# **Supporting Information**

# Electronic Modulation of Iridium Single Atomic Sites on NiCr Layered Double Hydroxide for an Improved Electrocatalytic Oxygen Evolution Reaction

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# 1. Experimental methods

#### 1.1. Chemicals and materials

Unless stated otherwise, all chemicals and electrochemical experiments were handled by using non-metallic materials and instruments (vials, containers, etc.) to avoid trace-metal contamination.

The following chemicals were used as received; any materials or chemicals requiring a separate preparation strategy are mentioned in the below subsections of methodologies. NiCl<sub>2</sub>.6H<sub>2</sub>O, CrCl<sub>3</sub>.6H<sub>2</sub>O, IrCl<sub>3</sub>.H<sub>2</sub>O were sourced from Sigma-Aldrich ( $\geq$  99.9% trace metal). IrO<sub>2</sub>; Alfa Aesar (99.9% trace metal). NaOH, KOH, NaCl, Na<sub>2</sub>CO<sub>3</sub> were procured from Merck Millipore. All the synthesis and electrochemical analyses were performed by using D.I water to minimize organic and trace-metal contamination. Carbon fiber paper; (Toray 060 - TGP-H-060, 5% wt-proofing, 190 µm thickness). Nafion perfluorinated 117 membranes; Fuel cell store (180 µm thickness).

#### 1.2. Synthesis, methodologies, and instrumentation

#### 1.2.1. Synthesis of NiCr LDH

In a typical synthesis procedure, NiCr LDH was synthesized by coprecipitating 40 ml aqueous solution of NiCl<sub>2</sub>.6H<sub>2</sub>O (6 mmol) and CrCl<sub>3</sub>.6H<sub>2</sub>O (2mmol) with 40 ml buffer solution of Na<sub>2</sub>CO<sub>3</sub> (3 mmol) and NaOH (21 mmol). With continuous stirring, the pH of the final solution was maintained carefully at 9. Vigorous stirring for 2 h followed by 24 h of aging formed the dark green sedimentation of our desired LDH. The resultant compound was washed several times with water and ethanol followed by sample drying in a vacuum oven at 70 °C for 12 h producing the Ni-Cr LDH.

#### 1.2.2. Synthesis of Ir<sub>1</sub>/NiCr LDH SAC

IrCl<sub>3</sub>.H<sub>2</sub>O precursor salt was solubilized in 40 ml of 0.01 M NaOH, and 0.2 g of NiCr LDH was dispersed in the solution followed by 24 h of continuous stirring under a nitrogen atmosphere. A dusky green precipitate was obtained which was washed with water and ethanol 5 times to remove the ionic traces. Overnight vacuum drying at 70 °C produced fine powder of the SAC. A similar procedure was mimicked to produce Ir SAC with different Ir loading by using 2, 4, 5, and 6 mg of IrCl<sub>3</sub>.H<sub>2</sub>O precursor salt.

#### 1.2.3. Material characterization and instruments

The morphology of the catalysts was analyzed through FESEM by using JEOL JSM-7800F Prime (JEOL, Japan). EDS of the samples were performed by LN2 free SDD X-max 80 detector (Oxford Instruments). HRTEM images of the catalyst were taken by a 200 kV JEOL JEM-ARM200F NEOARM instrument equipped with cold FEG Tungsten filament. Raman spectra were collected by Renishaw Raman spectrometer (GL 12 7 DW, UK) with a 514 nm laser source. XRD of the catalysts was performed by Malvern PANalytical Empyrean instrument from 5 to 70° with a step size of 0.02°. XPS of the samples was performed with Axis supra instrument having a monochromatic X-ray source of 1486.6 eV Al K $\alpha$ . XAS facility was availed by Indus-2 beamline of 2.5 GeV synchrotron radiation source (RRCAT Indore, India). Metrohm Autolab potentiostat was used to perform all the electrochemical analyses. To conduct the in-situ operando FTIR study, CHI electrochemical workstation (CHI660D) was used for applying potentials and React IR (Mettler Toledo; ReactIR 702L) was used to collect the FTIR spectra. ICP-MS data of the samples were collected by Agilent 7900 instrument.

