
Electronic Supplementary Information

NiCr-LDH-Co nanosheets on nickel foam as efficient oxygen evolution electrocatalysts in alkaline media

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EXPERIMENTAL SECTION

Materials.

Nickel (II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\geq 97.0\%$), chromium (III) nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\geq 99.0\%$), urea ($(\text{NH}_2)_2\text{CO}$), and absolute ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. Deionized (DI) water was used in all experiments. All chemicals used in this work were of analytical reagent grade and commercially available and used without further purification. The Ni foam (NF) was used as a substrate. The NF needs to be pretreated to remove the surface oxidation layer. Firstly, the NF was washed in an ultrasonic bath of acetone for 20 min. Subsequently, it was soaked in HCl solution (3 M) for 20 min, rinsed with deionized water, and ethanol for 20 min, respectively.

Synthesis of Co-(OH)₂/NF

5.0 mmol (1.455 g) Cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and 10.0 mmol (1.402 g) Methenamine ($\text{C}_6\text{H}_{12}\text{N}_4$) were dissolved in 40 mL H_2O and stirred 20 min to get a uniform solution. Then the solution and the treated nickel foam (1 cm × 2 cm) were put into a stainless steel autoclave lined with Teflon in 100 mL, held at 100 °C for 8 h, cooled to room temperature, and washed three times in turn with deionized water and ethanol, respectively. Then the Co (OH)₂ grown on nickel foam was obtained by drying in the oven at 70 °C for 3 h.

Synthesis of NiCr-LDH-Co/NF

3.75 mmol (1.090 g) nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), 2.5 mmol (1.010 g) chromium nitrate hexahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and 30.0 mmol (1.800 g) urea (H_2NCONH_2) were dissolved in 75 mL deionized water (H_2O), stirred for 20 min, and a uniform solution was obtained. Then the solution and the foamed nickel (cm × cm) obtained above were put into a 100 mL stainless steel autoclave lined with Teflon, kept at 120 °C for 12 h, cooled to room temperature, washed 3 times with deionized water and ethanol respectively, and then dried in an oven at 70 °C for 3 h to obtain NiCr-LDH-Co nanosheets growing on foamed nickel.

Synthesis of NiCoCr-LDH/NF, NiCr-LDH/NF and CoCr-LDH/NF

NiCr-LDH /NF was synthesized by the same method, except that Co(OH)₂/NF was not added. However, CoCr-LDH /NF was synthesized by hydrothermal reaction of 6 mmol (1.745 g) Co(NO₃)₂·6H₂O, 3 mmol (0.24 g) Cr(NO₃)₃·9H₂O and 10 mmol urea (0.6 g) on treated nickel foam at 120 °C for 12 h. NiCoCr-LDH /NF was synthesized by hydrothermal reaction of 6 mmol (1.745 g) Co(NO₃)₂·6H₂O, 3 mmol (0.87 g) (Ni(NO₃)₂·6H₂O), 3 mmol (0.24 g) Cr(NO₃)₃·9H₂O and 10 mmol urea (0.6 g) on treated nickel foam at 120 °C for 12 h. Cool to room temperature, wash with deionized water and ethanol for several times, oven at 60 °C for 4 h

Preparation of RuO₂ modified electrode

Typically, 4 mg of commercial RuO₂ (20 wt%) was independently dissolved into 2 mL of the mixed solution containing 800 μL of water + 970 μL of ethanol+30 μL of Nafion under ultra-sonication, and then the homogeneous suspension was dropped onto the cleaned NF, termed as RuO₂ for clarity.

Electrochemical Measurements.

