The Effect of Interlayer Anion Grafting on Water Oxidation Electrocatalysis: A Comparative Study of Ni- and Co-Based Brucite-Type Layered Hydroxides, Layered Double Hydroxides and Hydroxynitrate Salts

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Experimental Section

All starting materials Ni(NO$_3$)$_2$·6H$_2$O, Co(NO$_3$)$_2$·6H$_2$O, Al(NO$_3$)$_3$·6H$_2$O, and urea reagents, as well as Chelex resin, K$_2$[Fe(CN)$_6$] and 5 wt.% Nafion dispersion in a mixture 45 % water and 55 % aliphatic alcohols were purchased from Sigma-Aldrich or Merck (India) and used as such. KOH (reagent grade, 85.9 %) and ethanol absolute (reagent grade 99.97%) were purchased from VWR chemicals. All solutions were prepared using Milli-Q water, with a resistivity below 18.2 MO cm.

Material preparations

*Metal hydroxides:* Reagent grade Ni(OH)$_2$ and Co(OH)$_2$ procured from Sigma-Aldrich were used as control samples without further treatment.

*LDH synthesis:* Both, NiAl-CO$_3$, and CoAl-CO$_3$ LDHs with interlayer carbonate were synthesized by making use of the urea hydrolysis method.$^{[3]}$ In a typical synthesis, 0.5 M mixed metal nitrate solution with M$^{2+}$:M$^{3+}$ ratio as 2:1 was prepared by mixing suitable amounts of divalent and trivalent salts. Then solid urea was dissolved in 40 mL of this mixed metal nitrate solution by maintaining a urea/total metal ratio of 3.3 to 5. Finally, this clear solution was transferred to a Teflon lined stainless steel autoclave and hydrothermally treated at 110 or 180 °C for 24 hours. Then the autoclave was cooled before filtration, the solid was washed with water a couple of times and finally dried in an air oven at 60 °C for 24 hours.

*Hydroxynitrate synthesis:* Ni- and Co-hydroxynitrate were synthesized using previously reported urea hydrolysis of metal salt melts.$^{[1-2]}$ A slurry was prepared by mixing 18 g of nickel nitrate or cobalt nitrate, 2 g urea and 2 mL of water in a round bottom flask. This slurry was heated at 140 to 160 °C by placing the flask on a heating mantle for 2 to 3 hours until all water evaporated completely leaving behind a solid green (for Ni sample) or a pink cake (for Co sample) at the bottom. Finally, the solid cake/paste was recovered using Milli-Q water after cooling, washed with Milli-Q water 5 times by centrifugation and finally freeze-dried overnight.

Material characterization

Powder X-ray Diffraction (PXRD) traces for Ni-compounds were measured in transmission mode on a STOE STADI P powder diffractometer with a Cu K$_{\alpha1}$ radiation source ($\lambda = 1.540598$ Å) with a Ge monochromator and a linear position-sensitive detector. To circumvent heavy fluorescence, PXRD patterns of Co-samples were collected using a STOE STADI-P diffractometer with Ag K$_{\alpha1}$ radiation source ($\lambda = 0.5594075$ Å) in transmission geometry equipped with four MYTHEN2 R 1K detectors. The data collection was done in stationary mode for one hour with samples loaded in 0.5 mm glass
capillaries. To assist comparability, the diffraction traces shown in Figure 2 were, however, recalculated assuming Cu Kα1 radiation. The solid-state infrared (IR) spectra of samples were collected using a JASCO FTIR 6100 spectrometer (range 400-4000 cm⁻¹; resolution 4 cm⁻¹). The specific surface area was measured with a Quantochrome Nova A with N₂ as adsorbate at 77 K applying the Brunauer-Emmet-Teller (BET) method. The Scanning Electron Microscopy (SEM) micrographs were acquired using a Zeiss Ultra Plus. Post-mortem EDX measurements were acquired using the same device equipped with a UltraDry-EDX-Detector (Thermo Fisher Scientific NS7) unit.

Sample compositions: The metal (Ni, Co and Al) contents were determined using a Varian, Vista-Pro Radial Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). All solutions were prepared by two-fold dilution to reduce the original metal concertation to the ICP-OES detection range of 1 to 10 mg L⁻¹ using 5 % HCl (high purity spectroscopic grade). The nitrate and carbonate anions were estimated based on N and C contents determined by CHN analyses using an Elementar Vario EL III equipment. The water contents in samples were calculated from the first step weight loss observed in the thermogravimetric analysis (TGA) curves obtained by heating samples in a platinum crucible under Ar from 25 to 800 °C using a Netzsch STA 449c system (heating rate = 10 K min⁻¹).

