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Effect of Interlayer Anions in Ni–Fe Layered Double Hydroxides for Electrochemical Seawater Splitting

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Abstract

Nickel–iron layered double hydroxides (Ni–Fe LDHs) are among the active earth abundant electrocatalysts for the oxygen evolution reaction (OER) in alkaline media. The electrocatalytic performance is strongly influenced by both catalyst composition and the intercalated ions. However, there are lack of systematic comparison of the effect of intercalated anions which are abundantly found in sea water towards electrochemical water splitting. Here, Ni–Fe LDHs intercalated with chloride, nitrate, sulfate, and carbonate anions were synthesized via a hydrothermal route and systematically evaluated the role of interlayer anions under idealized and realistic electrolytes. Structural and compositional analyses confirm the formation of well-defined LDH phases with comparable Ni:Fe ratios with different interlayer compositions based on the precursor used. In 0.1 M KOH, divalent oxyanion intercalated LDHs (SO_4^{2-} and CO_3^{2-}) exhibit enhanced OER activity, achieving lower onset potentials (1.26–1.30 V vs Ag/AgCl/sat. KCl) than monovalent anion systems (Cl^- and NO_3^-). In contrast, when natural seawater is used as the electrolyte, all samples display nearly identical onset potentials (~1.60 V vs Ag/AgCl/sat. KCl), indicating that the intrinsic benefits of interlayer anion engineering are largely suppressed by the complex ionic environment. These results demonstrate that interlayer anion chemistry provides an effective approach for tuning Ni–Fe LDH activity in alkaline media but becomes secondary under seawater conditions.

Keywords: Oxygen evolution reaction, Ni-Fe layered double hydroxides, Seawater electrolysis, Intercalated anions, Hydrogen production

1. Introduction

Renewable-powered water electrolysis is at highest interest as it produces high purity fuel without major pollutants. The large overpotentials associated with the oxygen evolution reaction (OER) which is 1.23 V under standard conditions remain a major barrier for efficient electrolysis[1]. In alkaline media, Ni–Fe layered double hydroxides (LDHs) have emerged as benchmark earth-abundant OER catalysts, often matching or potentially surpassing noble metal oxides[2]. Their layered structure, composed of positively charged metal hydroxide sheets separated by charge-balancing interlayer anions, offers extensive compositional and structural tunability which adds modified properties for catalytic applications[3].

Transition metals are well known to have opto-electronic properties which can be utilized as catalysts for useful reactions[4]. Out of that, Ni shows enhanced catalytic activity for oxygen evolution reaction (OER)[4]. The addition of Fe to Ni improves better surface adsorption of the intermediate of OER (*OH and *OOH). Ni-Fe LDH therefore shows synergistic effect towards efficient electrocatalytic performance towards water splitting. As the anions are incorporated in the layers to neutralize the charge of the layers, the variety of anionic size results diverse group of materials with modified properties[1,5]. It was found that the intercalated anion in the double layers modifies the electronics structure of the Ni-Fe layers. Such modifications would eventually affect the binding energies and capabilities of the intermediates and products[6]. While the influence of metal cation composition, defect density, and morphology on Ni–Fe LDH activity has been extensively studied, the comparative understanding on such influence by the anions are still lacking.

Electrocatalysis of seawater is one of the promising approaches instead of using drinkable fresh water. The high ion concentrations, specifically the presence of high Cl^- concentration (~0.54 M) can alter the structural properties of the anion-intercalated LDH and then their respective performance[6]. High Cl^- concentration can trigger ion exchange with the anions incorporated with the synthesized Ni-Fe LDH[7]. Other than the structural modification, the chloride evolution reaction which has a reduction potential of 0.89 V ($Cl^- + 2OH^- = ClO^- + H_2O + 2e$) under basic

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conditions may compete the desired water splitting reaction[19]. The selective catalytic process of Ni-Fe LDH has demonstrated to remove any interferences and enhancing OER. Electronic structure modification by incorporating intercalated anion can provide further enhancement to its performance. A systematic understanding on how the intercalated ions influence for the electrocatalytic performance and their behavior under the seawater would provide an applicable approach to such materials in larger scale. In this study, we synthesized Ni-Fe LDH for water splitting application with modified interlayer environment. For that, chloride, nitrate, sulfate, and carbonate anions were intercalated and the materials were characterized using PXRD and FTIR spectroscopy techniques. Initially, the electrocatalytic performance was determined in KOH medium. To compare the electrochemical properties of the material under seawater was then carried out focusing on the direct seawater spitting applications.