All the electrochemical curves were carried out in a conventional three-electrode system on an CHI760 electrochemical station (Shanghai Chenhua, China). Glassy carbon electrode clamped with in situ growth of active material in nickel foam are used as working electrodes (the active area of 1×2 cm², mass loading 1.54 mg cm⁻²), carbon rod as the counter electrode, and the normal Hg/HgO electrode as the reference electrode. Before the LSV measurement, all samples were activated by cyclic voltammetry (CV) with 100 cycles. All linear sweep voltammetry (LSV) tests were performed at a potential range of 0 ~ 0.7V vs. Hg/HgO with a sweep speed of 5mV s⁻¹, and 90% iR compensation was used. All the final potentials are converted to reversible hydrogen electrodes with the conversion rate $E(\text{vs. RHE}) = E(\text{vs. Hg/HgO}) + 0.098V + 0.059 \times \text{PH}$. Accurate Tafel plots of NiCr-LDH-Co nanosheets and other related catalysts were deduced from the corresponding Koutecky-Levich plots. Electrochemically active surface areas (ECSA) were calculated by dividing the double-layer capacitance (*C_{dl}*) with the specific capacitance of these samples. In detail, a series of CV curves were performed at the scan rates varying from 20~100 mV s⁻¹ in 1.13~1.23 V vs. RHE and the sweep segments of the measurements were set to 6 to ensure consistency. By plotting the current density difference between the anode scan and the cathode scan divided by two ($(j_{\text{anodic}} - j_{\text{cathodic}})/2$) at 1.17 V vs. RHE against the scan rate, a linear trend was observed. The slope of the fitting line is *C_{dl}*.

The electrochemically active surface area (ECSA) was calculated from the *C_{dl}* value following the equation:

$$ECSA = \frac{C_{dl}}{40 \mu F cm^{-2} per cm_{ECSA}^2}$$

C_s is 0.04 mF·cm⁻². In the range of 0.01~100000Hz frequency, the potential range of electrochemical impedance spectroscopy is 1.49 to 1.565V (vs. RHE), *R_{ct}* is the charge-transfer resistance across the electrode/electrolyte interface, *R_s* is the solution resistance, and CPE is the constant phase component. The solution impedance (*R*) of 1 M KOH measured was 5 Ω at room temperature. Faradaic efficiency (FE) was calculated by the equation: $FE = 4 \times F \times n / Q$, where *F* represents the Faraday constant, *n* is the moles number of totally produced O₂ and *Q* represents the accumulated charges passing through the working electrode. BET normalized current density (mA·cm⁻²_{BET}) = Current density obtained by line sweep (mA·cm⁻²) / (Electrocatalyst loading (g·m⁻²) × BET (m²·g⁻¹)). Stability tests were carried out without iR-compensation. The i-t test was performed for 24 h at voltages corresponding to current densities of 10 (1.43 V vs. RHE) and 50 (1.50 V vs. RHE) mA cm⁻², respectively. A multi-step current test was carried out under the condition that the current density changed from 30 mA·cm⁻² to 190 mA·cm⁻² at a rising rate of 20 mA·cm⁻² per 500 s.

The crystal structures of the obtained samples were characterized using Bruker D8 Focus Advance X-ray diffraction (XRD, diffractometer with Cu-Kα radiation, λ = 0.15406 nm, receiving slit, 0.2 mm, scintillation counter, 40 mA, 40 kV) with scatter-ing angles of 5° to 70° 2θ range at 0.02 s⁻¹. In situ XRD tests were carried out using a special sample holder. The X-ray transmission window and current collector of the in situ XRD cell was a Be disc. Micro-structural properties were determined using HITACHI SU-70 field-emission scanning electron microscopy (FESEM) and JEOL JEM-2010 high-resolution transmission electron microscopy (HRTEM) at an accelerating voltage of 200 kV. Elemental mapping was performed using a JEOL JEM-2010F transmission electron microscope

operating at 200 kV. X-ray photoelectron spectroscopy (XPS) analysis was carried out on a Kratos Axis Ultra DLD spectrometer.