Electrochemical measurements

Working electrode preparation: Disk-shaped glassy carbon (GC) electrodes having a geometric area of 0.1134 cm² mounted in a Teflon sheath were used as the current collectors. To ensure a reproducible mirror-like surface in all the experiments, the GCs were polished using 3, 1, and 0.3 µm of abrasive particle size polishing papers, followed by 5 min polishing with a suspension of alumina (0.05 µm particle size) in water. Finally, to remove the remaining alumina, the GCs were rinsed thoroughly with Milli-Q water, sonicated for 1 min in a mixture Milli-Q water and absolute ethanol, and left to dry under a nitrogen stream. A catalyst ink was obtained by dispersing 5 mg catalyst in 1 mL solvent mixture (490 µL ethanol absolute, 490 µL Milli-Q water, and 20 µL of a 5 wt.% Nafion dispersion). Finally, the mixture was sonicated for 30 minutes at room temperature to ensure a stable dispersion. A certain volume of this dispersion was pipetted on the GC to generate homogeneous catalyst films with a mass loading of 0.2 mg cm⁻².

OER measurements were performed using an Autolab potentiostat/galvanostat (PGSTAT302N, Methrom) and a rotating disk electrode (RDE) (Autolab RDE-2 rotator and motor controller, Methrom). A standard three-electrode configuration containing the catalyst modified GC, a Pt wire, and a double junction Ag/AgCl 3 M KCl as working, counter, and reference electrodes, respectively, were used. A glass frit was employed to separate the counter electrode from the bulk electrolyte. KOH solution (1 M KOH, pH 13.5) was used as the electrolyte in all electrochemical experiments. It was purified using a
cation-exchange resin in its potassium form (Chelex 100, Sigma-Aldrich) following the procedure recommended by the producer.

The electrocatalytic activity of the materials was investigated in O$_2$ saturated 1 M KOH using linear sweep voltammetry (LSV) recorded from 0 to +1 V vs. Ag/AgCl (3 M KCl), with a scan rate of 5 mV s$^{-1}$ and a rotation speed of 1600 rpm. Three measurements were conducted for each material, and the average values of these measurements were reported. Before recording the LSV, electrochemical impedance spectroscopy (EIS) was conducted at open-circuit potential (OCP) in the frequency range from 100 kHz to 100 Hz using an AC perturbation of 10 mV (RMS). All the potentials shown in this work were referred to the reversible hydrogen reference electrode (RHE) scale, and the conversion from the Ag/AgCl 3 M KCl to the RHE scale, was done using the following expression:

$$E_{\text{RHE}} = E_{\text{app}} + E^0_{\text{Ag/AgCl/3M KCl}} + 0.059 \cdot \text{pH} \quad \text{[Eq. 1]}$$

where $E_{\text{RHE}}$ is the electrode potential in the RHE scale (in V); $E_{\text{app}}$ is the applied potential versus Ag/AgCl/3 M KCl (in V); $E^0_{\text{Ag/AgCl}}$ is the standard potential of the Ag/AgCl (3 M KCl) reference electrode (0.21 V). Potential values were 100% manually $iR$-corrected using the following formula:

$$E'_{\text{RHE}} = E_{\text{RHE}} - iR_u \quad \text{[Eq. 2]}$$

Where $E'_{\text{RHE}}$ is the $iR$-drop compensated potential (V), $i$ is the measured current intensity (in A) and $R_u$ is the uncompensated resistance determined by EIS (in Ω) in the high-frequency range.