#### 1.2.4. EXAFS measurement and fitting parameters

Ir L<sub>3</sub>-edge XAS spectra for Ir<sub>1</sub>/Ni-Cr LDH, IrO<sub>2</sub>, IrCl<sub>3</sub>. H<sub>2</sub>O and Ir-foil were collected by the Indus-2 beamline of the RRCAT synchrotron radiation facility (Applied spectroscopy division, BARC, India). The Dispersive Extended X-ray Absorption Fine Structure (DEXAFS) beamline (BL08) of the Indus-2 beamline is dedicated for X-ray absorption in transmission as well as fluorescence mode using dispersive optics. The beamline operates at 2.5 GeV and a bent crystal (Si 111) polychromator is used to select a band of energy from the white synchrotron beam which is horizontally dispersed and focused on the sample. All the collected EXAFS data were processed through ATHENA module and FEFF software package by taking Ir-foil and IrO<sub>2</sub> as reference material. The overall absorption spectra were normalized according to the edge jump step and the post-edge background was subtracted from the overall absorption spectra to obtain the k<sup>2</sup> -weighted EXAFS spectra. Subsequent Fourier transformations of these k-space spectra to R-space were done to distinguish the EXAFS contribution from different coordination shells. Fitting of these EXAFS curves was performed using FEFF module of the ARTEMIS software package so that structural parameters around the central metal atom can be evaluated precisely. The EXAFS equation used for the fitting is mentioned below,

$$\chi(\mathbf{k}) = \sum \frac{N_j S_0^2 F_j(k)}{kR_j^2} \exp\left[-2k2\sigma_j^2\right] \exp\left[\frac{-2Rj}{\lambda(k)}\right] \sin\left[2kR_j + \phi_j k\right]$$

 $S_0^2$  = Amplitude reduction factor

 $F_j(k) =$  Effective curved-wave backscattering amplitude

- $N_j$  = No. of neighbors in the jth atomic shell
- $R_j$  = Distance between the X-ray absorbing central atom and atom in the jth atomic shell
- $\phi_i$  (k) = Phase shift

 $\sigma_i^2 = \text{Debye-Waller parameter}$ 

#### 1.3 In-situ operando-FTIR study

An open-top cell setup filled with electrolyte solution was used for the analysis in which three electrodes were placed through their corresponding holes. The IR probe was dipped into the electrolyte solution and placed close to the surface of catalyst-mounted carbon fibre paper without touching it. Starting with OCP, 5 mins of bulk electrolysis was performed with each varying potential, and their corresponding FTIR spectra were collected. The range of the spectrum was set between 500-1500 cm<sup>-1</sup>.

Before taking the spectra through the IR probe, background spectra were collected in air and electrolyte solution itself so that they can be subtracted from the spectra collected at each varying potential.

#### 1.4. ICP-MS data calculation

Calculation of Ir loading in Ir<sub>1</sub>/NiCr LDH catalyst was done in the following way.

Sample weight of extraction = 0.005 g

The volume of extraction = 45 ml (0.045 L)

From ICP-MS data, the concentration of Ir was found to be 15.937 ppb. The actual sample was diluted 100 times before analysis. So the final concentration of Ir = 1593.7 ppb = 1.5937 mg/L

Conc. of Ir (mg/g) =  $\frac{\text{Conc. of Ir } (\frac{mg}{L}) \times \text{Volume of extract } (L)}{\text{Weight of Ir}_1/\text{NiCr LDH}}$ 

$$= \frac{1.5937 \left(\frac{mg}{L}\right) \times 0.05 L}{0.005 \text{ g}} = 15.937 \text{ mg/g} = 1.59 \%$$

Similar calculation parameters were used to identify the content of other metallic species.

#### **1.5. Electrochemical measurements**

All the electrochemical measurements were performed in freshly prepared 1 M KOH electrolyte solution. For the simulated seawater medium, a mixed solution of 1 M KOH and 0.5 M NaCl was used. A three-electrode setup with Ag/AgCl as the reference electrode and Pt mesh as the counter electrode was used for the electrolysis. Both glassy carbon electrodes (3 mm diameter) and carbon fibre paper  $(1 \text{ cm}^2)$  have been used as working electrodes. To prepare the catalyst ink, 4 mg of the as-prepared catalyst and 1mg of carbon black were finely dispersed in 1 ml of water by sonicating for 30 mins. After adding 25 µl of 5% Nafion solution, the catalyst was further sonicated for 15 mins. 10 µl of the prepared catalyst ink was drop cast onto the glassy carbon electrode, 200 µl of the catalyst ink was mounted on a 1 cm x 1 cm area. All the LSV polarization curves were taken at 1 mV/sec. To avoid bubble formation on the working electrode surface, 1600 rpm was fixed when the glassy carbon electrode was used as a working electrode in the RDE setup. Non-faradaic scans were measured in the capacitive region (0.9 V-1 V).