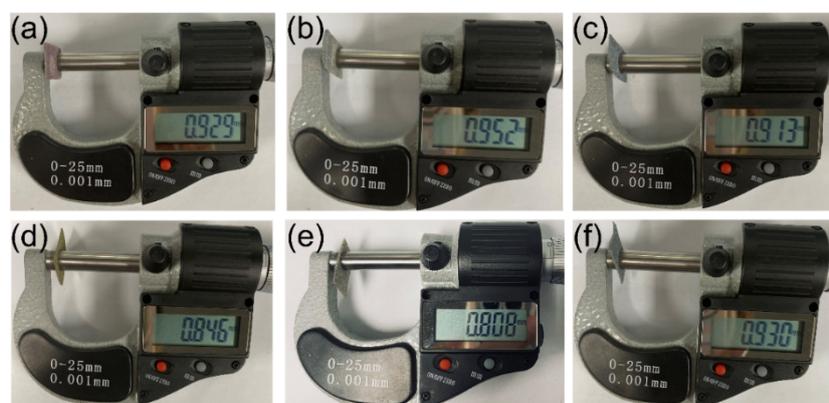


Fig. S1. Vernier calipers measure the thickness of different catalysts and pure nickel foam, (a) $\text{Co(OH)}_2/\text{NF}$, (b) NiCr-LDH/NF , (c) CoCr-LDH/NF , (d) NiCr-LDH-Co/NF , (e) NF and (f) NiCoCr-LDH/NF .

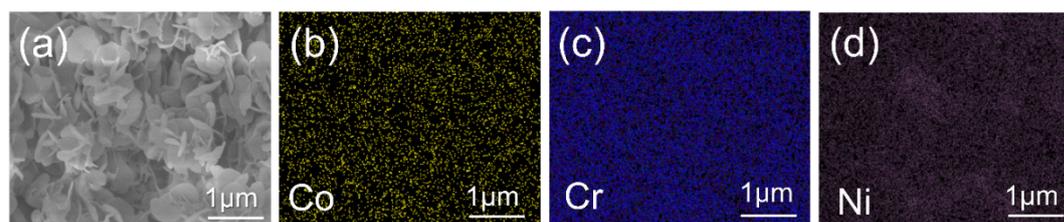


Fig. S2. (a) SEM image of NiCr-LDH-Co/NF composites and the corresponding EDS elemental mapping images of Co (b, green), Cr (c, blue) and Ni (d, purple), respectively.

