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Supplementary information

for

Decoupling the contributions of industrially relevant conditions to the stability of binary and ternary FeNi-based catalysts for alkaline water oxidation

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Experimental Section

Material

Nickel sulfate hexahydrate ($NiSO_4 \cdot 6H_2O$), chromium sulfate basic ($Cr_4(OH)_2(SO_4)_5$), potassium chloride (KCl), and potassium hydroxide (KOH) were supplied from Chem-Supply Australia. The Fe foam was purchased from Jia Shi De foam Metal Co., Ltd (Suzhou, China). All solutions were prepared by Milli-Q water.

Synthesis of FeNiCr/FF

The self-supporting FeNiCr/FF electrodes were prepared by a one-step oxygen corrosion method according to our previous report[27]. First, Fe foam was cleaned by ultrasonic treatment in 1.0M HCl solution, deionized water, and ethanol each for 10 min, respectively. Then, the clean Fe foam was immersed in a 300 mL solution containing 0.2 M $NiSO_4$ and 0.005M $Cr_2(SO_4)_3$ for 3h at room temperature for FeNiCr catalyst synthesis. The corroded Fe was then carefully washed with deionized water several times and dried under N_2 flow.

Synthesis of FeNi/FF

The binary FeNi/FF electrodes were prepared using a one-step oxygen corrosion process. After being treated with 1.0 M HCl solution, deionized water and ethanol for 10 mins each, the Fe foam was immersed in a corrosive solution containing 0.2 M $NiSO_4$. After 3 hours, the Fe foam was washed and dried under N_2 flow.

Physical Characterizations

Scanning electron microscopy (SEM) was performed using a JEOL 7001F FE microscope. Transmission electron microscopy (TEM) with high resolution (HRTEM), as well as energy dispersive X-ray spectrometry for elemental mapping (TEM-EDS), were performed by a JEOL JEM-F200. Raman spectroscopy was performed on a Renishaw inVia spectrometer using a 514 nm laser. The X-ray photoelectron spectroscopy (XPS) was employed using ESCALAB250Xi Thermo scientific spectrometer. The X-ray source is mono-chromated Al K alpha (energy 1486.68 eV). All the XPS spectra were calibrated with the standard C 1s peak of 284.8 eV for adventitious hydrocarbon. ICP-MS experiments were performed by Nexion 5000, PerkinElmer. 1 ml of electrolyte was taken by every 24 hours and analysed during the long-term stability test. Due to the high KOH (1-10 M), samples were diluted before analysis.

Electrochemical Measurements

CHI 760E electrochemical workstations with a booster were used to conduct all electrochemical tests in a typical three-electrode electrochemical cell. FeNiCr/FF and FeNi/FF served as the working electrodes with a geometric surface area of 1 cm^2 exposed to the electrolyte solution. Graphite plate and Hg/HgO served as the counter and reference electrodes, respectively. The electrolyte was kept stirring during all measurements to avoid local pH changes near the electrode surface. The recorded potentials were converted to reversible hydrogen electrode (RHE) system using the following equation:

$E_{RHE} = E_{Hg/HgO} + 0.098\ V + 0.059 \times pH$

The potential of the reference electrode was calibrated prior to each measurement under different industrially relevant conditions through cyclic voltammetry at a scan rate of 1 mV s^{-1} in KOH solution saturated with hydrogen. Calibration of the reference electrode to the reversible hydrogen electrode (RHE) in the non-standard condition is measured by the CV method.[40] Pt plate was used as both working and counter electrodes, and Hg/HgO served as the reference electrode. The electrolyte was saturated with hydrogen before test. The average of the two potentials of CVs when the current equal to 0 was taken as the potential gap between RHE and the tested reference electrode.

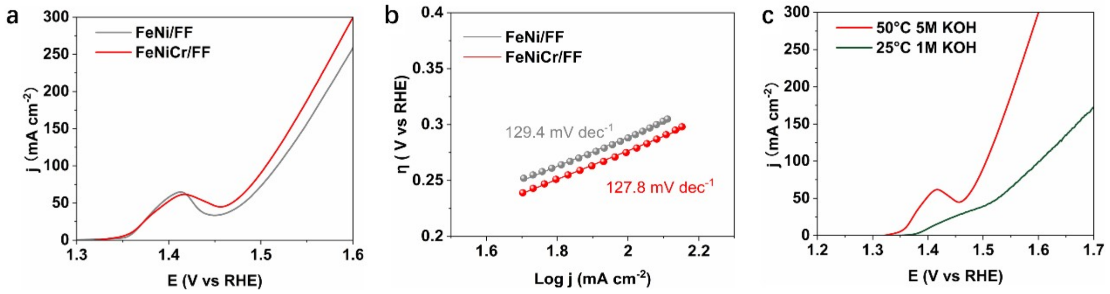

Figure S1 (a) Polarization curves and (b) Tafel slope of FeNi/FF and FeNiCr/FF. (c) Comparison of the LSV curves of the as-prepared ternary FeNiCr catalyst in standard lab-scale (25°C, 1M KOH) and simulated industrial scale conditions (50°C, 5M KOH).

