Supplementary Materials for

Anionic Insertion Prompted Corrosion Resistance in Metal-Organic Framework Anode for Seawater Oxidation

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Materials and Methods

Chemicals:

Nickel (II) nitrate hexahydrate (Ni(NO₃)₂.6H₂O, 98%), Iron (III) chloride hexahydrate (FeCl₃.H₂O, 99%), Dimethylformamide (DMF) 99%, Terephthalic acid (BDC) 99%, Sodium tungstate dihydrate (Na₂WO₄.2H₂O, 99%) were purchased from Sigma-Aldrich (Germany). Nickel foam was purchased from Alfa Aesar. All chemicals were used as purchased without further treatment.

Fabrication of NF-MOF:

The nickel foam was used as a support material for the fabrication of the catalyst. The as puchansed nickel foam generally have surface oxide layer which need to be remove before the growth of the catalyst, for removing the same it was initially treated with acid (3M HCl solution (37 wt%)) and sonicating for 15 minutes. A hydrothermal method was employed to synthesize the metal-organic framework (MOF). In the first solution, 6 mL of deionized water containing 0.02 mmol of Ni(NO₃)₂·6H₂O and 0.06 mmol of FeCl₃·H₂O was stirred for 30 minutes. Separately, 33.2 mg of terephthalic acid was dissolved 18 mL of DMF and sonicated for 30 minutes. The first solution was then added to the second and stirred for an additional 15 minutes. This mixture was transferred to a 30 mL autoclave containing the pre-treated NF and heated at 160°C for 6 hours. The resulting NF-MOF was washed and dried at 60°C for 12 hours.

Fabrication of WNF-MOF:

The synthesis procedure for WNF-MOF mirrored that of NiFe MOF, with the addition of 0.01 mmol of $Na_2WO_4 \cdot 2H_2O$ to the first solution.

Electrochemical measurement:

Electrocatalytic performance was evaluated using a three-electrode system connected to a potentiostat (Autolab PGSTAT; Metrohm) under real alkaline seawater conditions (1MKOH + seawater). The system comprised the self-supporting catalyst as the working electrode, an Ag/AgCl reference electrode, and a graphite counter electrode. Nitrogen was purged into the electrolyte prior to measurements. The working

electrode's exposed surface area was 0.25 cm². For IrO₂ and RuO₂, inks were prepared by dissolving 5 mg of each sample in 490 μ L of ethanol and 10 μ L of Nafion; 30 μ L of this ink was drop-cast onto the NF. Polarization curves were recorded at a scan rate of 5 mV s⁻¹. Potentials were converted to the reversible hydrogen electrode (RHE) scale using the equation: E(RHE) = E(Ag/AgCl) + 0.059 × pH + E°(Ag/AgCl). Polarization curves were corrected for 100% iR drop. Electrochemical impedance spectroscopy (EIS) was conducted at open circuit potential (OCP) over a frequency range of 0.1 to 100 kHz with a 5 mV sinusoidal amplitude. Tafel slopes were derived from the iR-corrected linear sweep voltammetry (LSV) curves using the equation: $\eta = b \log j + a$, where b is the Tafel slope, j is the current density, and η is the overpotential.

Determination of turn over frequency (TOF):

TOFs of the samples for OER were estimated by using the following equation,

$$TOF = j X A / (4 X F X N_s)$$

, where j, A, F, Ns are the current density (A cm⁻²) at a fixed potential, the area of the electrode (cm⁻²), the Faraday constant (96485 C mol⁻¹), and the concentration of the active sites (mol cm⁻²). (Noted that the Ns was obtained from the Linear sweep voltammetry (LSV) curve measured at different scan rates under a alkaline seawater solution, in which peak current has a linear relationship with the N_s as,

$$Slope=n^{2}F^{2}AN_{s}/4RT$$

, where the number of electrons transferred is n (here n = 1), the ideal gas constant and the temperature are R and T, respectively. The slopes value of LSVs for the WNF-MOF and NF-MOF were estimated as 0.5526 and 0.711, respectively. And the Ns value for the W-NF-MOF and NF-MOF were 2.35308E-06 mol cm⁻² and 3.02758E-06 mol cm⁻², respectively.

Determination of electrochemical double layer capacitance (Cdl):

CV curves were measured in an O_2 -saturated alkaline seawater solution. The potential for CV scans was determined where no Faradaic currents are generated using various scan rates. The C_{dl} of catalyst can be acquired from the slopes in linear plots between the current density difference (J_{anodic} - $J_{cathodic}$) at the middle of potential and the scan rate.

Determination of electrochemical surface area (ECSA):

The ECSAs of samples have been attained from the measured C_{dl} . The current generated in the non-Faradaic region is associated with double layer charging, that has a linear relationship with the active surface area. Notably, the specific capacitance of 1cm2 flat surface area corresponds to an average C_{dl} value of 40 μ F cm⁻².

