Supporting Information

W-promoted OER Kinetics of Bimetallic hydroxide: An Experimental Analysis via Operando EIS and Temperaturedependent Study

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This file contains **25** pages of the details of reagents, electrochemical results, electrochemical characterizations, and characterizations like post-HR-TEM, FE-SEM, and EDS spectra results are provided.

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Reagents and Instruments:

Cobalt nitrate Hexahydrate $(Co(NO_3)_2.6H_2O)$, Nickel nitrate Hexahydrate (Ni(NO₃)₂.6H₂O), Tungsten Tetrachloride (WCl₄), Urea, Ammonium fluoride (NH₄F) were obtained from Sigma-Aldrich and used as received. Acetone, 1N HCl and Ethanol were purchased from Merck and used as received. Ni foam was purchased from Sigma-Aldrich and used after surface cleaning. Characterization of the catalyst was done by HR-TEM, (TecnaiTM G² TF20), operating at an accelerating voltage of 200 kV and elemental color mapping by Talos F-200-S with HAADF. Energy Dispersive X-ray Spectroscopy (EDS) analysis was performed by SUPRA 55VP Carl Zeiss with a separate EDS detector. Scanning Electron Microscopy (SEM) analysis was carried with a Hitachi, Japan (Model S-3000H) having magnification varying from 30X to 300 KX with the accelerating voltage ~ 0.3 to 30 kV. XRD analysis was carried out with a scanning rate of 5° min⁻¹ in the 2θ range 10-90° using a Rigaku X-ray powder diffractometer (XRD) with Cu K_a radiation ($\lambda = 0.154$ nm). The electrochemical analyser AURT-M204 was used for all electrochemical characterizations.¹ Hg/HgO reference electrode (1M KOH) from CH instruments and platinum as counter electrode from Alfa-Aesar were used throughout the electrochemical studies. The entire experiments were conducted using deionised water. The overall potential data was obtained by utilising Hg/HgO (reference electrode), which was converted into a RHE (E_{RHE}) scale by the Nernst equation

$$E_{RHE} = E_{ref} + 14 \times 0.059 + 0.098...$$
 equation S1

Over potential (η) value of NiCo-LDH and W_{2.4}-NiCo-LDH to attain current density of 50 mA/cm² is calculated by the following equation:

$$\eta = E_{RHE} - 1.23 V$$
 (for OER) equation S2

The Tafel equation was fitted to match η vs. log (current density) after determining the Tafel slope from data of the LSV polarization curve.

$\eta = a + b \times \log(j)$ equation S3

where j-current density, b-Tafel slope value. To carry out Electrochemical impedance spectroscopy (EIS) measurements the frequency ranges chosen from 10^5 to 0.1 Hz at 325 mV of overpotential value for OER. Also, Operando-EIS study was performed by using a carbon cloth (CC) electrode-working electrode at a various applied potential. The double layer capacitance (C_{dl}) value can be calculated by evaluating as given below:

$$\Delta J = v \times C_{dl}$$
 equation S4

 ΔJ - current in double-layer capacitance obtaining from scan-rates (v) in the non-faradic potential region.²

For the RRDE experiment, 4 mg of $W_{2,4}$ -NiCo-LDH catalyst was added to a solution containing 200 µL of ethanol, 750 µL of H2O, and 50 µL of 5% Nafion solution. To prepare a homogeneous catalyst ink mixture was sonicated for 20 min. Later, 15 µL of homogeneous ink was drop-casted over the GC disk of RRDE set up with an effective surface area of ≈ 0.197 cm². The Pt ring was used with a constant potential of -0.3V versus RHE to reduce the asformed O₂ in situ.³ The FE was calculated from the ratio of the ring current to the disk using the following expression:

$$FE = I_{ring} / (I_{disk} \times N) \times 100 \dots equation S5$$

where, " I_{ring} " and " I_{disk} " are the ring and disk current density in mA cm⁻², respectively; "N" is the collection efficiency having a constant value of 0.249.



Figure S1: EDS spectrum of (a) W-NiCo-LDH and (b) $W_{2.4}$ -NiCo-LDH from FE-SEM showing the presence of all the expected elements.



