

Supporting Information

Large-scale fabrication of ZIF-derived electrocatalysts toward industrial oxygen evolution

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1. Experimental Section

1.1 Pre-oxidation of nickel foam

The nickel foam (NF) was cut into the size of 3 cm × 4 cm, and then it was washed with 3 M hydrochloric acid, ethanol, and deionized water under vigorous stirring for 20 mins in sequence. After that, the washed NF was dried at 120 °C for 12 h in the atmosphere.

1.2 Preparation of Mo-Co-O-ZIF

Firstly, 1.5 mmol $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.5 mmol Na_2MoO_4 were dissolved in 20 ml deionized water and stirred evenly to form solution A. Then, 8 mmol dimethylimidazole was dissolved in 20 ml deionized water and stirred evenly to form solution B. After that, solution A was quickly poured into solution B to form the final solution C. The pre-oxidized NF was immersed into solution C vertically for 1h. In addition, the blue NF electrode was washed with deionized water three times and dried at 60 °C. Then blue NF electrode was placed in a porcelain boat and transferred to a muffle furnace to keep at 300 °C for 4 h with the heating rate of 2 °C/min. Finally, the Mo-Co-O-ZIF was obtained after the muffle furnace was naturally cooled to room temperature. The method to gain Co-O-ZIF was similar to Mo-Co-O-ZIF except without adding 0.5 mmol Na_2MoO_4 into solution A. In addition, adding different types of sodium salts (Na_2MoO_4 , Na_2SO_4 , NaCl , NaH_2PO_2 and NaF) when preparing solution A can prepare a variety of ZIF-derived catalysts. For the preparation of large-area electrodes, it is only necessary to increase the solution C and NF size proportionally.

1.3 Characterization

X-ray diffraction patterns (XRD) were obtained from X-ray diffractometer (Rigaku, MiniFlex600) to detect the composition and crystallinity of various catalysts. X-ray photoelectron spectroscopies (XPS) were recorded by an Image Photoelectron Spectrometer (Thermo Fisher Scientific, K-Alpha). XPS and Raman microscope (LabRAM HR Evolution) were used to obtain information on the surface components of the catalysts. Scanning electron microscopy (SEM, ZEISS ULTRA 55) and transmission electron microscopy (TEM, FEI Talos F200x) were used to analyze the morphology and structural properties of various electrocatalysts.

1.4 Electrochemical measurements

All electrochemical measurements were performed on the Chenhua CHI 760E electrochemical workstation with a three-electrode system at room temperature. The electrolyte was 1M KOH. The self-supporting electrode, carbon rod and Hg/HgO were used as working electrode, counter electrode and reference electrode, respectively. The preparation of commercial IrO₂ on NF was as follows: 5 mg IrO₂ and 5 mg carbon black were dispersed into the mixed solution of 980 μ L ethanol and 20 μ L Nafion solution. A uniform ink was formed after ultrasound for 30 minutes. 100 μ L ink was dropped onto 1 cm \times 1cm NF and dried at 60 $^{\circ}$ C. Linear sweep voltammetry (LSV) was measured at the range 0.2 V to 0.9 V (vs. Hg/HgO) with a scanning rate of 5 mV/s. The IR compensation was 80% comes from the automatic calibration of the electrochemical workstation. All potentials were converted to Reversible Hydrogen Electrode (RHE) with the formula of $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.0592 \times \text{pH} + 0.098$. Chronopotentiometric curves recorded the long-term stability at various current densities (10 and 500 mA cm⁻²). Different scan rates of cyclic voltammetry (CV) including 20 mV/s, 40 mV/s, 60 mV/s, 80 mV/s, and 100 mV/s under the voltage window of 0.15 V to 0.25 V (vs. Hg/HgO). Then linear fitting of the charging current density differences $\Delta j = (j_a - j_c)/2$ at a potential of 1.126V (vs. RHE) against the scan rate was done to fit the slope, and the slope is the double-layer capacitance C_{dl} . The electrochemical impedance spectroscopy (EIS) tests were measured at the initial voltage of 0.63 V vs. Hg/HgO and the frequency range from 1×10^5 Hz to 0.01 Hz. All electrocatalysts were activated by CV (1.2-1.8 V vs. RHE) before testing to exclude the effect of surface reconstruction or early phase transition during the OER process.