ECSA=Cdl of catalyst (mF cm⁻²)/0.04 mF cm⁻²

Structural and chemical characterizations:

Scanning electron microscopy (SEM, Hitachi model S4800) was used to analyze the morphological characteristics of the specimens. Transmission electron microscopy (TEM, Thermo Fisher Scientific, Talos F200X) was used to capture the microstructures, whereas an energy dispersive X-ray (EDX) spectroscopy system integrated with TEM was used to analyze the elemental distributions within the samples. X-ray diffraction (XRD) analysis was conducted with Cu K α radiation at 40 kV and 100 mA. A diffractometer (Rigaku D/Max 2550) was used for XRD data acquisition. X-ray photoelectron spectroscopy (XPS; Thermo Fisher Scientific, VG ESCALAB 200i) was used to analyze the surface electronic structures of the samples. The C1s correction has been performed, and the peak was positioned at 284.8 eV. The spectrometer was calibrated based on the position of the C peak. Pass energies of 100 eV and 20 eV were used for the surveys and high-resolution scans, respectively. The FTIR spectra was

recorded on Shimadzu spectrometer. Raman spectrums were carried out by using a model of LabRam Soleil.



Fig. S1. PXRD pattern of the NF-MOF and WNF-MOF



Fig. S2. FT-IR spectra of NF-MOF and WNF-MOF



Fig. S3. Raman spectra of NF-MOF and WNF-MOF



Fig. S4. SEM images of the individual NF-MOF



Fig. S5. XPS analysis of the WNF-MOF, showing the XPS spectra of Ni2p, Fe2p, W4f, O1s and C1s present in the catalyst



Fig. S6. XPS analysis of the NF-MOF, showing the XPS spectra of Ni2p, Fe2p, C1s and O1s present in the catalyst



Fig. S7. Cyclic voltammetry curve for the estimation of the double layer capacitance (C_{dl})



Fig. S8. Stability study of the NF-MOF



Figure S9. SEM images of WNF-MOF after durability test



Fig. S10. Elemental mapping of the WNF-MOF electrode after stability showing the presence of Ni, W, Fe, C and O element even after the prolonged stability test.



Fig. S11. PXRD pattern of the WNF-MOF after the long-term durability test



Figure S12. XPS analysis of the WNF-MOF after durability test (a) Ni2p, (b) Fe2p, (c) W4f and (d) O1s spectra



Figure S13. (a) TEM image of the catalyst WNF-MOF after durability test (b) & (c) HRTEM image of the catalyst along with (d) fringe width



Fig. S14. Digital photographs for iodide titration experiments for (upper) NaClO reference solution and (lower) the electrolyte solution after the durability test



Figure S15. Cl 2p XPS spectra of the WNF-MOF before and after stability test



Fig. S16. ECSA values of NF-MOF and WNF-MOF



Fig. S17. In-situ EIS Nyquist plot of WNF-MOF



Fig. S18. In-situ EIS Nyquist lot of NF-MOF



Fig. S19. Faradaic efficiency of the WNF-MOF



Fig. S20. TOF calculation of WNF-MOF



Fig. S21. TOF calculation of NF-MOF

S.No	catalyst	Tafel (mV dec ⁻¹)	Overpotentia l	Reference
1	NiFe MOF/NF (acetone)	55 mV dec ⁻¹	270 mV at 50 mA/cm ²	1
2	FeNi-MOF	49 mV dec ⁻¹	270 mV at 50mA/ cm ²	2
3	MFN@Ga/NF	66 mV dec ⁻¹	299 mV at 100 mA/cm ²	3
4	Co@Ni/Fe-MS/MOF	52.37 mV dec ⁻¹	287 mV at 50 mA/ cm ²	4
5	NiFe-PBA	40.29 mV dec ⁻¹	368 mV at 200 mA/ cm ²	5
6	NiFe-LDH/MOF	61 mV dec ⁻¹	275 mV at 100 mA/ cm ²	6
7	Ni3Fe-BDC	90 mV dec ⁻¹	280 mV at 10 mA/ cm ²	7
8	NiFe-25	48.9 mV dec ⁻¹	299 mV at 100 mA/ cm ²	8
9	Ru/NiFe(OH) _x /NiFe- MOF	30.63 mV dec ⁻¹	320 mV at 100 mA/ cm ²	9
10	NiFe-NDC0.9BDC0.1	19.8 mV dec ⁻¹	295 mV at 400 mA/ cm ²	10
11	NFN-MOF/NF	44 mV dec ⁻¹	288 mV at 200 mA/ cm ²	11
12	WNF-MOF		270 mV at 50 mA/cm ²	This work

Table1. Comparison of the activity of the WNF-MOF with the recently published work

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