Figure S2 (a-f): The electrochemically effective surface area for NiCo-LDH and W_x -NiCo-LDH (x=0.6, 1.2, 2.4, 3.6, 4.8 mol%) respectively.

1. Estimation of the electrochemical double-layer capacitance (C_{dl})

To calculate the electrochemical double-layer capacitance for NiCoLDH and W_x-NiCo-LDH (X=0.6, 12, 2.4, 3.6 and 4.8 mol%), the cyclic voltammetry methods were performed with various scan rates ranging from 30 mV/s to 150 mV/s with a step of 30 mV/s. The potential is scanned from 0.2 to 0.3 V vs Hg/HgO where no faradic current was observed. The center of this working potential (i.e., 0.25 V) was selected to calculate ΔJ_0 (vs Hg/HgO). Hence, we plotted the differences in current densities ($\Delta J = J_a - J_c$) at 0.25 V (vs. Hg/HgO) against the scan rates. Hence, the electrochemical double-layer capacitance was calculated using the formula below.

Hence, the electrochemical double-layer capacitance was measured by using the formula

a. For NiCo-LDH in 1.0 M KOH

$$C_{dl} = \frac{(0.772 - (0.22)(mA/cm^2))}{(150 - 30)(mV/s)} = 4.6 \text{ mFcm}^{-2}$$

b. For W_{0.6}-NiCo-LDH in 1.0 M KOH

$$C_{dl} = \frac{(0.948 - 0.3)(mA/cm^2)}{(150 - 30)(mV/s)} = 5.4 \text{ mFcm}^{-2}$$

c. For W_{1.2}-NiCo-LDH in 1.0 M KOH

$$C_{dl} = \frac{(1.34 - 0.54)(mA/cm^2)}{(150 - 30)(mV/s)} = 6.7 \text{ mFcm}^{-2}$$

d. For W_{2.4}-NiCo-LDH in 1.0 M KOH

$$C_{dl} = \frac{(1.43 - 0.398)(mA/cm^2)}{(150 - 30)(mV/s)} = 8.6 \text{ mFcm}^{-2}$$

e. For $W_{3.6}$ -NiCo-LDH in 1.0 M KOH

 $C_{dl} = \frac{(0.956 - (0.32)(mA/cm^2))}{(150 - 30)(mV/s)} = 5.3 \text{ mFcm}^{-2}$

f. For $W_{4.8}\mbox{-NiCo-LDH}$ in 1.0 M KOH

 $C_{dl} = \frac{(0.94 - (0.328)(mA/cm^2))}{(150 - 30)(mV/s)} = 5.1 \text{ mFcm}^{-2}$

The ECSA can be calculated from the $C_{dl}\xspace$ according to:

ECSA for NiCo-LDH
$$= \frac{4.6 \ mFcm^{-2}}{0.04 \ mF \ cm^{-2} \ cm_{ECSA}^{2}} = 115 \ cm_{ECSA}^{2}$$

ECSA for W_{0.6}-NiCo-LDH =
$$\frac{5.4 \ mFcm^{-2}}{0.04 \ mF \ cm^{-2} \ cm_{ECSA}^{-2}} = 135 \ cm_{ECSA}^{-2}$$

ECSA for W_{1.2}-NiCo-LDH =
$$\frac{6.7 \ mFcm^{-2}}{0.04 \ mF \ cm^{-2} \ cm_{ECSA}^{-2}} = 167 \ cm_{ECSA}^{2}$$

ECSA for W_{2.4}-NiCo-LDH =
$$\frac{8.6 \ mFcm^{-2}}{0.04 \ mF \ cm^{-2} \ cm_{ECSA}^{-2}} = 215 \ cm_{ECSA}^{2}$$

ECSA for W_{3.6}-NiCo-LDH =
$$\frac{5.3 \ mFcm^{-2}}{0.04 \ mF \ cm^{-2} \ cm_{ECSA}^{-2}} = 132 \ cm_{ECSA}^{2}$$

ECSA for W_{4.8}-NiCo-LDH =
$$\frac{5.1 \ mFcm^{-2}}{0.04 \ mF \ cm^{-2} \ cm_{ECSA}^{-2}} = \frac{127 \ cm_{ECSA}^{2}}{127 \ cm_{ECSA}^{2}}$$



Figure S3: ECSA normalized LSV polarisation curve plot of NiCo-LDH and W_x -NiCo-LDH (x=0.6, 1.2, 2.4, 3.6, 4.8 mol %) respectively.