2. Supplementary Figures

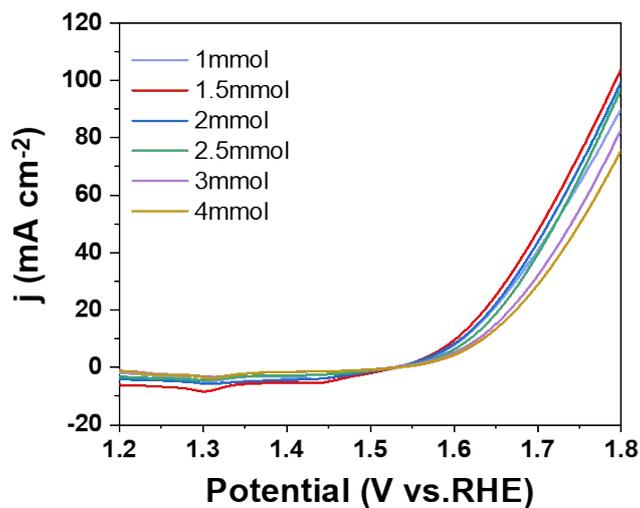


Figure S1. The LSV polarization curves without IR compensation of various Co content electrocatalysts in 1 M KOH and the Co contents were adjusted by varying the added amount of $\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ in the prepared solution.

