peak disappears after electrochemical ageing, which indicates a reconstruction of surface structure during the initial OER process. The N 1s spectrum of the unaged sample presents two peaks at 399.9 eV and 404.4 eV in Figure 2f, which belong to pyridinic N and graphite N, respectively. The pyridinic N in OER electrocatalysts tends to receive electrons, and graphite N tends to provide electrons, both of which positively influence the OER activity [51, 52]. To explore the real intrinsic nature of the alkaline OER, the NiFeCoCN electrode was also subjected to an ageing of 5000 seconds at a current density of 100 mA cm⁻² in a 1 M KOH solution. Figure S6 displays the XPS spectra of the NiFeCoCN electrode before and after electrochemical ageing. Studies have shown that metal catalysts can be reconstructed as metal oxides in the initial stage of OER under acidic conditions, while catalysts including transition metals can be reconstructed as metal (oxy)hydroxides under alkaline conditions, which is consistent with previous work [33, 36].

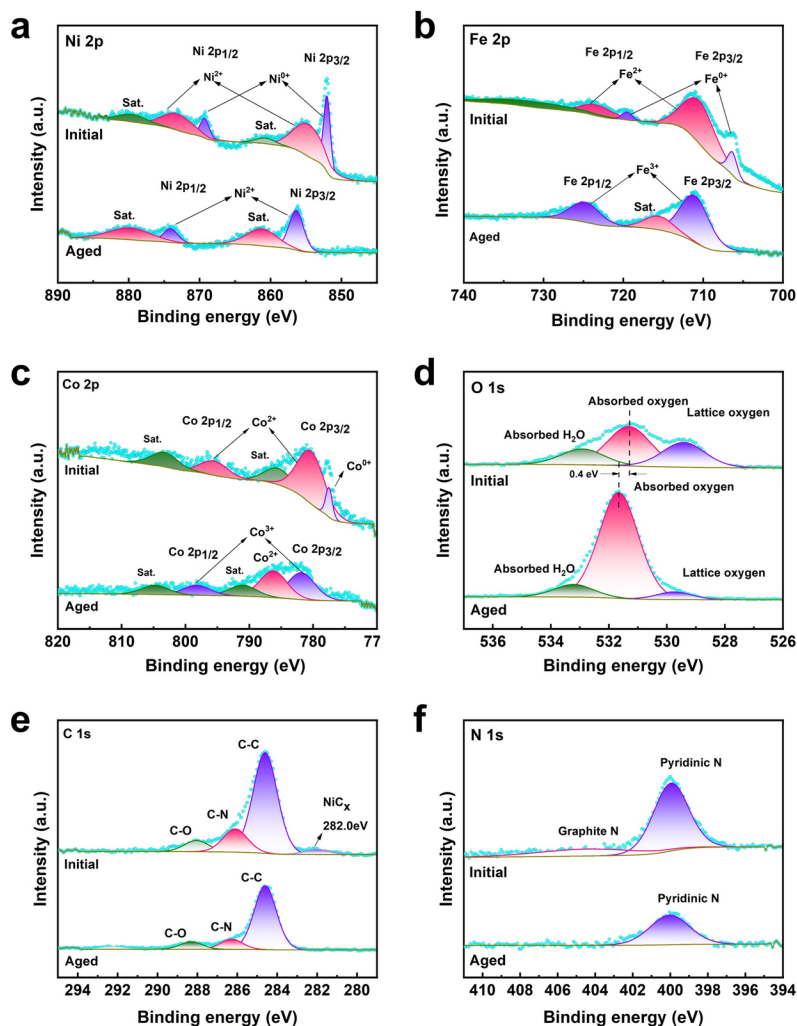


Figure 2 (a) Ni 2p, (b) Fe 2p, (c) Co 2p, (d) O 1s, (e) C 1s and (f) N 1s XPS spectra of NiFeCoCN before and after electrochemical ageing in a 0.5 M H_2SO_4 solution.

Figure 3a shows the linear sweep voltammetry (LSV) curves of NiFeCo, NiFeCoCN and IrO_2/Ti in a 0.5 M H_2SO_4 solution at a scan rate of 1 mV s^{-1} . NiFeCoCN electrode has the best electrocatalytic activity for the acidic OER in comparison with other electrodes. The overpotentials of the NiFeCoCN electrode for the acidic OER at current densities of 10 mA cm^{-2} and 100 mA cm^{-2} are only 432 mV and 567 mV, respectively, which are significantly lower than those of NiFeCo (526 mV and 664 mV) (see Table S6). The consequence indicates an obvious improvement in electrocatalytic activity due to the incorporation of C/N species, which may be attributed to a change of the electronic structure of active sites and an increase of the coordination unsaturated metal active sites for the OER. In addition, the NiFeCoCN electrode achieves a low Tafel slope of 52.4 mV dec^{-1} (see Figure 3b), which is even lower than the value of 58.6 mV dec^{-1} of the noble IrO_2/Ti electrode.