2. Experimental Section

2.1 Materials

All chemicals were of analytical grade and used as received without further purification. Distilled water was used throughout synthesis and washing procedures. Natural seawater was collected from Bentota, Southern Province, Sri Lanka, (pH=7.65, Conductivity=49.2 mS) filtered to remove suspended particulates, and used without chemical modification.

2.2 Synthesis of Anion Intercalated Ni–Fe LDHs

Ni–Fe LDHs intercalating Cl^- ions was synthesized using an adapted hydrothermal method[1]. Aqueous solutions containing $NiSO_4$ and $Fe_2(SO_4)_3$ were mixed with a NaOH solution containing NaCl under continuous stirring. The resulting suspension was transferred to Teflon-lined autoclave and heated at 120 °C for 24 h. After cooling to room temperature, the precipitate was collected by centrifugation. It was washed thoroughly with distilled water to dissolve any unreacted solid precursors and dried under ambient conditions. The Ni:Fe molar ratio was maintained at approximately 2:1.

To obtain other anions intercalated Ni-Fe LDHs, the alkaline solution was prepared by adding a salt having the target interlayer anion. To obtain nitrate and carbonate intercalated Ni-Fe LDH, $NaNO_3$ and Na_2CO_3, respectively, were mixed with alkaline solution. Sulfate intercalated LDH was obtained following the similar procedure without adding any chloride, nitrate, and carbonate salts.

2.3 Characterization

Powder X-ray diffraction (XRD) was employed to examine phase composition and crystallinity. Fourier-transform infrared (FTIR) spectroscopy was used to identify any functional groups involve and specifically, the interlayer anions. Elemental compositions were determined by X-ray fluorescence (XRF) analysis. Morphological features were examined using scanning electron microscopy.

2.4 Electrochemical Measurements

Electrochemical measurements were conducted in a three-electrode configuration using a glassy carbon working electrode (geometric area = 0.07 cm^2), a platinum wire counter electrode, and an Ag/AgCl/sat. KCl reference electrode. Catalyst was deposited on the glassy carbon surface by preparing a LDH dispersion in ethanol, followed by drop-casting onto the working electrode with identical loadings for all samples.

Cyclic voltammetry and linear sweep voltammetry were performed at a scan rate of 10 mV s^{-1}. The onset potential was defined as the potential at which the current density exceeded the non-faradaic background by 0.1 mA cm^{-2}.

3. Results and Discussion

All current densities discussed below are normalized to the geometric area of the working electrode. Because catalyst loading, ink preparation, and electrode fabrication were kept identical for all samples, the discussion focuses on comparative trends rather than absolute activity values.

3.1 Structural and Compositional Characteristics

Powder X-ray diffraction patterns (Fig 1) of all synthesized samples exhibit the characteristic reflections of hydrotalcite-like layered double hydroxides, including the (003), (006), (012), (015), and (202) planes, confirming successful formation of the LDH phase irrespective of the interlayer anion[1]. The absence of significant peak shifts in the in-plane reflections indicates that substitution within the metal hydroxide layers is minimal and that the Ni–Fe framework remains structurally consistent across the series.

Subtle differences are observed in the basal (003) reflection, reflecting variations in interlayer spacing associated with the identity of the intercalated anion[1] as indicate in (**Error! Reference source not found.**). Chloride-intercalated LDHs display the smallest basal spacing because of its smaller size compared to the other ions which is used. carbonate- and nitrate-intercalated samples show slightly expanded interlayer distances compared to that of chloride intercalated sample, which can be attributed to the strong electrostatic interaction of CO_3^{2-} with the positively charged hydroxide layers[8].

Further, the influences from differences in anion geometry, hydration, and hydrogen-bonding interactions would also affect the interlayer spacing[9]. Nitrate-intercalated LDHs exhibit comparatively broader basal reflections, suggesting a less ordered interlayer environment[8]. Presence of minor reflections in some samples can be attributed to the presence of crystal defects and trace oxides[10]. However, their low intensities indicate that these phases are present only in negligible quantities and are unlikely to dominate the electrochemical response. X-ray fluorescence analysis (**Error! Reference source not found.**) confirms that all samples possess comparable Ni:Fe

ratios close to 2:1 value, indicating that any electrochemical differences arise primarily from interlayer chemistry rather than variations in bulk composition, and the presence of significant amount of metal oxides can be eliminated.

