The Degradation of Ni_4Mo/MoO_2 Catalysts under Fluctuating Current Conditions

Supporting Information

Experimental Section

Synthesis of Ni_4Mo/MoO_2 electrodes

In a typical synthesis, 0.370g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and 0.349g of $Ni(NO_3)_2\cdot 6H_2O$ were dissolved in 30 mL of deionized water under ultrasonication. Nickel foam (2×4cm) was ultrasonically cleaned in 3 M HCl for 5-10 min and rinsed thoroughly with ethanol and deionized water. The precursor solution and pretreated nickel foam were transferred into a Teflon-lined autoclave and heated at 150 °C for 10 h. The obtained sample was washed with water and ethanol, dried at 80 °C for 1 h, and subsequently annealed in a tubular furnace under 5% H_2/Ar (100 sccm) at 500 °C for 2 h with a ramping rate of 5 °C min^{-1}. After natural cooling, NiMo alloy electrodes were obtained.

Characterization

X-ray diffraction (XRD, Rigaku D/max 2500) was performed over 2θ = 20-80° at a scan rate of 2° min^{-1}. Morphology and microstructure were examined by scanning electron microscopy (SEM, Zeiss SUPRA 55) and high-resolution transmission electron microscopy (HRTEM, JEM-2010). Elemental leaching during electrochemical tests was quantified using inductively coupled plasma optical emission spectroscopy (ICP-OES, ICAP6300 Radial).

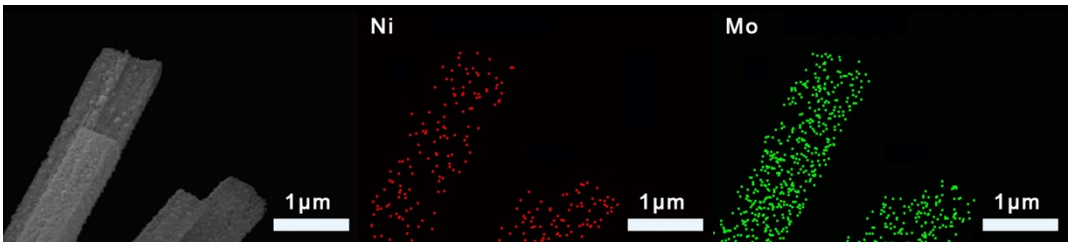
Electrochemical measurements

Electrochemical tests were conducted on a DH7003B workstation in alkaline electrolyte. Linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS)were performed in a three-electrode setup with a Hg/HgO reference electrode, Pt foil counter electrode, and Ni_4Mo/MoO_2 working electrode. The LSV tests at a scan rate of 5 mV s^{-1} were performed after 40 cycles of CV. The final potentials were converted with respect to the reversible hydrogen electrode (RHE) based Nernst equation:

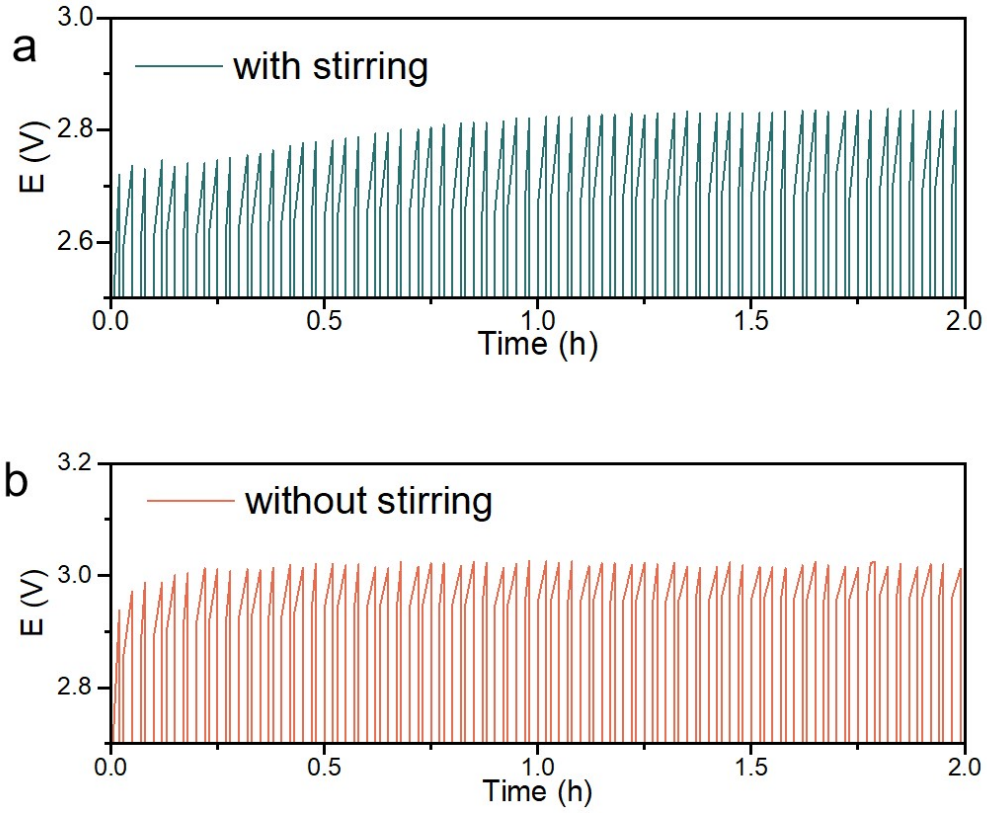
$$E\,(RHE, iR\ corrected) = E(SCE) + 0.244\ V + 0.059\ pH - iR \quad (1)$$

where i is the measured current density and R is the solution resistance determined by electrochemical impedance spectroscopy at a high frequency.

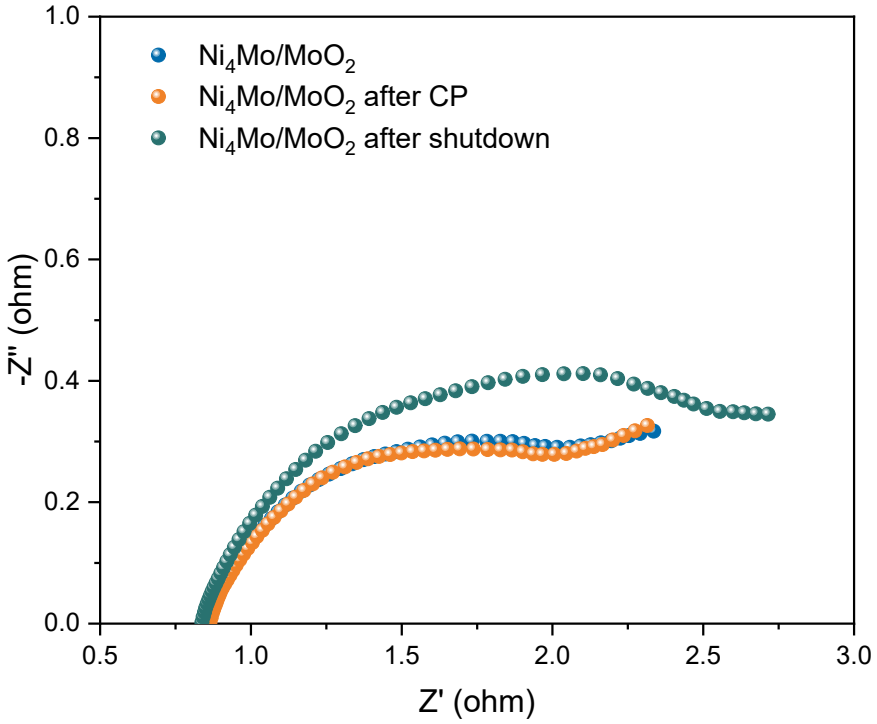
Long-term durability and intermittent start–stop tests were performed in a two-electrode configuration setup with Ni foam counter electrode, and Ni_4Mo/MoO_2 working electrode.