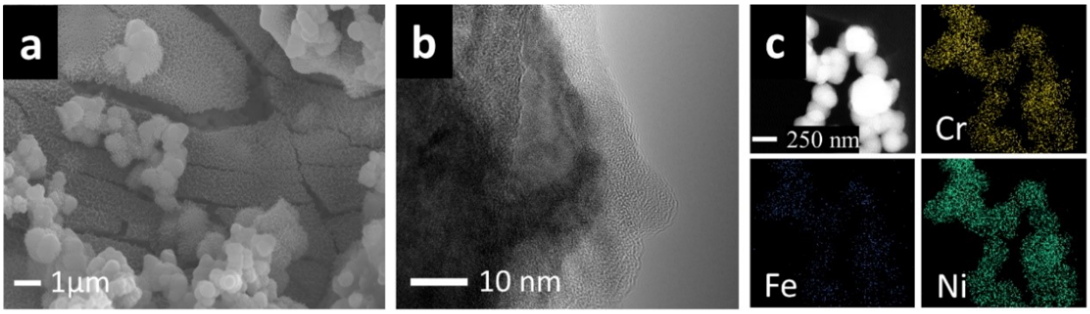

Figure S2 As-prepared FeNiCr/FF (a) SEM, (b) HRTEM, and (c) EDS images.

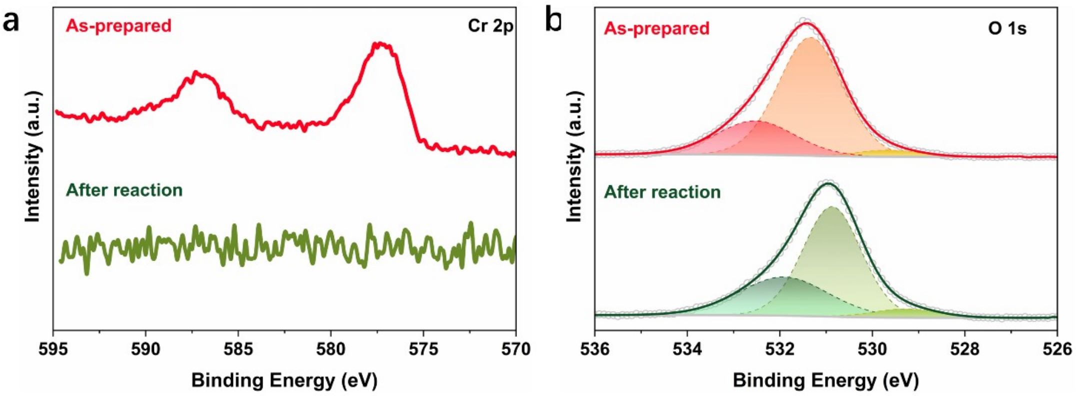

Figure S3 High-resolution XPS spectrums of as-prepared and after-reaction (under 500mA cm^{-2}, 50°C, 5M KOH) FeNiCr/FF: (a) Cr 2p, (b) O 1s.