Electrochemical impedance spectroscopy (EIS) is the preferred technique to study the kinetic mechanism of porous electrodes for the OER, because the output is directly affected by the electrode porosity. Figure 3c shows the EIS of NiFeCo, NiFeCoCN and IrO_2/Ti electrodes. All data are fitted using the equivalent circuit of $(R_s(Q_{dl}R_{ct}))$, where R_s , Q_{dl} and R_{ct} are the solution resistance, electric double layer capacitance

and charge transfer resistance in the OER process, respectively [53, 54]. As shown in Figure 3c and Table S7, the R_{ct} value of NiFeCoCN is $0.15 \Omega \text{ cm}^{-2}$, which is much smaller than that of NiFeCo ($14.36 \Omega \text{ cm}^{-2}$) and similar to that of IrO_2/Ti ($0.17 \Omega \text{ cm}^{-2}$), which indicates superior charge-transfer ability and high OER activity in acidic media. Moreover, NiFeCoCN electrode also exhibits an excellent Faradaic efficiency of 94.7% in a 0.5 M H_2SO_4 solution (see Figure S7).

The electrochemical active surface area (ECSA) is proportional to the catalytic performance and the specific activity of the catalyst can be obtained by calculating the ratio between the current density corresponding to a given voltage (I_{OER}) and ECSA. The ECSA is usually calculated by using the electric double layer capacitance value (C_{dl}) based on CV data. Figure 3d shows the electric double layer capacitance data calculated based on Figure S8. As shown in the figure, the NiFeCoCN electrode has a higher C_{dl} value than NiFeCo. The ECSA and specific activity can be estimated as follows:

$$\text{ECSA} = C_{dl} / C_s \quad (1)$$

$$\text{Specific activity} = I_{OER} / \text{ECSA} \quad (2)$$

where C_s is the specific capacitance of the electrode material and takes the general value of the transition metal surface oxide: $40 \mu\text{F cm}^{-2}$ [55]. After calculation, the NiFeCoCN electrode obviously has higher ECSA of 105 cm^2 and specific activity of 2.7 mA cm^{-2} than that of the NiFeCo (67.5 cm^2 and 1.6 mA cm^{-2}), indicating an increase of the intrinsic activity owing to an incorporation of C/N species (see Table S8).

Stability is another important indicator for evaluating OER catalysts, especially in acidic electrolytes. Figure 3e shows the stability of the NiFeCoCN electrode in a 0.5 M H_2SO_4 solution. The NiFeCoCN electrode can stably perform for 10000 seconds at a current density of 100 mA cm^{-2} , and the oxygen evolution potential tends to stabilize over time. To further confirm the true stability, the long-term stability of the NiFeCoCN was determined in a 0.5 M H_2SO_4 solution, which could stably operate for approximately 28 hours at a current density of 100 mA cm^{-2} (see Figure S9), which indicates the excellent stability for the acidic OER. There is not a change of the phase on the surface of aged sample compared to initial sample (see Figure S10). However, the increased binding energy and O content shown in the XPS data indicate that the sample surface has an oxidation occurred, which is consistent with the data in Table S3. Figures 3f-h further exhibits the HRTEM images of the NiFeCoCN electrode before and after 5000 seconds of electrochemical ageing at a current density of 100 mA cm^{-2} in 0.5 M H_2SO_4 solution. As shown in Figures 3g and h, an amorphous metal oxide layer of approximately 7-10 nm thickness is formed on the surface of the aged electrode, which is consistent with the XPS analysis results. The surface and interior of the NiFeCoCN electrode without electrochemical ageing (see Figure 3f) show the ordered crystal structure of the γ -Ni solid solution, while the aged electrode undergoes obvious surface reconstruction. The relative reference also confirms the amorphous metal oxide layer that has formed on the outer surface of the electrocatalysts [56-58]. The metal oxide layer of the active centre for the OER in acidic medium is generally considered to be reconstructed by the dissolution/deposition or electromigration mechanism in the OER process [24, 59].