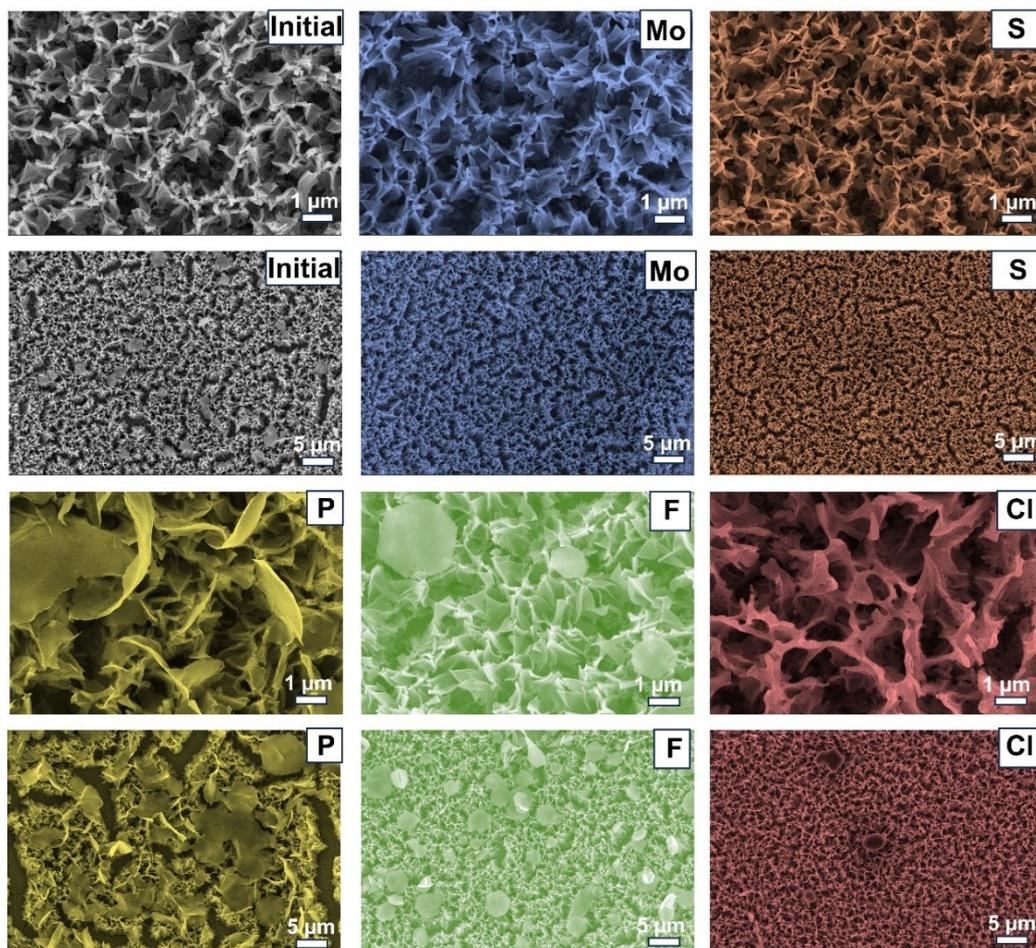


Figure S2. The SEM images of various anion-doped cobalt oxide nanosheets at different resolutions.

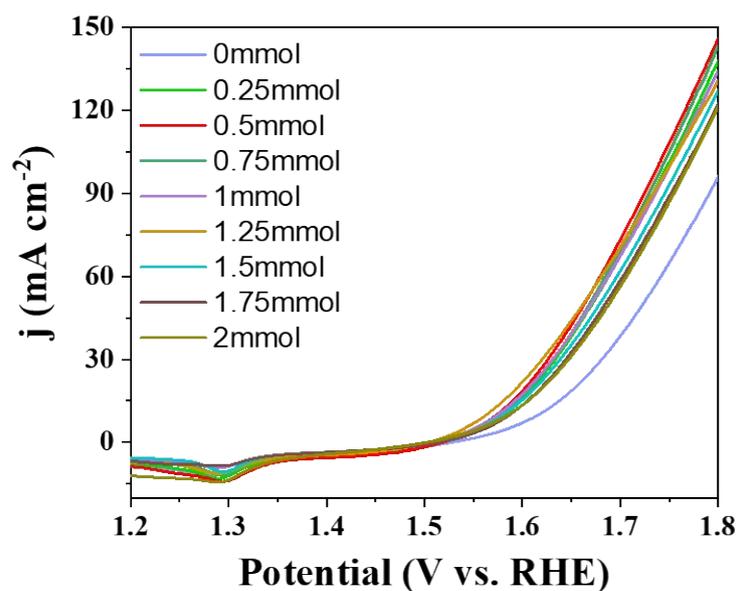


Figure S3. The LSV polarization curves without IR compensation of various Mo anions incorporation electrocatalysts in 1 M KOH and the Mo contents were adjusted by varying the added amount of Na₂MoO₄ in the prepared solution.

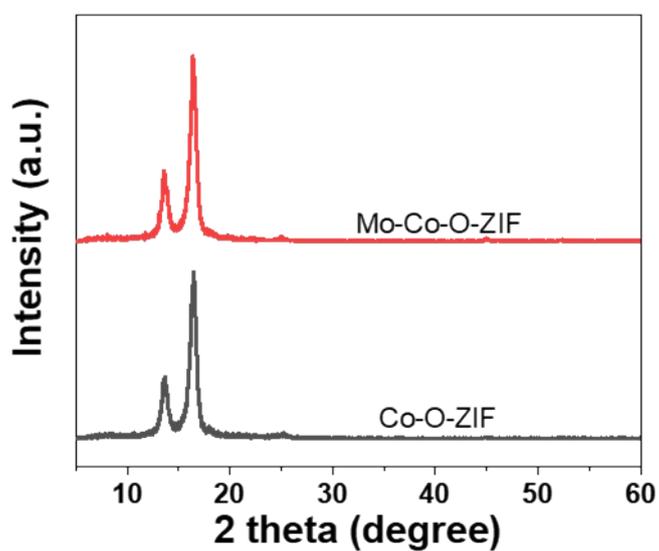


Figure S4. The X-ray diffraction (XRD) patterns of Mo-Co-O-ZIF and Co-O-ZIF.