Figure S4 (a-f): The area of reduction peak for NiCo-LDH and W_x -NiCo-LDH (x=0.6, 1.2, 2.4, 3.6, 4.8 mol %) respectively.

S.No	Concentration (M) of W ⁴⁺ in NiCo-LDH	Overpotential (mV) at current density of 10 mA cm ⁻²	Reduction surface area (VA)	Charge over the electrode surface (C)
1	0.003	340	0.00658	0.116
2	0.006	330	0.00686	1.32
3	0.012	260	0.00775	1.55
4	0.024	300	0.0083	1.66

Table S1: Comparison table for OER activity of various concentrations of W4+ in NiCo-

LDH.



Figure S5: Volcanic plot of charge accumulated over the catalyst surface vs current density value at 1.62 V vs RHE.



Figure S6: LSV responses of the taken RRD electrode for the redox reaction of ferroferri in 0.1 M KNO₃ with 10 mM of K_3 [Fe(CN)₆] at various rotation speed by using RRD electrode.

Table S2. Collection Efficiency (N) value for the redox reaction of ferro-ferri in 0.1 M KNO3
with 10 mM of $K_3[Fe(CN)_6]$ at various rotation speed by RRD electrode

S.No	Rotation speed (RPM)	Disc current (mA)	Ring current (mA)	Collection Efficiency (N)	
1	100	0.224561	0.05796	0.258103589	
2	400	0.316	0.07779	0.246170886	
3	900	0.3881	0.098266	0.25319762	
4	1600	0.446	0.10919	0.244820628	
5	2500	0.491	0.11857	0.241486762	
			Average	0.248755899	

Calculation of Faradaic Efficiency (FE):

The Faradaic Efficiency for NiCo-LDH in OER process was calculated by using Rotating Ring-Disk (RRD) technique as follows:

Ring current for complex 1 (I_{ring}) = 0.040 mA

Disc current for complex 1 (I *disc*) = 0.199 mA

Collection Efficiency (N) = 0.249 (The Collection Efficiency (N) value calculated experimentally by using ferri/ferrocyanide system in 0.1 M KNO₃ with 10 mM K_3 [Fe(CN)₆], the data are given in Figure S8d and Table S5)

Faradaic Efficiency in complex 1 in OER process

$$= \frac{I_{ring}}{N * I_{disc}}$$

$$= \frac{0.040 \ mA}{0.249 \ * \ 0.199 \ mA} = 0.928 \ *100 = 80.36\%$$

The Faradaic Efficiency for $W_{2,4}$ -NiCo-LDH in OER process was calculated by using the Rotating Ring-Disk (RRD) technique as follows:

Ring current for complex 1 (I_{ring}) = 1.57 mA

Disc current for complex 1 (I disc) = 6.79 mA

Collection Efficiency (N) = 0.249

Faradaic Efficiency in complex 1 in OER process

$$= \frac{I_{ring}}{N * I_{disc}}$$

 $= \frac{0.048 \ mA}{0.249 \ * \ 0.146 \ mA} = 0.928 \ *100 = 92.63\%$

Determination of various Surface concentration in W-doped NiCo-LDH from the redox features of CV:

• Calculated area associated with the reduction of Ni³⁺ to Ni²⁺ of NiCo--LDH

Hence, the associated charge is = $0.0067 \text{ VA} / 0.005 \text{ Vs}^{-1}$ (Equation S6)

Now, the number of electrons transferred is

= $1.34 \text{ C} / 1.602 \times 10^{-19} \text{ C}$ (Equation S7)

 $= 0.8364 \times 10^{19}$

Since, the reduction of Ni³⁺ to Ni²⁺ is a single electron transfer reaction, the number electron calculated above is exactly the same as the number of surface-active sites.