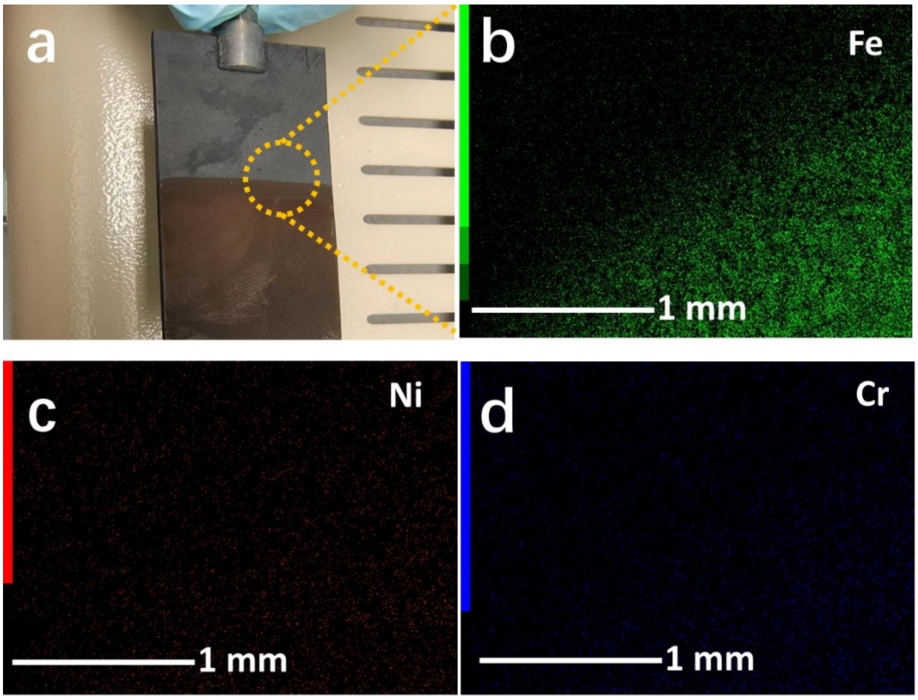

Figure S4 (a) Optical photo of the graphene counter electrode after reaction, (b-d) SEM-EDS mapping of the counter electrode after reaction.

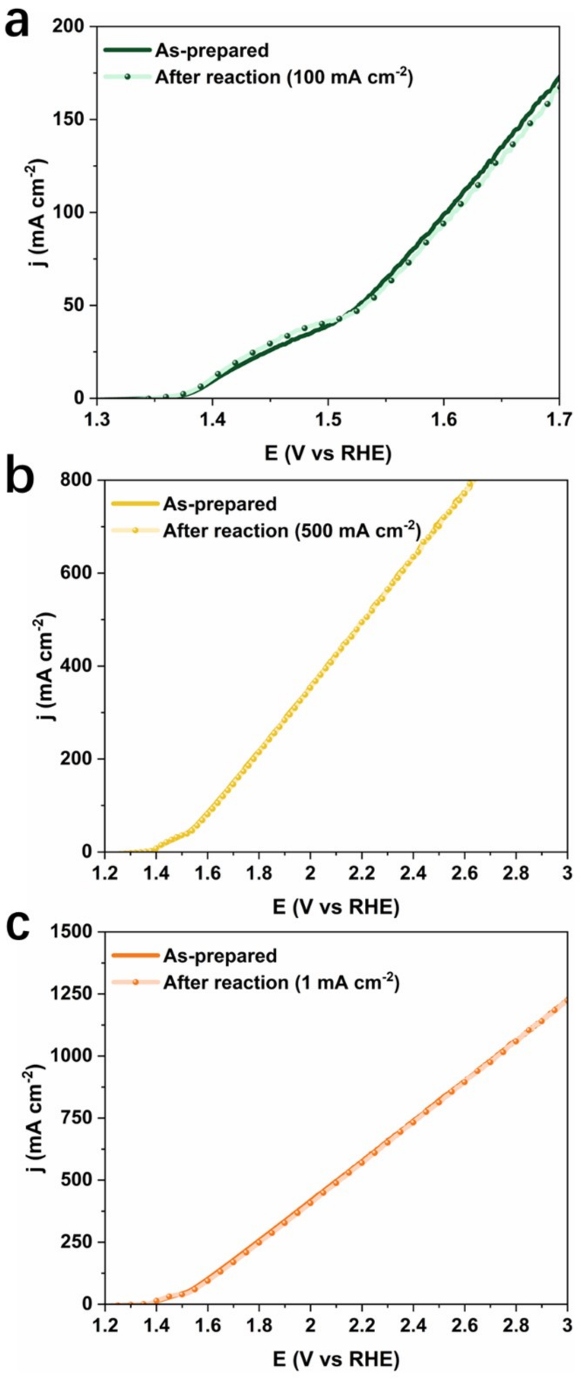

Figure S5 Polarization curves before and after stability test at the current densities of (a) 100 mA cm^{-2}, (b) 500 mA cm^{-2} and (c) 1000 mA cm^{-2}.