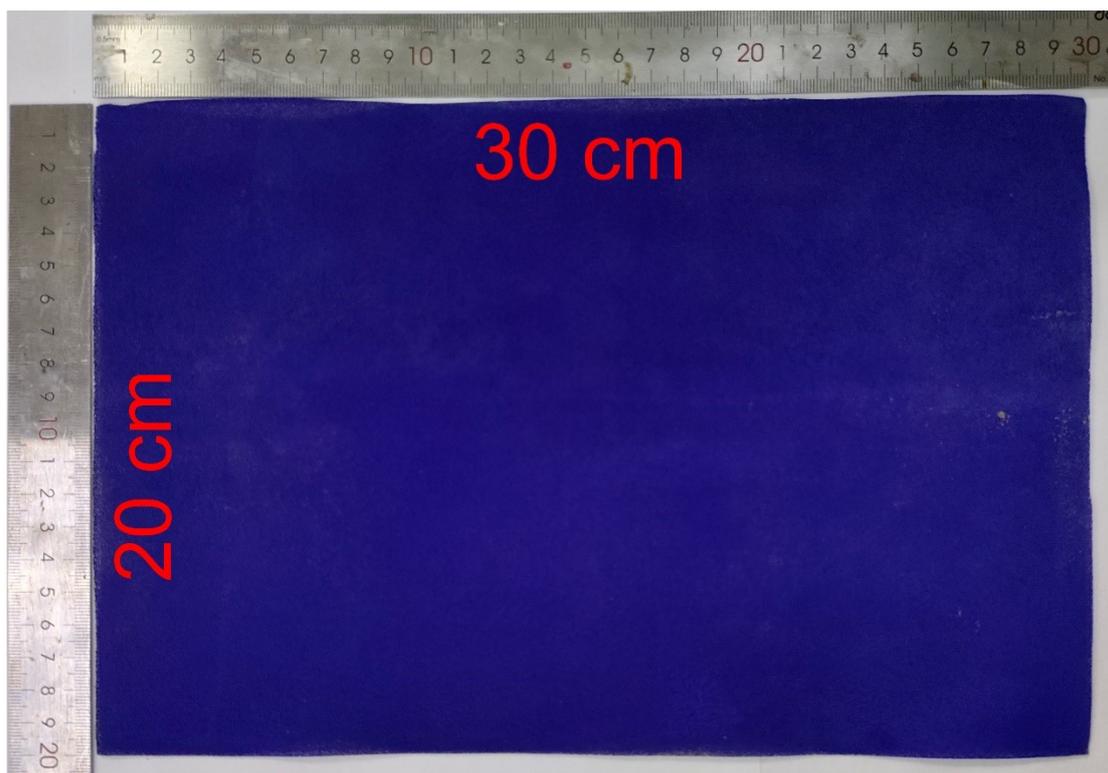


Figure S5. Digital image of ZIF's large-area electrode.