#### 1.5.1. Chronoamperometry measurement

Fresh catalyst ink prepared with the earlier mentioned concentration ratio was mounted on carbon fibre paper and kept at 1.48 V (vs RHE) for 36 h. No significant decay in current density was observed throughout. The appearance of the rough spectra is because of the continuous bubble formation and bursting throughout the analysis period. After performing the long-term stability study, electrolyte solutions were collected for ICP-MS analysis to quantify the metal leaching in all three catalyst systems.

## 1.5.2. Faradaic efficiency performance

An H-type cell being separated by a perfluorinated Nafion117 membrane was used for the experimental setup to calculate Faradaic efficiency. One side of the cell contained reference (Ag/AgCl) and the working electrode (Catalyst loaded CFP) whereas the other side held up to

the counter electrode (Pt mesh). The probe of the dissolved oxygen meter was dipped into the electrolyte side of the working electrode and made completely airtight from both sides to avoid any kind of leakage and gas escape. Bulk electrolysis was carried out keeping the potential at 1.47 V vs RHE (11 mA/cm<sup>2</sup> current density) for 6 h. Increased ppm level of dissolved oxygen was noted and a similar cycle was conducted 5 times to collect 30 h results for Faradaic efficiency.

Before using the dissolved oxygen meter, a two-point calibration was performed with air and zero oxygen liquid to avoid any instrumental error. Calibration was repeated each time before the 6 h measurement cycle.

#### **1.5.3. ECSA calculation**

Electrochemical active surface area (ECSA) of a catalyst has a linear relation with the electrochemical double-layer capacitance ( $C_{dl}$ ) of the electrocatalyst. CV plots at different scan rates in the non-faradaic capacitive current region will provide its direct measure. Considering this, potential sweeps between 0.9 V to 1 V vs RHE with varying scan rates (10-50 mV/s) were collected. The relation between double-layer charging current ( $i_c$ ) and scan rate can be described as

$$i_c = vC_{dl}$$

The slope obtained from the plot of  $i_c$  and scan rate (v) can be identified as  $C_{dl}$ . Further ESCA was calculated by dividing  $C_{dl}$  with  $C_s$ ,

$$ECSA = C_{dl}/C_s$$

where  $C_s$  is the specific capacitance of a catalyst with an atomically smooth planar surface per unit area in a particular electrolyte medium. General consideration for  $C_s$  in 1 M NaOH lies between (0.035-0.06) mF/cm<sup>2</sup>. Here we have considered the upper limit value for  $C_s$  as 0.04 mF/cm<sup>2</sup> for ECSA calculation. The surface roughness factor (S) was taken as 0.196 here.

#### 1.5.4. Faradaic efficiency calculation

Faradaic efficiency in the case of OER can be defined as the ratio between the actual yield of oxygen to the theoretical yield of oxygen.

$$FE = \frac{Experimental mmole of O_2 gas}{Theoretical mmole of O_2 gas} \times 100$$

The theoretical oxygen gas produced can be calculated by Faraday's law equation

$$n = \frac{I \times t}{z \times F}$$

where *n* is the number of moles of O<sub>2</sub>, *I* correspond to the current in ampere, *z* is the electrons transferred (for OER, z = 4), t is the time in seconds and *F* is the Faraday's constant (96485.3 C mol<sup>-1</sup>).

Considering the experimental  $O_2$  production as m, Faradaic efficiency can be calculated as

$$FE = \frac{m}{n} = \frac{m \times z \times F}{I \times t}$$

 $O_2$  produced during the OER process was measured at 10 mA/cm<sup>2</sup> current density (0.01 ampere) by dissolved oxygen meter in ppm unit (1 ppm = 0.05556 mmol for  $O_2$ ).

#### 1.5.5. Turn Over Frequency (TOF) calculation

Turn over frequency for O<sub>2</sub> generation is calculated from the following formula.

$$TOF = \frac{\text{Total number of } O_2 \text{ turnover per geometric area (cm2)}}{\text{Total no of active sites per geometric area (cm2)}}$$

The total number of O<sub>2</sub> generation per unit area was calculated by using the equation of current density (j) from LSV polarization curves.

$$\left( \left| j \right| \frac{mA}{cm^2} \right) \left( \frac{1 C/s}{1000 mA} \right) \left( \frac{1 mol}{96458.3 C} \right) \left( \frac{1 mol}{4 e^{-1}} \right) \left( \frac{6.023 \times 10^{23}}{1 mol O_2} \right)$$
$$= 1.56 \times 10^{15} \left( \frac{O_2/s}{cm^2} \right) \text{ per } \left( \frac{mA}{cm^2} \right)$$