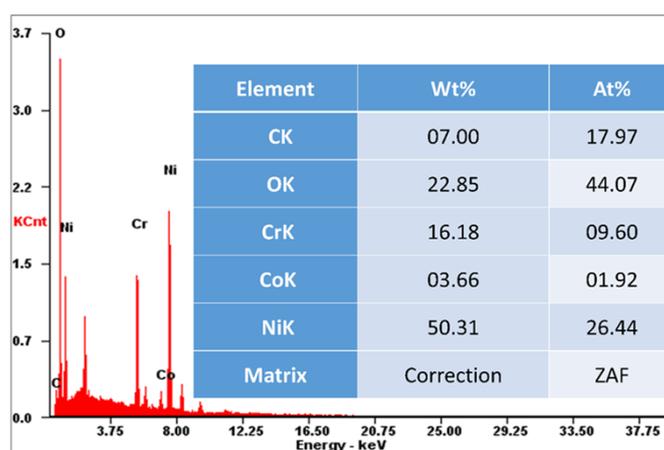
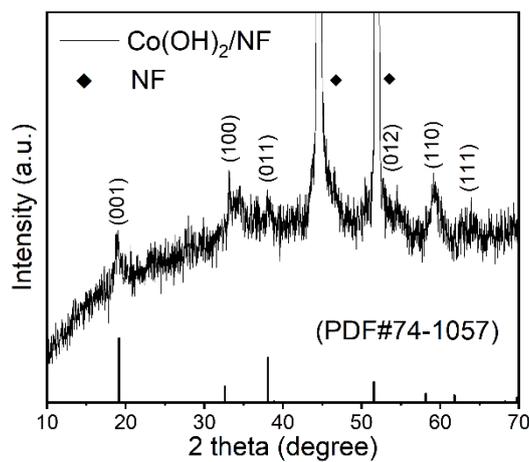
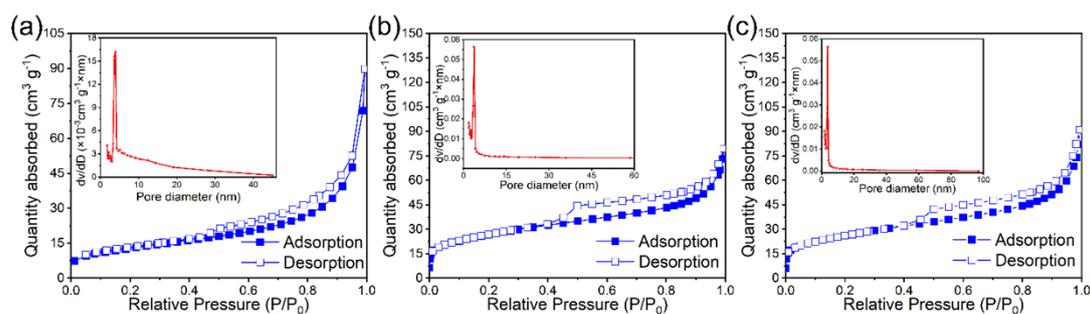
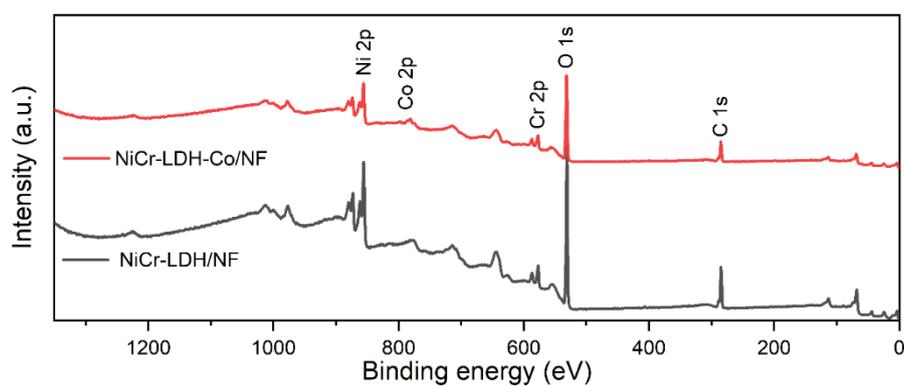


Fig. S3. EDS spectrum of the NiCr-LDH-Co/NF composites.

Fig. S4. XRD patterns of $\text{Co(OH)}_2/\text{NF}$ Fig. S5. N_2 adsorption-desorption isotherms of (a) $\text{Co(OH)}_2/\text{NF}$, (b) $\text{NiCr-LDH}/\text{NF}$ and (c) $\text{CoCr-LDH}/\text{NF}$ and pore distribution calculated from the desorption branch in the inset.Fig. S6. XPS survey spectra of $\text{NiCr-LDH-Co}/\text{NF}$ and $\text{NiCr-LDH}/\text{NF}$.

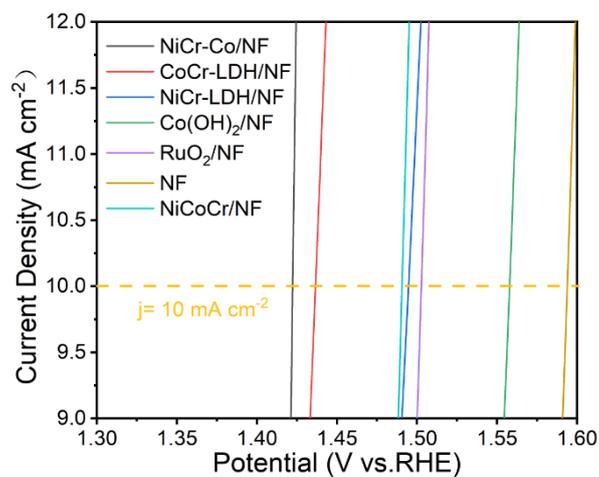


Fig. S7. Polarization curves of bare NF, $\text{Co(OH)}_2/\text{NF}$, CoCr-LDH/NF , NiCr-LDH/NF , NiCr-LDH-Co/NF , and RuO_2/NF at 10 mA cm^{-2} in 1 M KOH.