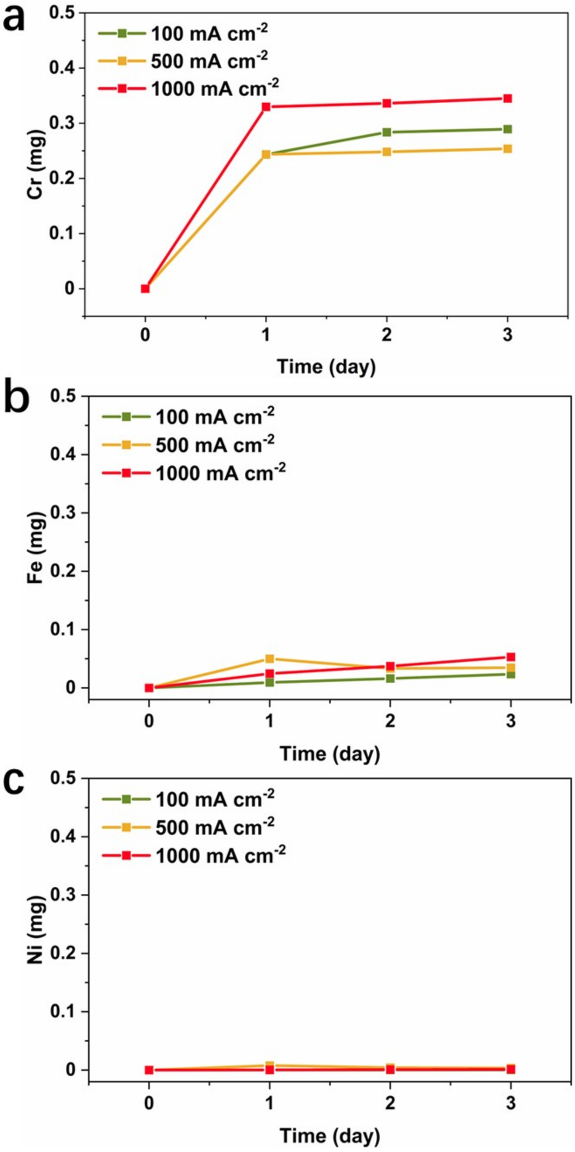

Figure S6 ICP measurements of the electrolyte during the stability test at 25°C and in 1M KOH, (a) Cr, (b) Fe and (c) Ni.