Assuming each Iridium center in the catalyst acts as an active site, the number of Ir atoms in Ir<sub>1</sub>/NiCr LDH was calculated from Ir molar mass and mass loading on the surface of the glassy carbon electrode. From the ICP-MS data, 1.59 % mass loading has been detected in the catalyst. Mass loading on the glassy carbon electrode was calculated to be 0.2857 mg/cm<sup>2</sup>. The upper limit of active sites per geometric area was calculated by the following equation, 0.2857 mg/cm<sup>2</sup> × 10 <sup>-3</sup> × 1.59 × 6.023 × 10<sup>23</sup>

192.22 g/mol =1.426 × 10<sup>16</sup> sites/cm<sup>2</sup> TOF at an overpotential of 232 mV (10 mA/cm<sup>2</sup>)

$$= \frac{1.56 \times 10^{15} \left(\frac{O_2/s}{cm^2}\right) \text{ per } \left(\frac{mA}{cm^2}\right) \times 10 \left(\frac{mA}{cm^2}\right)}{1.426 \times 10^{16} \text{ sites/cm}^2} = 1.093/\text{ site s}^{-1}$$

Similar calculation methods were implemented to calculate the TOF of  $Ir_1/NiCr LDH$  at 320 mV (common overpotential for comparison between  $IrO_2$  and  $Ir_1/NiCr LDH$ ).

ICP-MS data suggested the Ir content in IrO2 is 73.6 % and the corresponding upper limit for the number of active sites in  $IrO_2$  was calculated. Following the same protocol and calculation parameters, TOF for  $IrO_2$  at 232 and 320 mV was calculated.

#### 1.5.6. Mass activity calculation

Mass activity (A  $g_{metal}^{-1}$ ) of Ir<sub>1</sub>/NiCr LDH and IrO<sub>2</sub> were calculated from normalized current density (0.2857 mg/cm<sup>2</sup>) with respect to applied potential data. As per the following equation, the mass activity of Ir<sub>1</sub>/NiCr LDH was calculated.

Mass activity<sub>Ir1/NiCr LDH</sub> =  $\frac{|j|}{0.2857 \times 1.59\%}$  = 220.136 |j| A g<sub>metal</sub><sup>-1</sup> per cm<sup>2</sup>

At 232 and 320 mV overpotential, the current density of  $Ir_1/NiCr LDH$  is 10 and 65 mA/cm<sup>2</sup> respectively.

The calculated Mass activities are Mass activity<sub>232 mV</sub> = 2201.36 A  $g_{metal}^{-1}$ 

Mass activity<sub>320 mV</sub> = 14,308.84 A 
$$g_{metal}^{-1}$$

The mass activity of IrO<sub>2</sub> was calculated by the following equation.

Mass activity of  $IrO_2 = \frac{|j| \times 224.22 \text{ g/mol}}{0.2857 \times 73.6 \% \times 192.22 \text{ g/mol}} = 5.5473 \times |j|$ 

Current densities at 232 and 320 mV for  $IrO_2$  are 0.42 and 4.36 mA/cm<sup>2</sup> respectively.

Calculated Mass activity for IrO<sub>2</sub>, Mass activity<sub>232 mV</sub> = 2.2189 A g<sub>meta</sub>

Mass activity<sub>320 mV</sub> = 22.364 A  $g_{metal}^{-1}$ 

#### **1.6.** Computational details

All the computational simulations were performed using dispersion-corrected Density Functional Theory (DFT)-D3<sup>1</sup> as included CP2K simulation package.<sup>2</sup> Quickstep method was used for optimizing the structure as well as geometry. To simulate the LDHs in CP2K with reasonable accuracy, a plane-wave cutoff of 300 Ry is used. The Perdew-Burke-Erzerhof (PBE) functional within generalized gradient approximation (GGA) is considered for exchange and correlation interactions.<sup>3</sup> The interatomic forces are relaxed to less than 0.0027 eV.