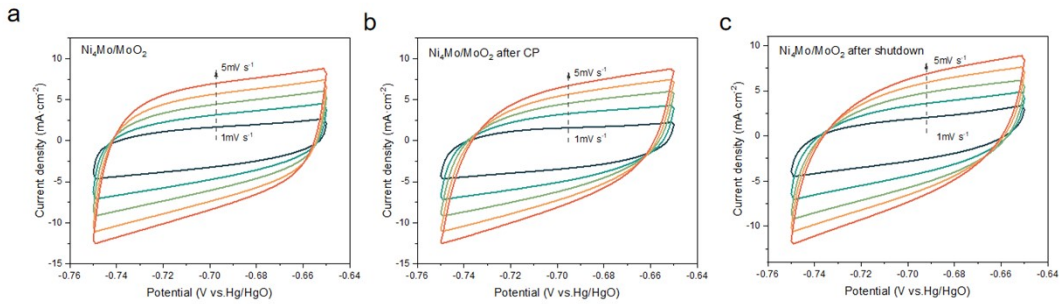
Supplementary Figure 1 | SEM-EDS elemental mappings of Ni_4Mo/MoO_2



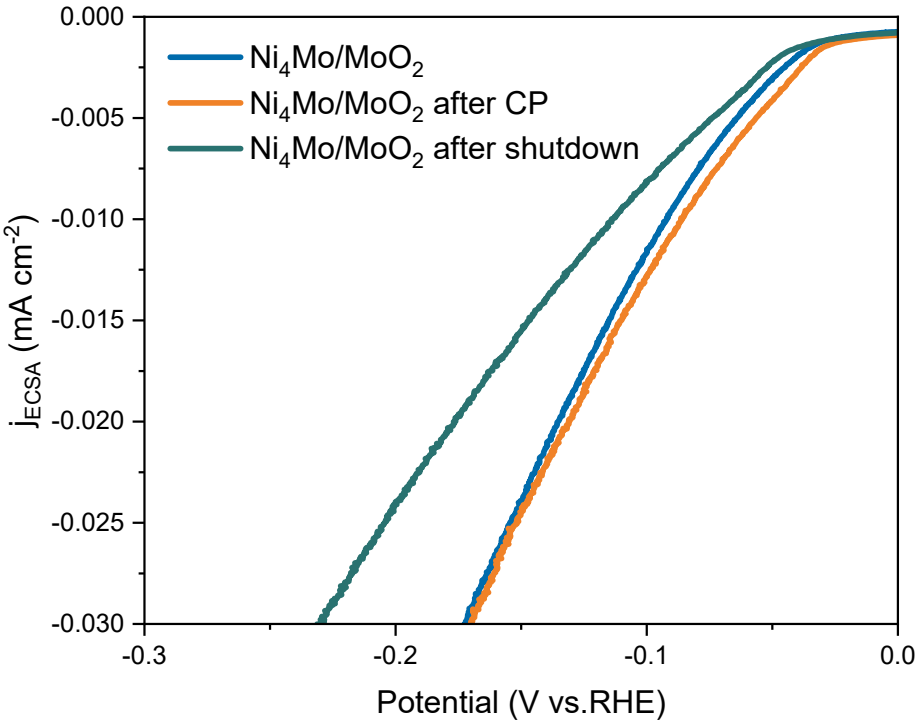
Supplementary Figure 2 | Voltage variation of Ni_4Mo/MoO_2 cathode vs. Ni foam anode in 1 M KOH at 1 A cm^{-2} with 1 min shutdown intervals:(a)with stirring (b)without stirring