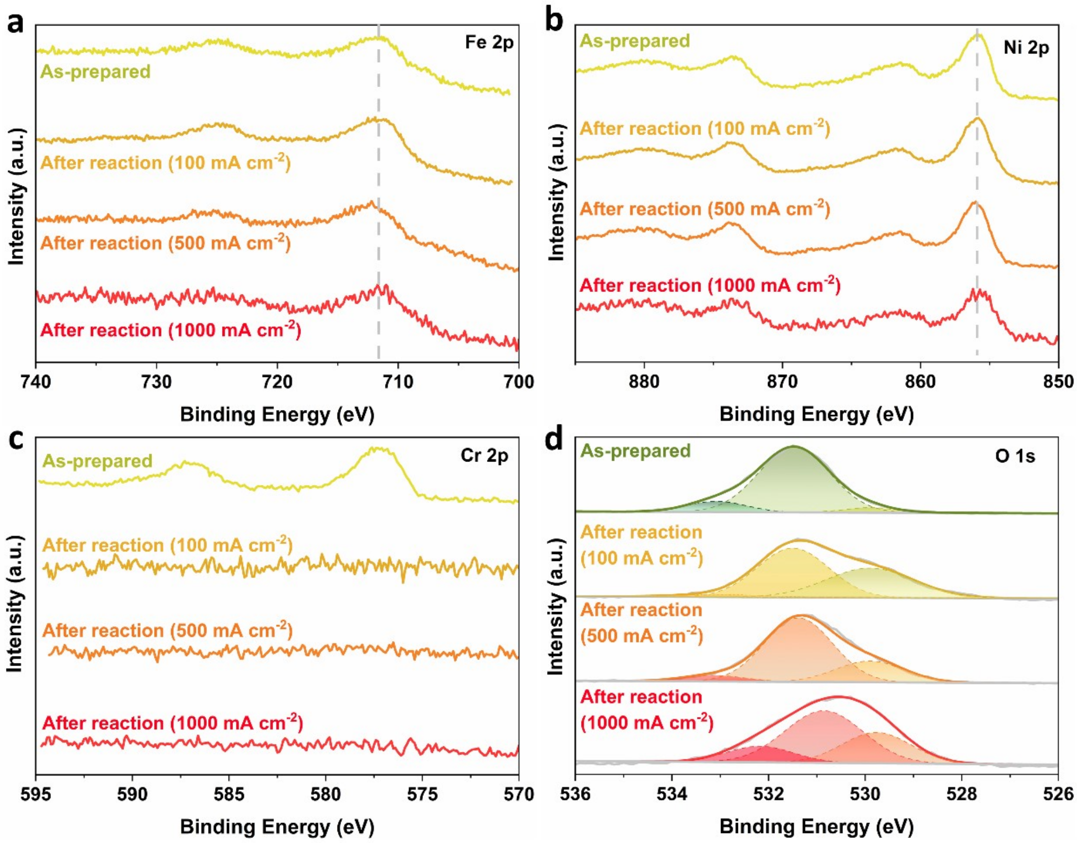

Figure S7 Post-OER FeNiCr/FF of the stability at different current densities: High-resolution XPS spectrums of (a) Fe 2p, (b) Ni 2p, (c) Cr 2p, (d) O 1s.

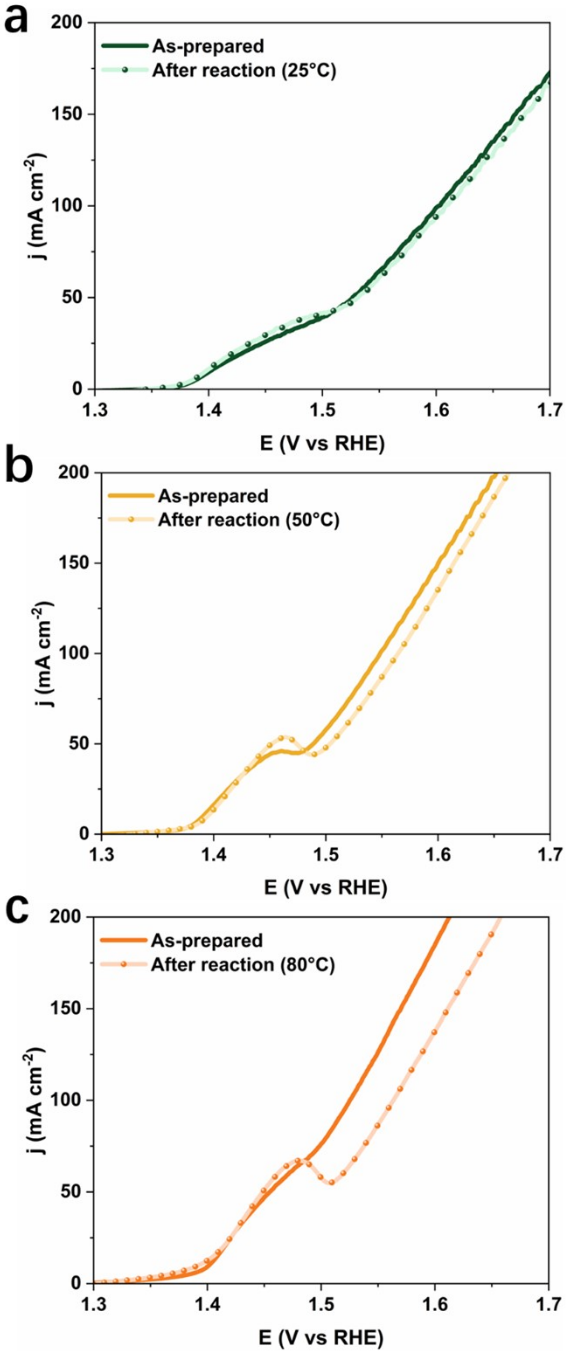

Figure S8 Polarization curves before and after stability test at (a) 25°C, (b) 50°C, (c) 80°C.