The electrochemical surface area (ECSA) was determined following protocols described in literature.$^{[3]}$ Cyclic voltammograms were recorded in the OCP ± 0.05 V potential window using different scan rates (ν): 0.005, 0.01, 0.025, 0.05, 0.1, 0.2 and 0.4 V s$^{-1}$. 10 s waiting time was used between the anodic and cathodic scans. From the CVs, the electrochemical double-layer capacitance ($C_{DL}$) was calculated using the following formulas:

$$C_{DL} = \frac{i_{\text{average}}}{\nu} \quad \text{[Eq. 3]}$$

$$i_{\text{average}} = \frac{(i_a - i_c)}{2} \quad \text{[Eq. 4]}$$

Where $i_{\text{average}}$ stands for the average value of anodic ($i_a$) and cathodic ($i_c$) currents in modulus at different scan rates, taken from the CVs at OCP. Then, ECSA was calculated by dividing the $C_{DL}$ value with the specific capacitance ($C_s$) approximated to be 0.04 mF cm$^{-2}$ in alkaline electrolyte.$^{[3]}$

$$\text{ECSA} = \frac{C_{DL}}{C_s} \quad \text{[Eq. 5]}$$
Screening of catalyst stability based on fast benchmarking protocol: Galvanostatic measurements investigated initial evaluation of the stability of the hydroxynitrates samples. A current of 0.0011 A (corresponding to a current density of 10 mA cm$^{-2}$) was applied for 2 h. After the stability measurement, an LSV was recorded from 0 to +1 V vs. AgCl/Ag (3 M KCl) to explore changes in the electrocatalytic performance. The experimental conditions were the same as those described above.

OER Faradaic efficiency

Faradaic efficiency (FE) of the Ni-hydroxynitrates was evaluated using rotating ring disk electrode (RRDE) measurements. A rotating ring disk electrode device (rotor and motor controller, Methrom) was used along with the PGSTAT302N in the bipotentiostat mode for these measurements. The experiments were performed in an Ar-saturated 1 M KOH solution and a rotation speed of 3000 rpm. The potential of the Pt ring electrode was set at -0.7 V vs. Ag/AgCl (3 M KCl). Initially, OCP was applied to the disk electrode for 60 s to establish the background currents for both ring and disk electrodes. The potential of the disk electrode was further increased to +0.50 V vs. Ag/AgCl (3 M KCl) and kept at this potential for 500 s. The FE was calculated using the following formula:

$$\text{FE} = \frac{|I_{\text{ring}}|}{N \cdot I_{\text{disk}}}$$

[Eq. 6]

where $N$ is the collection efficiency. The collection efficiency was determined using an Ar-saturated solution of 5 mM K$_3$[Fe(CN)$_6$] in 1 M KOH. The potential of the Pt ring electrode was kept at +0.4 V vs. Ag/AgCl/3 M KCl, while the potential of the disk electrode was swept from +0.5 to -0.2 V vs. Ag/AgCl (3 M KCl) with a scan rate of 5 mV s$^{-1}$. The calculated collection efficiency ($N$) is 0.18 for the Ni-hydroxynitrate sample and 0.25 for Co-hydroxynitrate.

Considering the high currents obtained with Co-hydroxynitrate, the O$_2$ FE was further investigated through gas chromatography. Experiments were conducted in an H-type cell with an air-tight electrode compartment connected to the gas chromatograph. An anion exchange membrane (fumasep® FAB-PK-75, Fumatech) was used to separate catholyte and anolyte compartments. The reference electrode was a leakless Ag/AgCl (3 M KCl) reference electrode immersed in the working solution (deoxygenated purified 1 M KOH). A Pt mesh was used as the counter electrode. The working electrode consisted of a Co-hydroxynitrate drop-coated carbon paper (H23, Quintech) with a catalyst loading of 1 mg cm$^{-2}$. The catalyst was drop-coated using the same ink composition mentioned above in this section. The piece of carbon paper used had a geometric area of 1 cm x 1 cm, and both sides of the paper were drop-coated (total geometric area = 4 cm$^2$). Oxygen was quantified during electrolyzes conducted at different current densities (3.75 up to - 50 mA cm$^{-2}$) for 15 min each. An aliquot of the oxygen produced in the anode chamber was automatically into the gas chromatograph and analyzed online in
all the experiments. The gas chromatograph used was an SRI 8610C MG1 Multiple Gas Analyzer System equipped with a packed 3 m HaySep D column (SRI instruments). O₂ was analyzed using a thermal conductivity detector (TCD), previously calibrated with O₂ and N₂ mixtures. High purity nitrogen (99.999 %) was used as the carrier gas in the gas chromatograph. N₂ was also used to deoxygenate the solution and carry the gases from the H-type cell to the chromatograph, with a flow rate of 10 mL min⁻¹ provided by a flow mass controller. The FE for O₂ was also calculated during 2 h electrolysis at 10 mA cm⁻². In this case, a constant current was applied for 2 h, and each 15 min, a sample was injected in the gas chromatograph and thus analyzed.