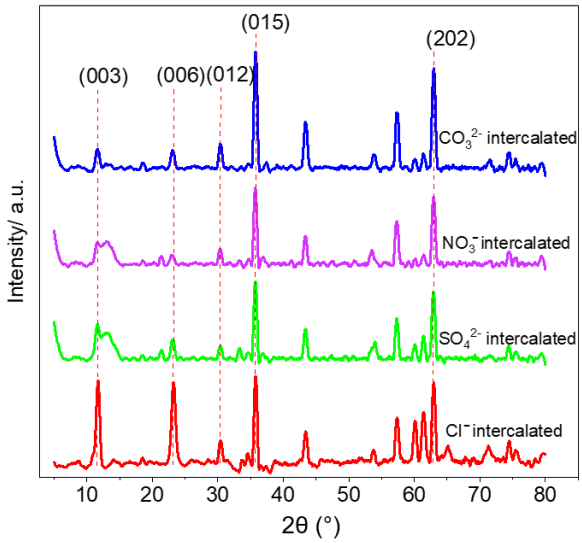

Fig 1. Powder X-ray diffraction patterns of Ni–Fe LDHs intercalated with CO_3^{2-}, NO_3^-, $SO4^{2-}$, and Cl^-, confirming the formation of layered double hydroxide phases with characteristic basal reflections.

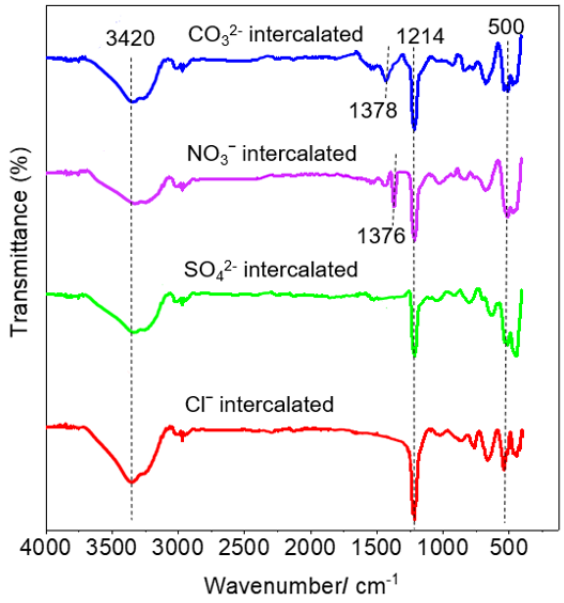

Fig 2. FT-IR spectra of anion-intercalated Ni–Fe LDHs showing hydroxyl stretching modes and characteristic vibrational features associated with the respective interlayer anions.

Fourier-transform infrared spectroscopy (Fig 2) further corroborates successful anion intercalation. All samples show broad O–H stretching bands associated with hydroxyl layers and interlayer water around 3420 cm^{-1} [1]. Distinct vibrational features characteristic to sulfate, nitrate, and carbonate anions are observed at their respective wavenumbers, confirming their presence within the interlayer spacing. The peaks corresponding to the N=O vibrations appear at 1376 cm^{-1} [3]. The peak corresponding to C=O vibrational modes show a slight shift that of N=O vibrational bond as the C=O possesses stronger bond compared to that of N=O. Asymmetric stretching of S-O bond is indicated from the peak centered at 1214 cm^{-1} (**Error! Reference source not found.**). The chloride-intercalated LDH lacks strong anion-specific IR features, as expected, but displays spectral signatures consistent with hydrated LDH structures. The lower wave number region (500-800 cm^{-1}) shows weak absorption bands attributed to M-O-H bending and metal-oxygen lattice vibrations[8].