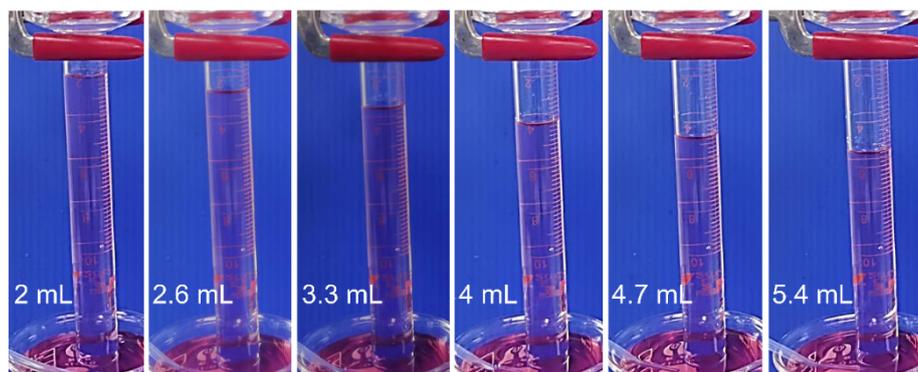


Fig. S8. In a H-type gas-tight electrochemical cell, O_2 generated at 0, 2, 4, 6, 8, 10 min.

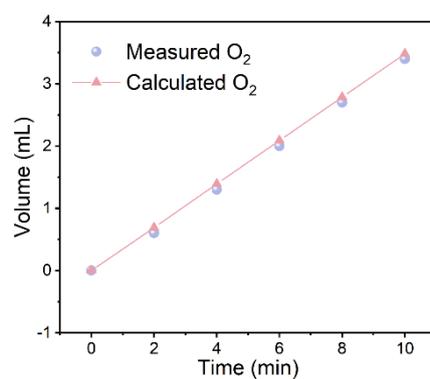


Fig. S9. The amounts of the experimentally generated and theoretically calculated O_2 for NiCr-LDH-Co/NF at a constant current density of 100 mA cm^{-2} .

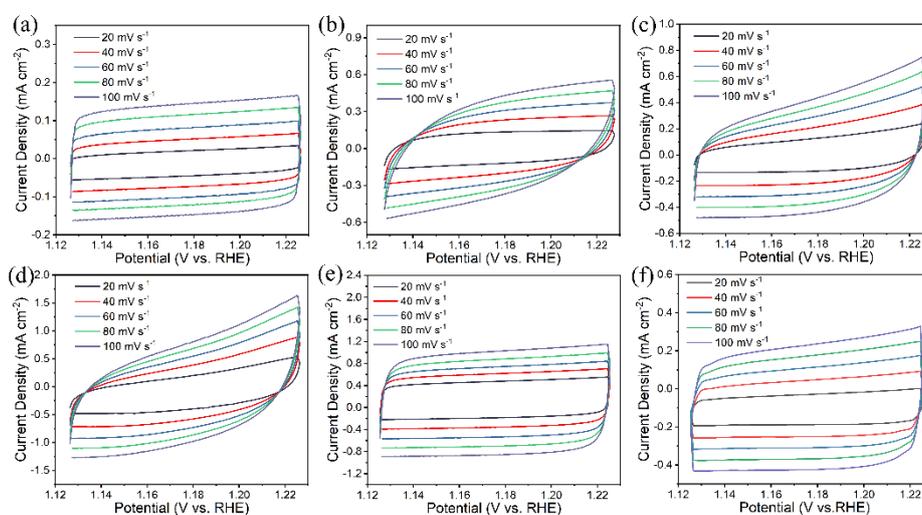


Fig. S10. CVs of (a) $\text{Co(OH)}_2/\text{NF}$, (b) $\text{NiCr-LDH}/\text{NF}$, (c) $\text{CoCr-LDH}/\text{NF}$, (d) $\text{NiCr-LDH-Co}/\text{NF}$, (e) $\text{NiCoCr-LDH}/\text{NF}$ and (f) NF in 1.0 M KOH solution at different scan rates.