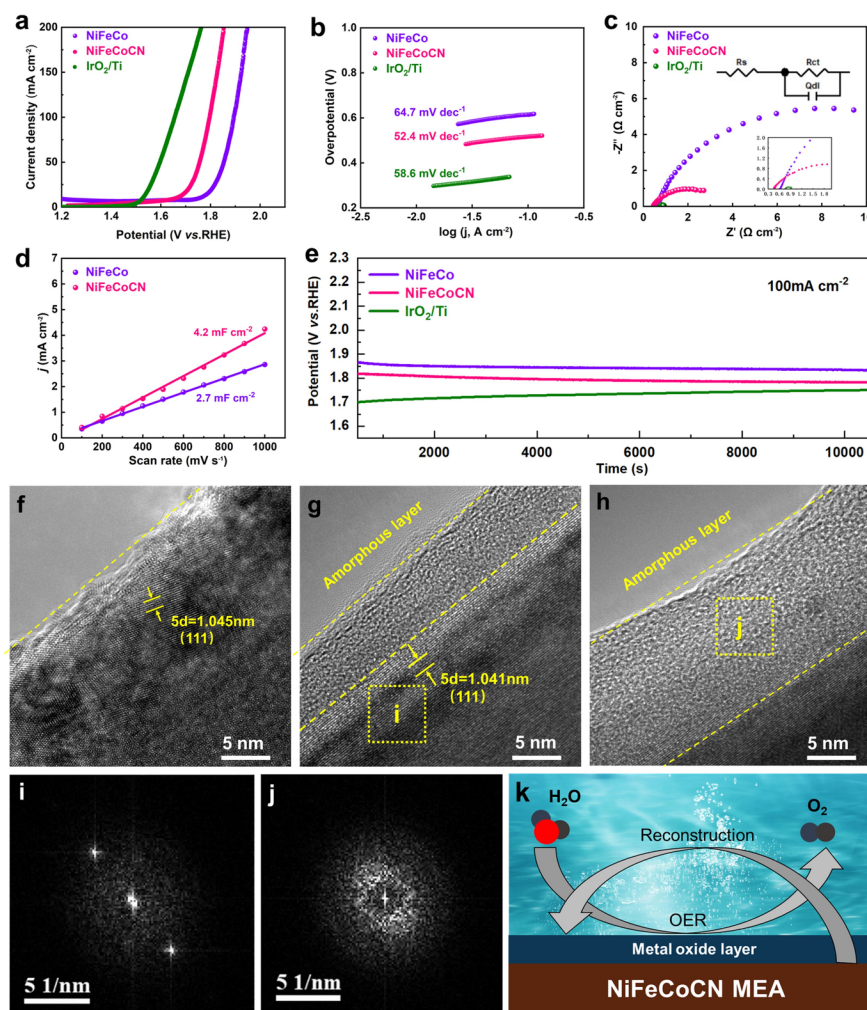


Figure 3 Electrocatalytic measurements. (a) LSV curves of the NiFeCo, NiFeCoCN and IrO₂/Ti electrodes in a 0.5 M H₂SO₄ solution with a scan rate of 5 mV s⁻¹. (b) The iR_s -corrected Tafel plots of all as-prepared electrodes derived from the curves of Figure 3a. (c) Nyquist plots of the EIS of all as-prepared electrodes measured at an OER voltage of 1.702 (*vs.* RHE) over a frequency range of 0.01 Hz–100 kHz in a 0.5 M H₂SO₄ solution. The insets are the equivalent circuit of R_s ($Q_{dl}R_{ct}$) and the plots in the high frequency region. (d) C_{dl} of NiFeCo and NiFeCoCN in a 0.5 M H₂SO₄ solution. (e) Galvanostatic tests of the electrodes at a constant current density of 100 mA cm⁻² in a 0.5 M H₂SO₄ solution. HRTEM images of the NiFeCoCN electrode (f) before and (g), (h) after electrochemical ageing. (i) SAED images of the NiFeCoCN bulk after ageing and (j) SAED images of the NiFeCoCN MEA surface after ageing. (k) Schematic diagram of the metal oxide layer reconstruction.

The alkaline OER performance of the NiFeCoCN was also measured to evaluate the potential prospect of practical application. Figure 4 shows the LSV, Tafel slope, EIS and multistep diagram of NiFeCo, NiFeCoCN and IrO₂/Ni foam during OER in a 1 M KOH solution. In Figure 4a, the overpotential of the NiFeCoCN electrode for the alkaline OER at a current density of 10 mA cm⁻² is only 177 mV, which is significantly lower than those of IrO₂/Ni foam (215 mV) and NiFeCo (239 mV). In Figure 4b, its Tafel slope reaches a low value of 36.1 mV dec⁻¹, which is also lower than IrO₂/Ni foam (68.8 mV dec⁻¹) and NiFeCo (46.2 mV dec⁻¹). In addition, the NiFeCoCN electrode has an extremely low charge transfer resistance (see Figure 4c and Table S7) and the NiFeCoCN electrode also has higher ECSA of 167.5 cm² and specific activity