The FE was calculated using the following formula:

\[
FE = \frac{C_{O2} \cdot j_{N2} \cdot 4 \cdot F}{V_m \cdot I} \cdot 100 \% \tag{Eq. 7}
\]

Where: \( C_{O2} \) is the O₂ concentration obtained from the gas chromatograms, \( j_{N2} \) is the N₂ flow- the carrier gas, \( F \) is the Faraday constant, \( V_m \) molar volume, and \( I \) is the electrolysis current.
S.1. Rotating ring disk electrode (RRDE) measurements.

**Figure S1.** Chronoamperometric measurement was performed using Ni-hydroxynitrate coaded GC to calculate the Faradaic Efficiency towards O₂ formation. The WE are set at OCP for the first 60 s and then swept up to +1.50 V vs. RHE for 500 s. RRDE measurements were recorded under 3000 rpm and with a constant electrode potential of +0.31 V vs. RHE in the Pt ring.

**Figure S2.** RRDE experiments performed to determine the collection efficiency (N) for the Ni-hydroxynitrate modified GC electrode using an Ar-purged 5 mM K₃[Fe(CN)₆] in 1 M KOH solution.
S.2. Faradaic efficiency for OER determined by gas chromatography measurements.

Figure S3. O₂ faradaic efficiencies were calculated at different current densities used for the galvanostatic water electrolysis using Co-hydroxynitrate as electrocatalyst. (Electrode geometric area = 4 cm²). The O₂ concentrations obtained based on two chromatograms were used to calculate the FE, and the data are averaged.

Figure S4. O₂ faradaic efficiencies evaluated over 2 h at the 15-minute interval while performing water electrolysis galvanostatically at 10 mA cm⁻² (40 mA) using Co-hydroxynitrate as electrocatalyst. O₂ quantification was performed by gas chromatography every 7.5 minutes.
S.3. Post-mortem SEM characterization.

**Figure S5.** SEM images of the Co-hydroxynitrate modified GC electrode before (left) and after (right) 2 h chronopotentiometry measurement performed at a current of 1.134 mA corresponding to 10 mA cm\(^{-2}\) current density.

**Figure S6.** SEM images of the Ni-hydroxynitrate modified GC electrode before (left) and after (right) 2 h chronopotentiometric measurement performed at a current of 1.134 mA, corresponding to 10 mA cm\(^{-2}\) current density.
S.4. Stability measurements.

**Figure S7.** LSVs performed for Ni-hydroxynitrate modified GC electrode before and after a stability measurement based on applying 10 mA cm\(^{-2}\) for 2 h. LSV were recorded in a O\(_2\)-saturated 1 M KOH solution with a rotation of 1600 rpm.
S.5. Post-mortem XRD characterization

**Figure S8.** Post-electrolysis XRD performed for Ni-hydroxynitrate after electrolysis performed at 0.55 V vs. Ag/AgCl 3 M KCl in 1 M KOH for 2 h.

**Figure S9.** Post-electrolysis XRD performed for Co-hydroxynitrate after electrolysis performed at 0.55 V vs. Ag/AgCl 3 M KCl in 1 M KOH for 2 h.
S.6. Post-electrolysis EDX characterization

Energy dispersive X-ray (EDX) spectroscopy measurements of Ni- and Co-hydroxynitrate samples were conducted to rule out the incorporation of secondary metals during the chronopotentiometry experiment (10 mA cm\(^{-2}\) for 2 h). The obtained results present no evidence of such metal (particularly Fe) incorporation. The only additional signals not belonging to the catalyst can be attributed to the Nafion binder (F, S) and traces of electrolyte (K). The investigation included probing each sample at 10 different spots from which two representative EDX spectra of points 1 and 2 are shown.

**Ni-hydroxynitrate**

![EDX characterization of Ni-hydroxynitrate after 2 h chronopotentiometry measurement performed at a current of 1.134 mA, corresponding to 10 mA cm\(^{-2}\) current density.](image)

**Figure S10.** EDX characterization of Ni-hydroxynitrate after 2 h chronopotentiometry measurement performed at a current of 1.134 mA, corresponding to 10 mA cm\(^{-2}\) current density.
Co-hydroxynitrate

Figure S11. EDX characterization of Co-hydroxynitrate after 2 h chronopotentiometry measurement performed at a current of 1.134 mA, corresponding to 10 mA cm\(^{-2}\) current density.

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