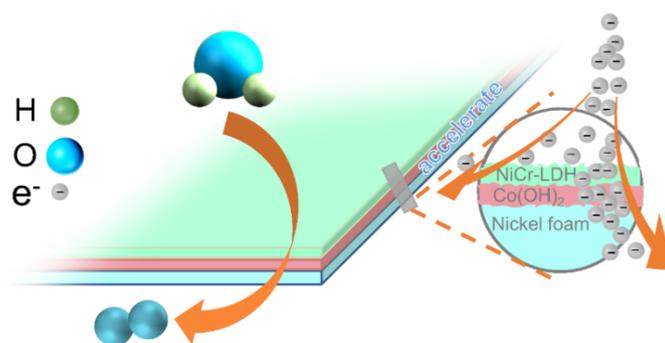


Fig. S11. Schematic diagram of electron transfer inside electrocatalytic materials.

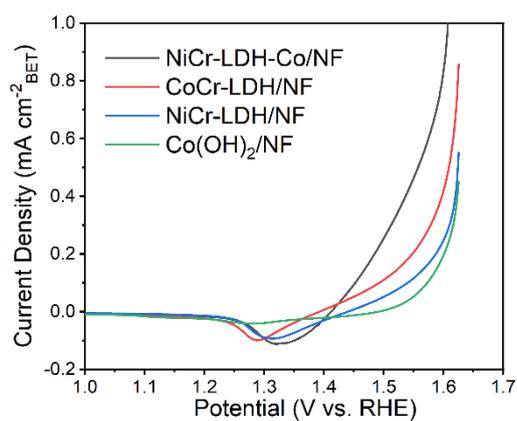
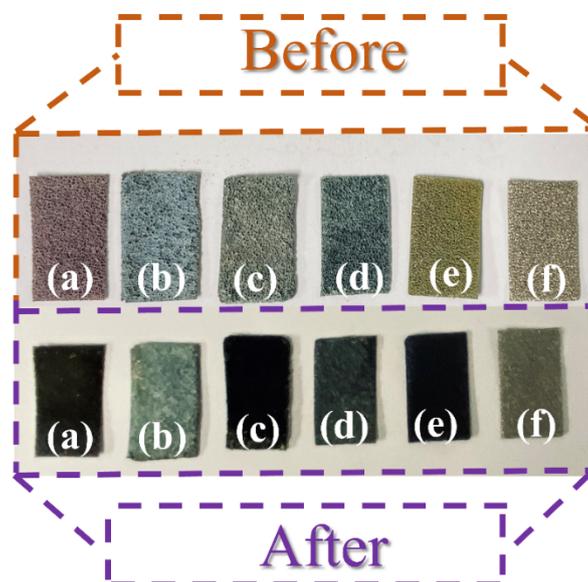
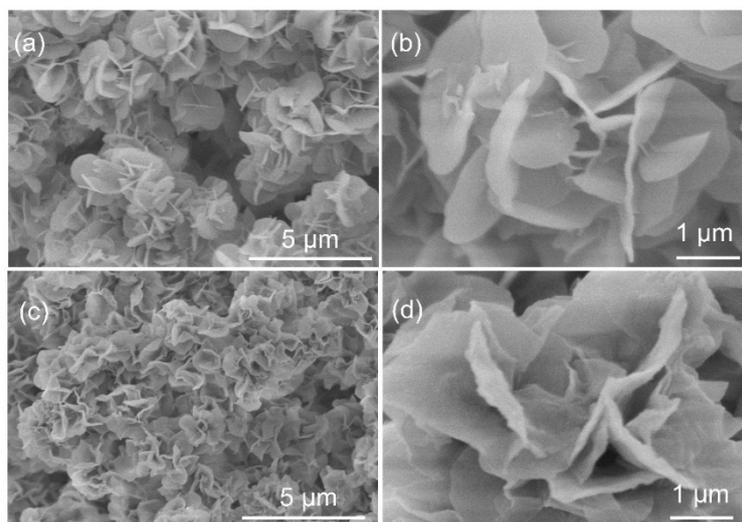


Fig. S12. BET-normalized LSV curves of different catalysts.