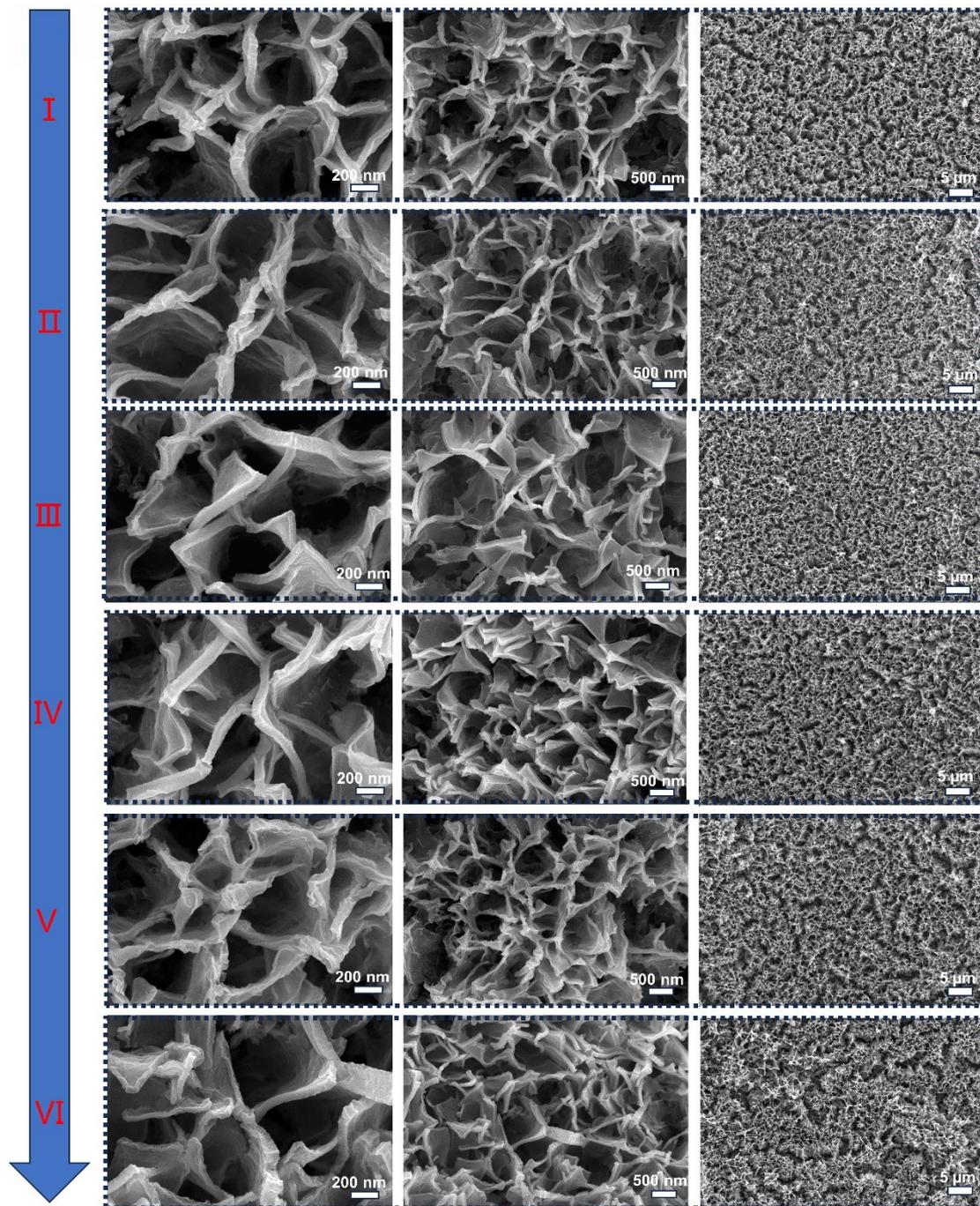


Figure S6. SEM images of the representative areas I-VI in the large-area electrode at different resolutions.