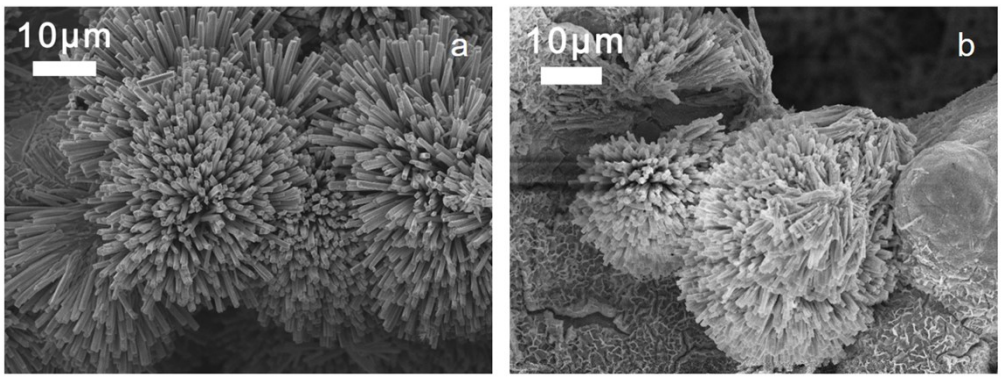
Supplementary Figure 3 | Nyquist plots of the three samples



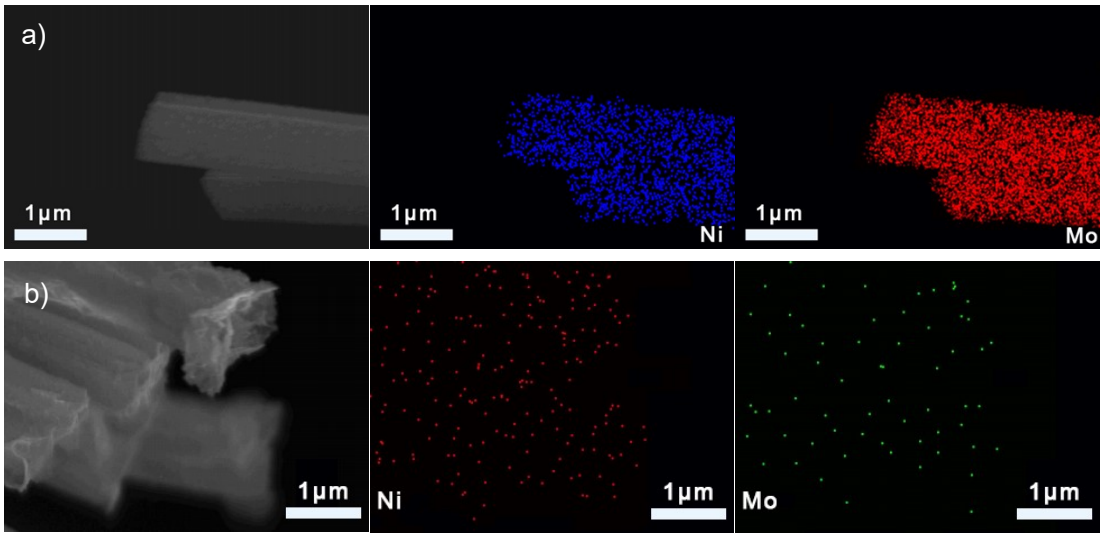
Supplementary Figure 4 | The capacitance of Ni_4Mo/MoO_2, Ni_4Mo/MoO_2 after CP, and Ni_4Mo/MoO_2 after shutdown was evaluated by a series of cyclic voltammetry (CV) scans at different sweep rates. Cyclic voltammograms were recorded in the potential window of -0.75 to -0.65 V (vs. Hg/HgO) at varying scan rates for: (a) Ni_4Mo/MoO_2, (b) Ni_4Mo/MoO_2 after CP, and (c) Ni_4Mo/MoO_2 after shutdown



Supplementary Figure 5 | ECSA-normalized polarization curves



Supplementary Figure 6 | (a) SEM of Ni_4Mo/MoO_2 after CP;(b)SEM of Ni_4Mo/MoO_2 after shutdown



Supplementary Figure 7 | (a) SEM-EDS elemental mappings of Ni_4Mo/MoO_2 after CP;(b)SEM-EDS elemental mappings of Ni_4Mo/MoO_2 after shutdown