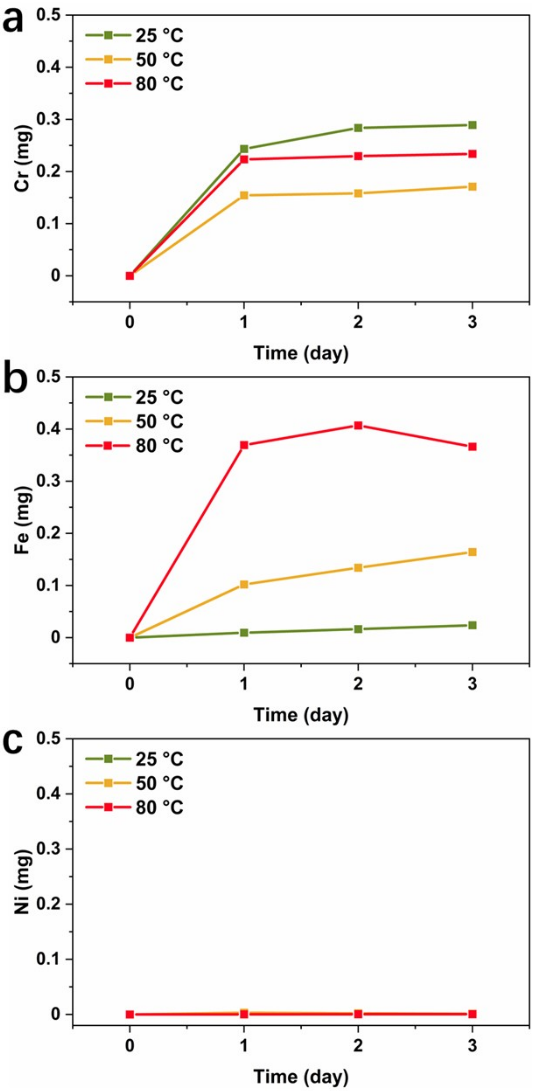

Figure S9 ICP measurements of the electrolyte during the stability test at 100 mA cm^{-2} and in 1M KOH, (a) Cr, (b) Fe and (c) Ni.

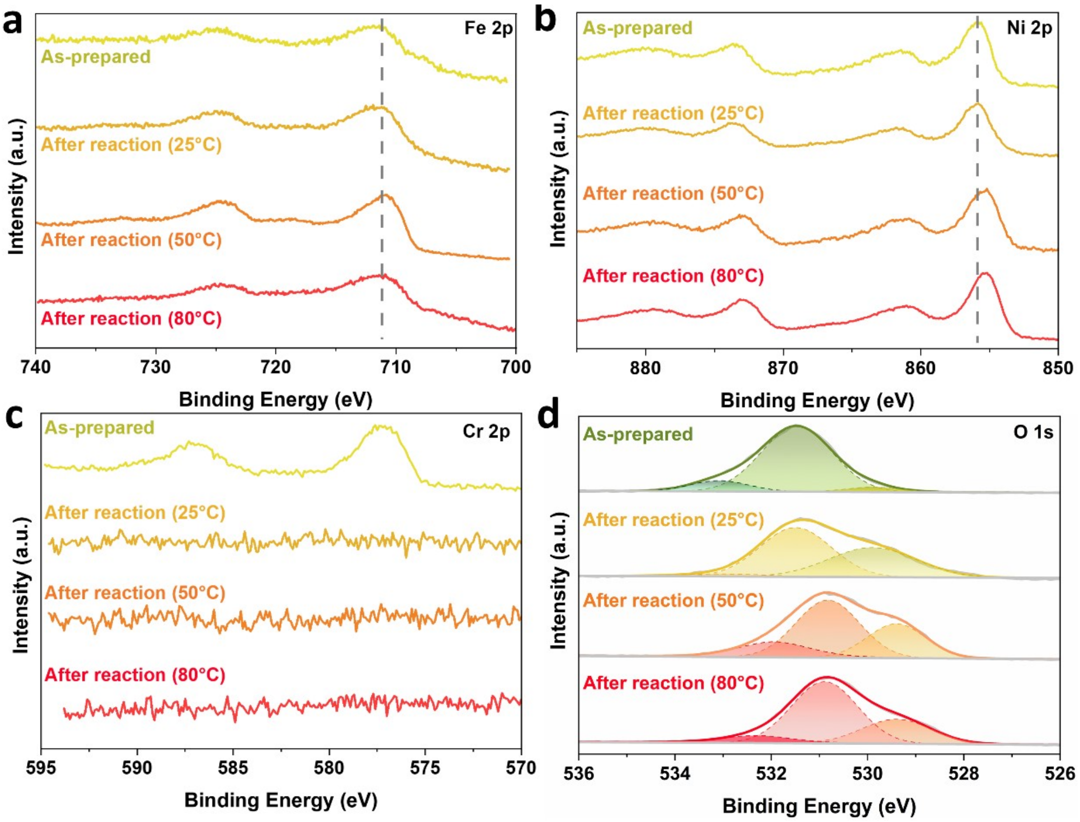

Figure S10 Post-OER FeNiCr/FF of the stability at different temperatures: High-resolution XPS spectrums of (a) Fe 2p, (b) Ni 2p, (c) Cr 2p, (d) O 1s.