of 2.2 mA cm^{-2} than the NiFeCo (80 cm^2 and 1.6 mA cm^{-2}) (see Figure 4d and Table S8), which indicates the higher intrinsic activity for the OER compared to other electrodes in a 1 M KOH solution. Figure 4e displays the multicurrent step experiment of all electrodes in a 1 M KOH solution at 10, 50, 100 and 200 mA cm^{-2} . The potential of the NiFeCoCN electrode exhibits almost no fluctuation at different currents, which confirms its excellent stability in alkaline solution. NiFeCoCN electrode also exhibits an excellent Faradaic efficiency of 97.6% in a 1 M KOH solution (Figure S7).

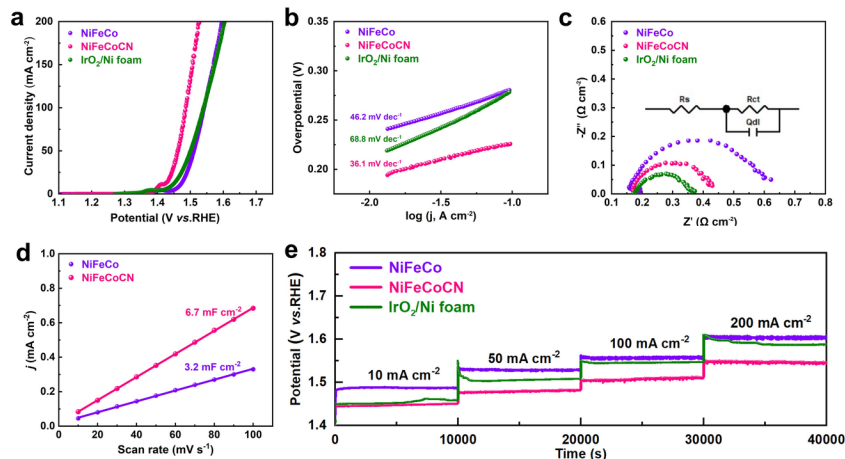


Figure 4 Electrocatalytic measurements. (a) LSV curves of the NiFeCo, NiFeCoCN and IrO_2/Ti electrodes in a 1 M KOH solution with a scan rate of 5 mV s^{-1} . (b) The iR_s -corrected Tafel plots of all as-prepared electrodes derived from the curves of Figure 4a. (c) Nyquist plots of the EIS of all as-prepared electrodes measured at an OER voltage of 1.503 (*vs.* RHE) over a frequency range of 0.01 Hz-100 kHz in a 1 M KOH solution. The insets are the equivalent circuit of $R_s (Q_{dl}R_{ct})$ and the plots in the high frequency region. (d) C_{dl} of NiFeCo and NiFeCoCN in a 1 M KOH solution. (e) Galvanostatic tests of the electrodes at constant current densities of 10-200 mA cm^{-2} in a 1 M KOH solution.

To further insight the intrinsic activity, DFT calculations were employed to study the process of modifying the electronic structure of the active sites by the C/N in the amorphous oxidation layer of NiFeCo and NiFeCoCN. In acidic media, the following steps can describe the four-electron OER pathways:

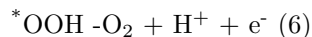
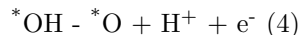


Figure 5a and Figure S11 show the models of intermediates (OH^* , O^* and OOH^*) adsorbed on the Fe site on the surface of NiFeCoCN MEA. The Gibbs free energies for each step of the reactions were calculated (0 and 1.23 V *vs.* RHE) (see Figure 5b, Table S9 and S10). The catalytic performance of OER is determined rate-determining step (RDS). At 1.23 V, O^* formation ($\text{OH}^* \rightarrow \text{O}^*$) with the NiFeCo MEA was the rate determining step (RDS) with a free energy difference of 0.768 eV. After introducing C/N, the formation energy of O^* on the NiFeCoCN MEA decreased to 0.45 eV. According to previous studies, the theoretical overpotential of OER can be determined by the adsorption free energy of O^* with respect to OH^* , referred to as $\Delta G(\text{O}^*) - \Delta G(\text{OH}^*)$ [14]. In other words, the NiFeCoCN MEA need a lower overpotential to drive water oxidation. The projected density of states (PDOS) of Fe s, Fe p and Fe d orbitals is calculated to insight the electronic structure (see Figure 5c). The total density of states (TDOS) of the Fe site in NiFeCoCN MEA is mainly contributed by d orbital, and the d-band center relative to Fermi level is -1.82 eV. For NiFeCo MEA,