The model structure was designed using VESTA<sup>4</sup> for the pristine Ni<sub>3</sub>(II)Cr<sub>1</sub>(III)–LDH system having the slab model of two layers of LDH. Geometry optimization is done by taking a supercell of dimensions  $2 \times 2 \times 1$  having 224 atoms and  $R\overline{3}m$  space group.<sup>5</sup> A vacuum of 20 Å is created in the supercell along the (001) plane to model a surface that contains an LDH layer as the exposed one. The atoms of the lower slab remain frozen during all simulations to model the bulk part of LDH. Another model has been designed where the edge-defect Ni<sub>3</sub>(II)Cr<sub>1</sub>(II) is made by creating a (110) surface on pristine, made up of three layers of LDH with a total of 168 atoms. Again, a vacuum is added along the x-axis, and atoms of the lowest slab are considered frozen. Moreover, to improve the OER activity we introduced Iridium (Ir) atoms on the (001) surface of pristine Ni<sub>3</sub>(II)Cr<sub>1</sub>(III)–LDH which is acting as a SAC (Ir<sub>1</sub>/NiCr LDH). And it is made by deprotonating four oxygen atoms on the surface, leading to the formation of a void for the Ir atom adsorption with a total number of 221 atoms. To compare the activity of SAC, we have taken the traditional IrO<sub>2</sub>-slab model consisting of five layers with inversion symmetry, and a vacuum is included along the (110) direction to use this plane as the reaction surface. Using the above-mentioned optimized models, we calculated energetics for each step of the reaction mechanism for individual models.

# **1.7. Electron microscopy analysis**

# 1.7.1. FESEM images of NiCr LDH



Figure S1. FESEM images showing the layered morphology of NiCr LDH.

# 1.7.2. FESEM images of Ir<sub>1</sub>/NiCr LDH



Figure S2. FESEM imaging of Ir<sub>1</sub>/NiCr LDH showing the retention of layered morphology.

# 1.7.3. HRTEM images of NiCr LDH



**Figure S3.** High-resolution TEM imaging of NiCr LDH showed the presence of layered morphology along with partial crystalline nature. Lattice fringes showed the d spacing to be around 0.57 nm.

# 1.7.4. HRTEM images of Ir<sub>1</sub>/NiCr LDH



**Figure S4.** HRTEM images of Ir<sub>1</sub>/NiCr LDH showed the retention of layered morphology after Ir stabilization. An important observation was the absence of nanoparticle formation on the surface of NiCr LDH, providing primary information about the single atomic existence of Ir. Undisturbed d-spacing in comparison to NiCr LDH proved the unchanged lattice parameter and structural dynamics.

# 1.7.5. EDS-Mapping images of NiCr LDH



**Figure S5.** The presence of Ni and Cr was confirmed through EDS mapping data. The ratio of Ni: Cr was found to be 3:1.



# 1.7.6. EDS-Mapping images of Ir<sub>1</sub>/NiCr LDH

**Figure S6.** EDS mapping data Ir<sub>1</sub>/NiCr LDH showed the primary significance for the presence of Ir on the NiCr LDH surface.

#### 1.7.7. Powder X-ray diffraction analysis



**Figure S7.** XRD pattern of NiCr LDH and Ir<sub>1</sub>/NiCr LDH showed no difference, providing evidence for undisturbed lattice dynamics after single atomic stabilization. The simulated XRD pattern also matches precisely with the obtained XRD pattern. The absence of any additional peak corresponding to Ir suggested that there was no nanoparticle formation.

#### 1.7.8. Raman spectra analysis



**Figure S8.** Raman spectra of Ir<sub>1</sub>/NiCr LDH match with NiCr LDH by having peaks  $v_1$ ,  $v_2$ , and  $v_3$  at similar wavenumber regions.  $v_1$ ,  $v_2$ , corresponds to  $E_g A_{1g}$  Raman active vibrational mode of Ni(OH)<sub>2</sub>. Broad and intense peak ( $v_3$ ) at 530-540 cm<sup>-1</sup> is a superposition of the Cr-O-H bending mode of Cr(OH)<sub>3</sub> and the second-order acoustic mode of Ni(OH)<sub>2</sub>. The effect of

atomic stabilization of Ir becomes substantial when Raman spectra of  $IrO_2$  are compared with  $Ir_1/NiCr LDH$ . The high intensity of  $v_4$  in  $Ir_1/NiCr LDH$  as compared to NiCr LDH is because of the presence of the  $B_{2g}$  band of Ir-O (present in  $IrO_2$ ). This provides a hint of Ir-doping and Ir-O interaction in  $Ir_1/NiCr LDH$ .

# **1.8. X-ray photoelectron spectroscopy**



1.8.1. XPS survey spectra

Figure S9. XPS survey spectra of NiCr LDH (A) and Ir<sub>1</sub>/NiCr LDH (B)



# 1.8.2.0 1s spectra comparison

**Figure S10.** Broadening of O1s spectra after atomic stabilization Ir appeared as a slightly broadened peak around 533 eV and was considered an Ir-O interaction.