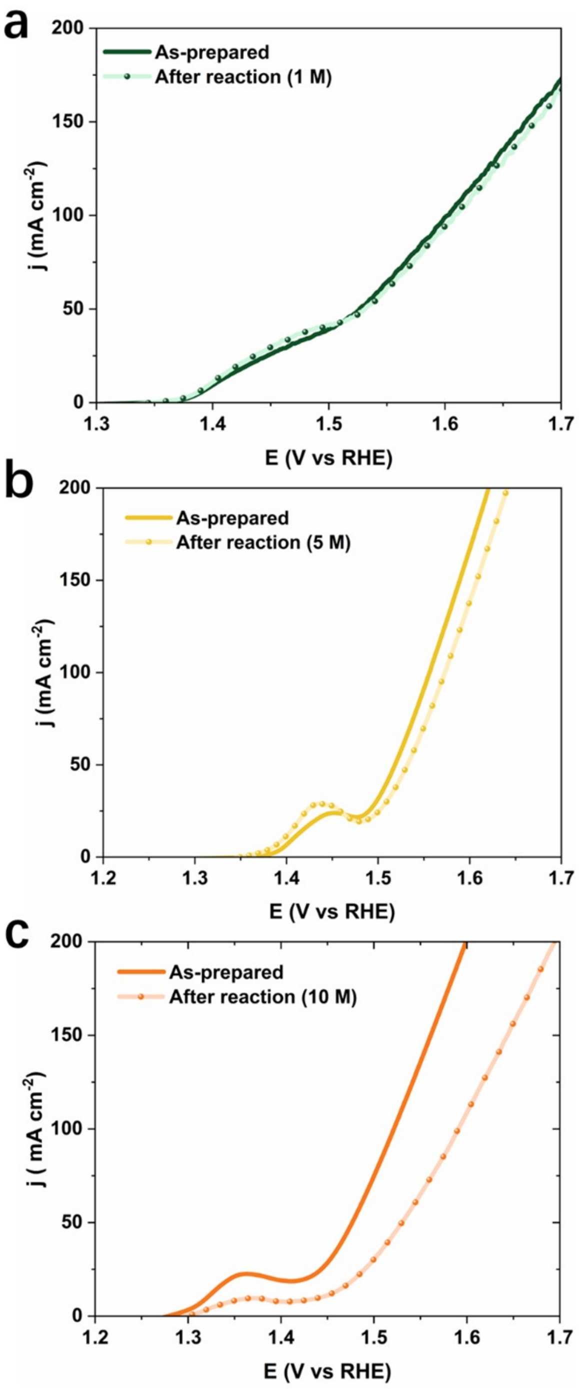

Figure S11 Polarization curves before and after stability test in (a) 1 M, (b) 5 M and (c) 10 M KOH.