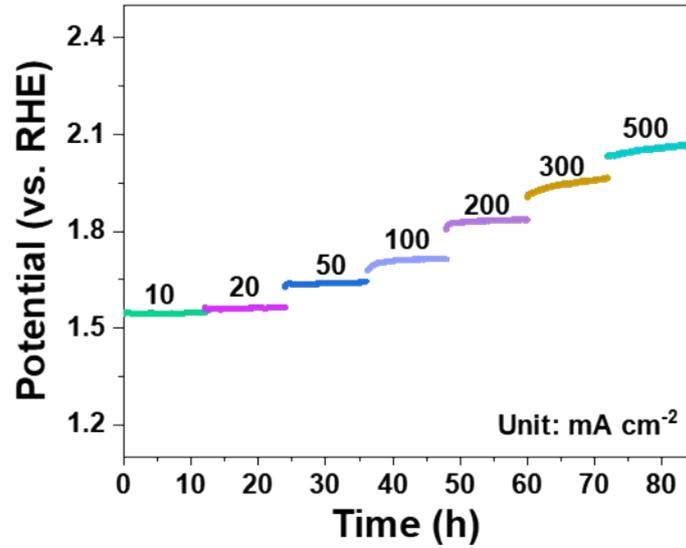


Figure S7. Durability potential–time plots of Mo-Co-O-ZIF at various current densities.

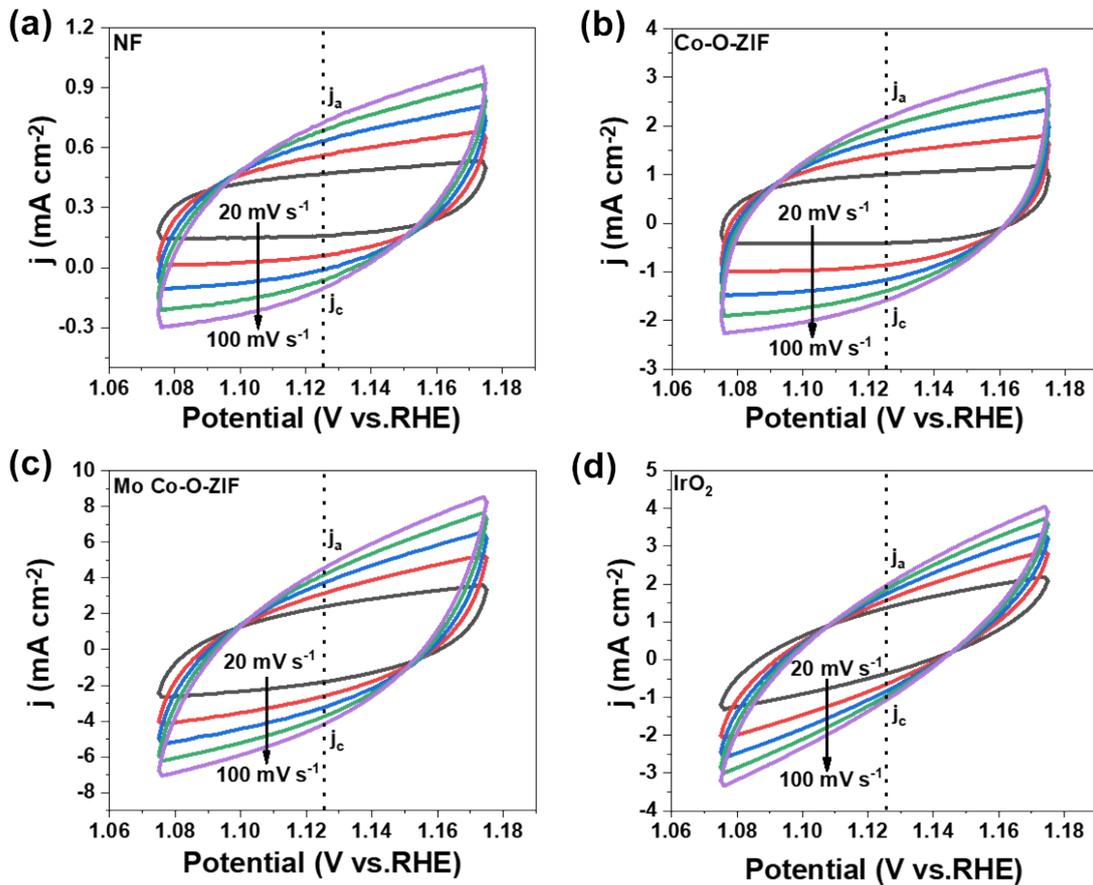


Figure S8. Cyclic voltammetry of a) NF, b) Co-O-ZIF, c) Mo-Co-O-ZIF, and d) IrO₂ at different scan rates.