#### 1.8.3. Ir 4f spectra comparison



**Figure S11.** Ir 4f spectra comparison of  $Ir_1/NiCr LDH$  with  $IrO_2$  and  $IrCl_3.H_2O$  showed evidence for its intermediate oxidation state as the peak appeared to be in between  $IrO_2$  and  $IrCl_3.H_2O$ , corresponding to +3 and +4 oxidation states respectively.

# 1.9. HAADF-STEM images of Ir/NiCr LDH



**Figure S12.** HAADF-STEM images of  $Ir_1/NiCr$  LDH confirmed the atomic existence of Ir as bright spots on a relatively darker NiCr LDH matrix. On the basis of Z-contrast imaging, the resolved images of  $Ir_1/NiCr$  LDH are present here in a 3-1 nm scale bar.



Figure S13. STEM- EDS mapping data of Ir<sub>1</sub>/NiCr LDH.

# 2. Additional information from X-ray Absorption Spectroscopy

#### 2.1. XANES analysis



**Figure S14.** Extrapolating the pre-edge excitation energy values, the oxidation state of Ir<sub>1</sub>/NiCr LDH was found to be 3.58.

# 2.2. EXAFS spectra fitting

## 2.2.1. EXAFS fitting of IrCl<sub>3</sub>.H<sub>2</sub>O



Figure S15: q, k, R-space fitting plot of IrCl<sub>3</sub>.H<sub>2</sub>O

## 2.2.2. EXAFS fitting of Ir-foil



Figure S16: q, k, R-space fitting plot of Ir-foil.

## 2.2.3. EXAFS fitting of IrO<sub>2</sub>



Figure S17: q, k, R-space fitting plot of IrO<sub>2</sub>

# 2.2.4. EXAFS fitting of Ir<sub>1</sub>/NiCr LDH



Figure S18: q, k, R-space fitting plot of Ir<sub>1</sub>/NiCr LDH

# 3. Electrochemical analysis



3.1. Ir loading at different concentrations for optimization of OER activity

**Figure S19.** LSV polarization curves at different Ir loadings on NiCr LDH. Optimum catalytic activity was observed at 4 mg Ir loading. (iR-compensated LSV plots)

#### 3.2 LSV polarization curves with and without iR compensation



Figure S20. 90 % iR-compensated LSV polarization curves of all three catalyst systems.

3.3. Catalyst stability after 3000 CV cycles



**Figure S21.** LSV polarization curve after 3000 CV cycle for Ir<sub>1</sub>/NiCr LDH showed its high catalytic stability.

3.4. Non-faradaic scan, specific capacitance, and ECSA plot in alkaline media OER activity



**Figure S22.** (A, B, C) Non-Faradaic scans in all three catalyst systems showed that the highest capacitive tendency existed in  $Ir_1/NiCr LDH$ . (D) The slope of the plot of current density and scan rate provides the double-layer capacitance value (C<sub>dl</sub>). (E) Dividing the specific capacitance C<sub>s</sub> with C<sub>dl</sub>, the ECSA of all three catalysts was obtained.

3.5. EIS analysis in alkaline medium



**Figure S23.** The EIS plot showed the least charge transfer resistance ( $R_{ct}$ ) in the case of Ir<sub>1</sub>/NiCr LDH. This proves the high charge transfer rate in the SAC system when compared to the other two catalyst systems.



**Figure S24.** Impedance spectroscopy of all three catalyst systems in a simulated seawater medium resulted in a lower charge transfer resistance value as compared to alkaline media. The additional ions present in the electrolyte solution resulted in a higher charge transfer rate. Even though  $IrO_2$  showed very high catalytic activity in the simulated seawater medium,  $Ir_1/NiCr$  LDH overpowered it by showing even less  $R_{ct}$  value.

3.7. Non-faradaic scan, specific capacitance, and ECSA plot in seawater medium OER activity



**Figure S25.** (A, B, C) Non-Faradaic scans in all three catalyst systems showed that the highest capacitive tendency existed in  $Ir_1/NiCr LDH$ . (D) The slope of the plot of current density and scan rate provides the double-layer capacitance value (C<sub>dl</sub>). (E) Dividing the specific capacitance C<sub>s</sub> with C<sub>dl</sub>, the ECSA of all three catalysts was obtained.

# **3.8.** Working electrodes used in the electrochemical analysis



**Image 1.** Two types of working electrodes Glassy carbon (3 mm) electrode and carbon fiber paper (CFP) used to conduct the electrochemical analysis.