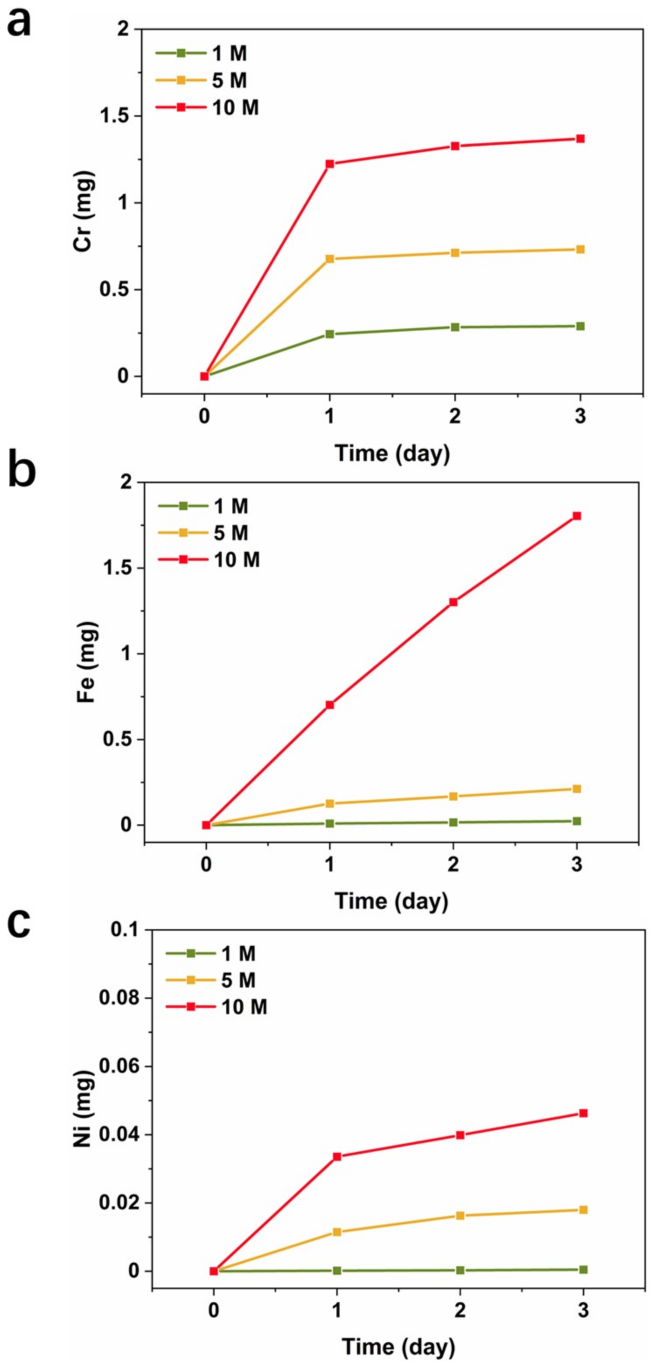

Figure S12 ICP measurements of the electrolyte during the stability test at 100 mA cm^{-2} and 25°C, (a) Cr, (b) Fe and (c) Ni.

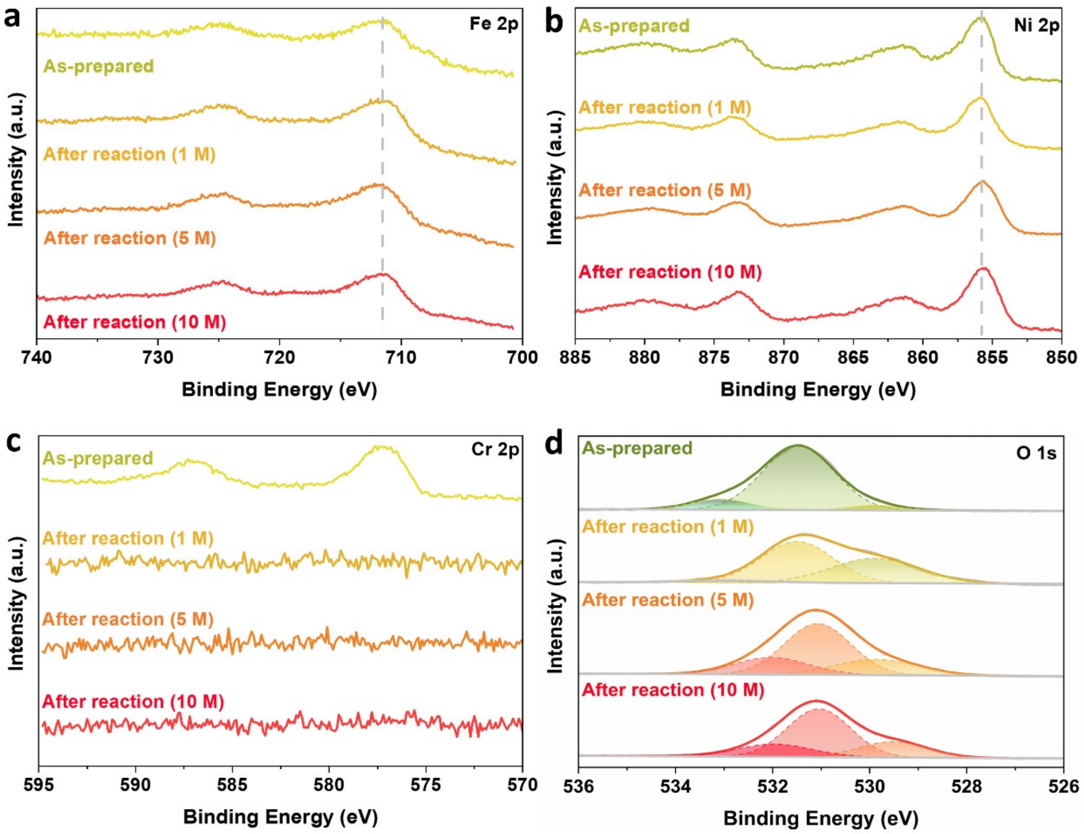

Figure S13 Post-OER FeNiCr/FF of the stability at different concentrations of electrolyte: High-resolution XPS spectrums of (a) Fe 2p, (b) Ni 2p, (c) Cr 2p, (d) O 1s.