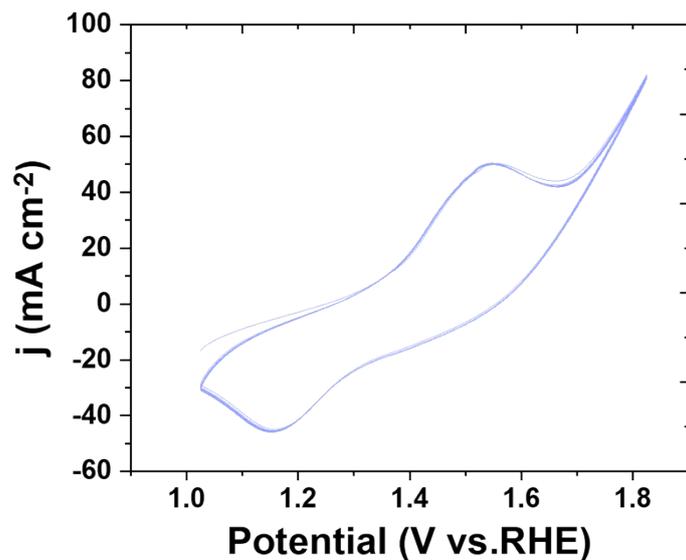


Figure S9. 60 CV cycles in the potential range of 1.025–1.825 V versus RHE at a scan rate of 50 mV s⁻¹.

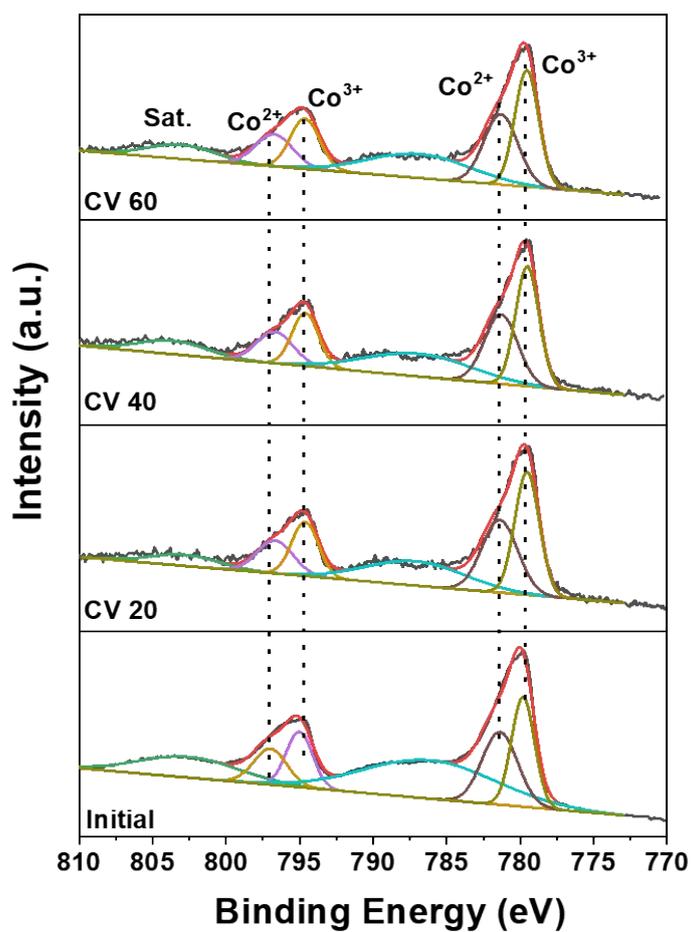


Figure S10. Co 2p XPS spectra of Mo-Co-O-ZIF at different CV cycles.