# <image>

# **3.9. Electrochemical cell setup**

**Image 2.** Electrochemical cell setup for electrochemical analysis where Ag/AgCl as reference electrode, and Pt mesh as counter electrode were used.

# 4. Post stability (36 h of chronoamperometry) analysis of Ir<sub>1</sub>/NiCr LDH

# 4.1. FESEM of Ir<sub>1</sub>/NiCr LDH



**Figure S26.** FESEM imaging of Ir<sub>1</sub>/NiCr LDH after a long-term stability study showed morphological stability without any significant deterioration.

# 4.2. HRTEM of Ir<sub>1</sub>/NiCr LDH



**Figure S27.** HRTEM imaging and SAED pattern also showed almost consistent results as before catalysis. This shows the robustness of the Ir<sub>1</sub>/NiCr LDH catalyst after stability study.

# 4.3. EDS mapping of Ir<sub>1</sub>/NiCr LDH



**Figure S28.** EDS mapping of Ir<sub>1</sub>/NiCr LDH after a long-term stability study showed that the elemental composition similar to before catalysis.

#### 4.4. Powder XRD analysis



Figure S29. XRD pattern comparison showed similar peaks without any significant shift.

## 4.5. Raman spectra analysis



Figure S30. Raman spectra presented a similar trend in before and after stability study.



4.6. Post catalytic XPS analysis of Ir<sub>1</sub>/NiCr LDH

**Figure S31.** XPS analysis after the stability study showed minimum shifts in individual spectra. The longevity and robustness of the catalyst are higher as all the elements are in their active states to show OER activity.

# 5. In-situ operando FTIR spectra of NiCr LDH



**Figure S32.** In-situ FTR spectra of NiCr LDH showed a peak corresponding to \*OOH at around 1050 cm<sup>-1</sup>. Peaks started intensifying beyond 1.5 V, where significant OER activity has been confirmed from the LSV polarization curve.

# 6. Computational studies

# 6.1. Optimized structure of NiCr LDH



Figure S33. Optimized structure of NiCr LDH (A) top view, (B, C) side views.

# 6.2. Optimized structure of Ir<sub>1</sub>/NiCr LDH



Figure S34. Optimized structure of Ir<sub>1</sub>/NiCr LDH (A) top view, (B, C) side views.

# 6.3. Optimized structure of IrO<sub>2</sub>



Figure S35. Optimized structure of IrO<sub>2</sub> (A) top view, (B, C) side views.

## 6.4. Local structure of Ir<sub>1</sub>/NiCr LDH



**Figure S36.** Zoomed view of the local structure of Ir<sub>1</sub>/NiCr LDH showing interaction with four lattice oxygen atoms.

# 6.5. pDOS plot of NiCr LDH



**Figure S37.** pDOS plot of NiCr LDH showed maximum states for the Ni center available for interaction with incoming oxygenated intermediates for OER activity. This gives the primary assumption for Ni as an active center for OER in NiCr LDH.

#### 6.6. Enthalpy change plot for NiCr LDH



**Figure S38.** Enthalpy change plot for (A) Ni as the active center, (B) Cr as the active center is shown here. Ni as an active center requires lower energy than Cr for the overall OER process with reduced rate determining step energy.

# 6.7. Spin-polarized pDOS plot of Ir<sub>1</sub>/NiCr LDH



**Figure S39.** pDOS plot of Ir<sub>1</sub>/NiCr LDH showed that Ir has maximum states available around Fermi energy level to interact with the 2p orbital of oxygenated intermediates.

6.8. Interlayer spacing of Ir<sub>1</sub>/NiCr LDH during \*O-Ir formation



**Figure S40.** Interlayer spacing of Ir<sub>1</sub>/NiCr LDH during the formation (A) \*Ir-OH and (B) \*Ir-O. Increased interlayer spacing in the case of \*Ir-O signifies stronger Ir-O interaction, leading to the negative energy of formation.



#### 6.9. Bader charge distribution plot

**Figure S41.** The Bader charge distribution plot shows the oxidation state change of the Ir active center with each intermediate addition step.

7.0. Electron density distribution in Ir<sub>1</sub>/NiCr LDH with different intermediate adsorbed



**Figure S42.** Electron density distribution with different intermediate adsorbed on Ir showed a continuous reduction in electron density on Ir center till the formation of Ir-O\*. Further, the Ir center is regaining electron density to get back to its active form. Valence band maxima (VBM) electron density analysis in both spin 1 and 2 showed a similar trend of electron density distribution.