Fig. S13. The image of the actual electrodes before and after the electrochemical test, (a) $\text{Co(OH)}_2/\text{NF}$, (b) $\text{NiCr-LDH}/\text{NF}$, (c) $\text{CoCr-LDH}/\text{NF}$, (d) $\text{NiCrCo-LDH}/\text{NF}$, (e) $\text{NiCr-LDH-Co}/\text{NF}$ and (f) pure NF.Fig. S14. SEM images of $\text{NiCr-LDH-Co}/\text{NF}$ before (a-b) and after (c-d) electrochemical measurement (i-t test at 50 mA cm^{-2} for 24 h).

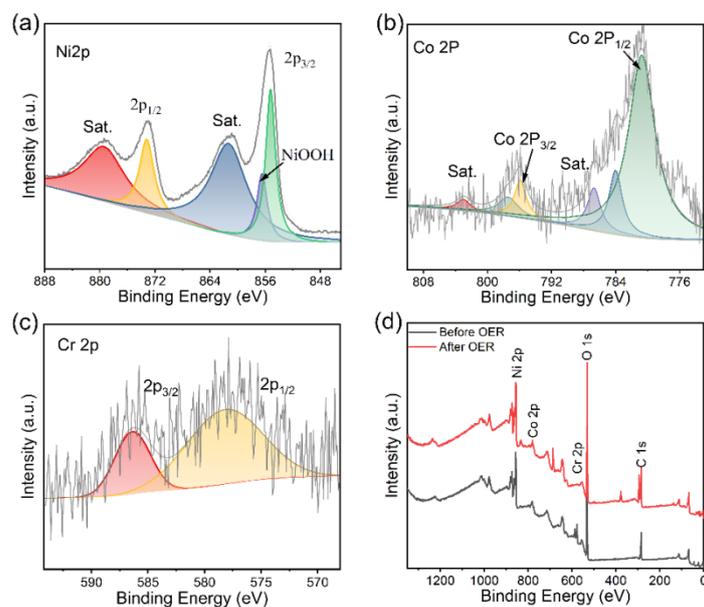


Fig. S15. XPS spectra for the post-OER NiCr-LDH-Co/NF in the a) Ni 2p, b) Co 2p (c) Cr 2p regions (d) XPS results of before OER and after OER

Catalysts	η at $j=10\text{mA cm}^{-2}$ (mV)	Tafel (mV dec^{-1})	References
NiCr-LDH-Co/NF	203	55.15	This Work
(Ni,Co)Se ₂ -GA	250	70	[1]
CoFeV-0.25/NF	242	57	[2]
CeO ₂ /Co-Mn-S/NF	239	93.2	[3]
Ni ₃ S ₂ @NGCLs/NF	271	99	[4]
α -NiOOH/NF	266	76.3	[5]
Fe-CoO/Co@NC-mNS/NF	257	41.56	[6]
Fe_{0.67}Ni_{0.33}OOH-Fe₂O₃@NF	232	34	[7]
MnCoP/CC	261	44.9	[8]
Ni doped CoS ₂ /CFP	270	79	[9]
6%Se-Co ₃ O ₄	281	70	[10]

Table S1. Comparison of the OER activities of the NiCr-LDH-Co/NF in 1 M KOH and other recently reported high-performance OER catalysts

Catalysts	Rs (Ω)	Rct(Ω)
Co(OH) ₂ /NF	5.45	20.33
NiCr-LDH/NF	5.39	23.26
CoCr-LDH/NF	4.55	14.31
NiCr-LDH-Co/NF	4.71	10.46
NiCoCr-LDH/NF	1.65	13.75

Table S2. Resistance Rs of the electrolyte during OER testing of the prepared material and internal resistance Rct of the material for electron transfer at the electrode/electrolyte interface.

Reference

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