Hence, the number of Ni participate in OER is = 0.836×10^{19}

Hence, Determination of Turnover Frequency (TOF) from OER Current Density TOF in our study was calculated assuming that the surface-active Fe atoms that had undergone the redox reaction just before onset of OER only participated in OER electrocatalysis. The corresponding expression is,

 $TOF=j \times N_A / F \times n \times \Gamma \quad \longrightarrow \quad \text{(Equation S8)}$

Where, j = current density N_A= Avogadro number F = Faraday constant n = Number of electrons Γ = Surface concentration.

TOF= $[(109 \times 10^{-3}) (6.023 \times 10^{23})] / [(96485) (4) (0.836 \times 10^{19})]$

 $= 0.00231 \text{ s}^{-1}$

• Calculated area associated with the reduction of Ni^{3+} to Ni^{2+} of $W_{2.4}$ -NiCo--LDH

$$= 0.00775 \text{ VA}$$

Hence, the associated charge is = $0.00775 \text{ VA} / 0.005 \text{ Vs}^{-1}$ (Equation S9)

Now, the number of electrons transferred is

$$= 1.55 \text{ C} / 1.602 \times 10^{-19} \text{ C} \qquad \longrightarrow \qquad \text{(Equation S10)}$$
$$= 0.967 \times 10^{19}$$

Since, the reduction of Ni³⁺ to Ni²⁺ is a single electron transfer reaction, the number electron calculated above is exactly the same as the number of surface-active sites.

Hence, the number of Ni participating in OER is = 0.967×10^{19}

Hence, the Determination of Turnover Frequency (TOF) from OER Current Density TOF in our study was calculated assuming that the surface-active Fe atoms that had undergone the redox reaction just before onset of OER only participated in OER electrocatalysis. The corresponding expression is,

 $TOF=j \times N_A / F \times n \times \Gamma \quad \longrightarrow \quad (Equation \ S11)$

Where, j = current density N_A= Avogadro number F = Faraday constant n = Number of electrons Γ = Surface concentration.

TOF= $[(454 \times 10^{-3}) (6.023 \times 10^{23})] / [(96485) (4) (0.967 \times 10^{19})]$

$$= 0.0732 \text{ s}^{-1}$$



Figure S7: (a and b) Nyquist plot measured at various applied voltages of NiCo-LDH and W_{2.4}-NiCo-LDH respectively.

Table S3	Comparison	table for	· OER	activity	of	W _{2.4} -NiCo-LDH/NF	with similar	r type	of
catalyst.									

SI.No	Catalyst	Overpotential @50 mA/cm2 (mV)	Tafel slope (mV/dec)	Stability (hours)	References
1	Ce ⁻ NiCo-LDH/NF	250	98	24	1
2	Ce-NiFe-LDH/CNT	227	33	8	2
3	CoNi-LDH/CoNiSe ₂	269	102	12	3
4	NiMn-LDH/NiCo ₂ S ₄	312	83	20	4
5	NiMn-LDH/NF	253	130	20	5
6	CoFe Borate-LDH	418	131	50	6
7	Co(OH)2@NiFe- LDH/NF	209	38	100	7
8	CuS/NiFe-LDH	249	81.84	24	8
9	Sm-NiCu-LDH	284	109	48	9
10	NiV-LDH@Mn ₂ O ₃	298	89	54	10
11	Se@CoFe-LDH	251	47	10	11
12	Ag@NiFeLDH	330	89	12	12

13	W _{2.4} -NiCo-LDH/NF	260	62.64	100	This work
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Figure S8: iR uncompensated LSV polarisation curve plot for $W_{2,4}$ -NiCo-LDH in different electrolytes such as LiOH, NaOH, KOH and CsOH with 0.1M concentration respectively.



Figure S9: (a and b) Low and high magnification FE-SEM images post-OER $W_{2.4}$ -NiCo-LDH/NF respectively.



2 µm

Figure S10: (a-b) Low and High magnification images (c) Lattice fringes (d) SAED pattern (e) HAADF color mapping (f-i) Uniform distribution of Ni, W, O and Co respectively of Post-OER $W_{2,4}$ -NiCo-LDH.



Figure S11: (a-d) The Deconvulated XPS spectra for Ni 2p orbital, Co 2p orbital, O 1s orbital and W 4f orbital of Post-OER study of $W_{2,4}$ -NiCo-LDH.

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