7.1. pDOS plots of Ir<sub>1</sub>/NiCr LDH at each intermediate formation step



**Figure S43.** Maximum states of Ir are available at the fermi energy level for interaction with the O 2p orbital of the intermediates.



7.2. Relative contribution of Ir d-orbitals in different intermediate formation states

**Figure S44.** The relative contribution of different d-orbital participation in different intermediate species formation by Local Density of States (LDOS)calculation.

Table S1. Ir L3-edge	<b>EXAFS curve fitting</b>	parameters of	Ir foil and	l IrO2,
and Ir <sub>1</sub> /NiCr LDH				

Catalyst	Shell	N	R (Å)	σ <sup>2</sup> ×10 <sup>2</sup> (Å <sup>2</sup> )	R-factor (%)	<b>Δ</b> E <sup>0</sup> (eV)	R-space range (Å)	K Range
IrO <sub>2</sub>	Ir-O	5.92	1.98	0.38±0.07	0.157	11.2±0.2	1-2.7	3-12.2
Ir-Foil	Ir-Ir	12	2.72	0.12±0.02	0.3558	8.2±0.7	1-4	3-11
Ir <sub>1</sub> /NiCr LDH	Ir-O	3.84	1.78	0.40±0.03	0.0676	$15.5 \pm 0.3$	1-3.2	3-11

**Note:** N represents the coordination number,  $S_0^2$  denoted the amplitude reduction factor (fixed to 1 for all samples), R is the bond length between the central atoms to surrounded coordinated atoms,  $\sigma^2$  is the Debye-Waller factor (a measure of thermal and static disorder in absorber scatterer distances,  $\Delta E^0$  is the inner potential correction (also known as edge energy shift, the difference between the zero kinetic energy value of the sample and that of the theoretical model), R factor is used to value the goodness of the fitting.

Catalyst	Solution resistance (R <sub>s</sub> )		Charge-transfer resistance (R <sub>ct</sub> )		
	1 M KOH	Simulated seawater	1 M KOH	Simulated seawater	
Ir <sub>1</sub> /NiCr LDH	5.2	7.3	42.8	16.4	
NiCr LDH	5.6	6.9	209.4	119.4	
IrO <sub>2</sub>	5.7	7.6	240.2	35.2	

# Table S2. Solution and charge-transfer resistance from EIS analysis

# Table S3. ICP-MS analysis for metal content in the electrolyte solution (1 M KOH) after 24 h chronoamperometry study

Catalyst	Ni	Cr	Ir
NiCr LDH	2.36 %	87.04 %	
Ir <sub>1</sub> /NiCr LDH	0.25 %	18.16 %	Below detection limit
IrO <sub>2</sub>			1.87 %

\* Ir content in Ir<sub>1</sub>/NiCr LDH and IrO<sub>2</sub> was found to be 1.59 % and 73.26 % respectively.

# Table S4. Comparison of OER activity with previously reported Ir-based catalysts

Catalyst	Overpotential (mV)	Tafel slope (mV/dec)	Reference
	η10		
Ir <sub>1</sub> /NiCr LDH	232	51	This work
IrO <sub>2</sub>	360	76	This work
Ir <sub>1</sub> -vo-CoNiO <sub>2</sub>	183	64.8	Ref <sup>6</sup>
Ir <sub>1</sub> Co <sub>13.3</sub> O <sub>20.1</sub>	154	62.3	Ref <sup>7</sup>
Ir-Ni(OH) <sub>2</sub>	262	41	Ref <sup>8</sup>
Ir <sub>1</sub> -Ni(OH)NF	223	58	Ref <sup>9</sup>
IrO <sub>x</sub> -Ir	308	48	Ref <sup>10</sup>

Ir@TiN	265	52.3	Ref <sup>11</sup>
IrO <sub>2</sub> @FeMF <sub>2</sub>	254	54	Ref <sup>12</sup>
IrO2@a-MnO2	275	59	Ref <sup>13</sup>
Co@Ir/NC-Core shell	300	73.8	Ref <sup>14</sup>
Ir-Ni NP aerogel	365	53.6	Ref <sup>15</sup>
Ir <sub>1</sub> -NiP	160	90.1	Ref <sup>16</sup>
Ir <sub>1</sub> /Ni-OOH	270	45.2	Ref <sup>17</sup>
Ir Fe-N-C	350	43	Ref <sup>18</sup>
Pd@Ir TOH	300	84.9	Ref <sup>19</sup>
Ir@Co nanosheet	273	99	Ref <sup>20</sup>
Ir-Co mixed oxide	310	58.6	Ref <sup>21</sup>

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