the d-band center relative to Fermi level is -1.57 eV. It means that the d-band center of Fe in NiFeCoCN MEA shifts far away from Fermi level. The adjustment in d orbital of Fe caused by involving C/N leads to the weakened adsorption ability of the oxygen-containing intermediates, facilitating the reduction of energy barrier. In addition, Figure 5d shows the Bader charge computations of the model. Initially, the metal atoms (Ni, Fe, Co) in the NiFeCoCN MEA model transfer charges to O atom, respectively. When N atom replaces O atom in the NiFeCoCN MEA model, the charge transfer from metal atoms to N atom becomes less, and the Fe atom changes most significantly (1.24 e^- - 1.08 e^-). This phenomenon of less charges transfer at metal sites will repeat when C atom replace O atom. The result shows that electrons tend to be enriched at metal sites dominated by Fe after introducing C/N. This difference directly represents the weakened adsorption of O on the electron-rich metal sites over amorphous oxidation layer of NiFeCoCN MEA, facilitating the lower energy barrier of RDS and thus has excellent OER activity in acidic media.

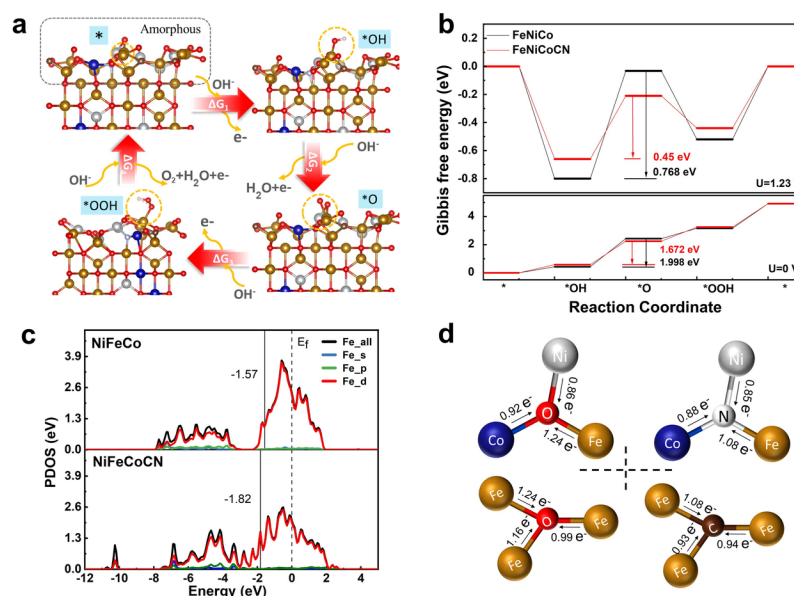


Figure 5 Calculation of density function theory. (a) Proposed 4e⁻ mechanism of OER on NiFeCoCN (110) in acidic media. The Fe coordinated O_h site is the active site. Ni, Fe, Co, C, N, O and H atoms are marked in silver, yellow, blue, brown, white, red and pink colors, respectively. (b) Gibbs free-energy diagrams of NiFeCo and NiFeCoCN. (c) Projected density of states of Fe total, Fe s, Fe p and Fe d orbitals in NiFeCo and NiFeCoCN. (d) The charge transfer before and after C/N replacement O is described by the electron transfer difference calculated based on the Bader charge computations. The black arrow shows the direction of electron transfer.

CONCLUSION

In summary, a nonprecious nanoporous NiFeCoCN MEA electrode was successfully fabricated by a facile method of high-temperature sintering with urea as a C/N source and pore-forming agent. The NiFeCoCN MEA electrode for the OER in 0.5 M H₂SO₄ has a lower Tafel slope (52.4 mV dec⁻¹) than noble IrO₂/Ti (58.6 mV dec⁻¹) and an overpotential of 432 mV at 10 mA cm⁻². The NiFeCoCN MEA electrode can be continuously operated for 28 hours at a current density of 100 mA cm⁻² in 0.5 M H₂SO₄, which confirms the superior stability for the acidic OER. In addition, NiFeCoCN MEA has an overpotential of 177 mV at a current density of 10 mA cm⁻² and a Tafel slope of 36.1 mV dec⁻¹, which are also lower than those of the IrO₂/Ni foam electrode (215 mV and 68.8 mV dec⁻¹, respectively). This work provides a novel strategy to design and fabricate OER electrocatalysts with low price and high performance in pH-universal media.

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