3.2 Morphological Features

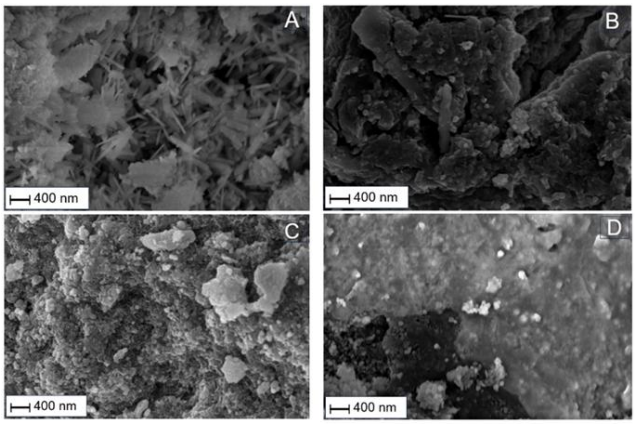

Fig 3. SEM images illustrating morphology variations among Ni–Fe LDHs with different interlayer anions; A) CO_3^{2-} intercalated, B) Cl^- intercalated, C) NO_3^- intercalated, and D) SO_4^{2-} intercalated.

Scanning electron microscopic images (Fig 3) shows differences in particle morphology of the as synthesized LDHs with different intercalated anions. The carbonate-intercalated Ni–Fe LDH (Fig 3A) forms well-developed, flower-like architectures composed of thin, radially oriented nanosheets. The chloride-intercalated LDH (Fig 3**Error! Reference source not found.**B) exhibit more compact and densely aggregated morphologies, with limited nanosheet separation. Absence of a surfactant in the synthesis can be attributed to the aggregated behavior of the particles. Heating the LDH at higher temperature further promotes fuse of crystallites together regardless of improving crystallinity. Such aggregation can restrict electrolyte access and reduce the effective electrochemically active surface area. Nitrate- and sulfate-intercalated samples (Fig 3C and **Fig** *3*D) display morphologies with stacked structures of LDH. Synthesis approach with variable anions would influence to morphologies of the particles. The images demonstrates that the intercalated anion influence the morphologies of LDH.

3.3 Electrochemical Behavior in Alkaline Electrolyte

The electrocatalytic performance of the Ni–Fe LDHs was evaluated in 0.1 M KOH (Fig 4A) to determine intrinsic OER activity under well-defined alkaline conditions. Linear sweep voltammetry (LSV) reveals differences in onset potential and current densities related to the LDH with different interlayer compositions. carbonate-intercalated Ni–

Fe LDH exhibits the lowest OER onset potential which is 1.26 V, followed closely by the sulfate and chloride intercalated LDH. Lower layer spacing and modified electron density by Cl^- may support stabilizing the intermediates on the LDH surface resulting higher OER activity[11]. The NO_3^- intercalation shows highest onset potential (1.34 V) among the anions considered indicating insufficient electronic structure modification to support stabilizing intermediates on the LDH surface[12]. The charge density of anion can enhance overall charge density of LDH supporting stabilizing the OER intermediate[13,14]. Carbonate possesses 2- charge which is also relatively smaller in size compared to the SO_4^{2-} ions so that CO_3^{2-} shows high charge density. Further, the -1 charge in NO_3^- ions has relatively low charge delocalized in relatively three O atoms. Therefore, the compared to other anions, NO_3^- possesses less charge density so that higher overpotential. SO_4^{2-} and Cl^- would have intermediate charge densities which lies between the overpotential of CO_3^{2-} and NO_3^- intercalated LDHs. The correlation between the charge density and the overpotential demonstrate its influence for the catalytic activity[13,14].

The changes in current densities of the LDH can be mainly due to their morphologies and exposed surfaces. CO_3^{2-} intercalated structure shows efficient charge transfers by resulting higher current. As the plate-like morphology of the material exposed more surfaces for catalytic reaction, the current density of such materials becomes larger than the other morphologies. As plates expose more edges and corners providing additional active sites for catalytic reaction. Such morphological features are absent to the other samples. The SO_4^{2-} and Cl^- intercalated LDH shows mostly aggregated behaviors which can be attributed to the similar current density variations[13]. NO_3^- intercalated sample shows rough surface and the plate or sheet like morphology is mostly absent. Such aggregations may reduce the current densities from the structure. Further, lack of active sites in (**Error! Reference source not found.**D) surface may reduce the current densities further. However, because all electrodes were prepared with identical loadings, these effects primarily influence relative kinetics rather than absolute current densities.

Cyclic voltammogram obtained in 0.1 M KOH (**Error! Reference source not found.**)indicates that differences in their electrocatalytic activity for the oxygen evolution reaction (OER). It demonstrates that the interlayer anions influence the catalytic activity of the sample towards OER. It also shows that there are no any other redox reactions rather than OER is occurring during the water splitting process.

The enhanced activity of divalent oxyanion-intercalated LDHs can be attributed to several factors. Stronger electrostatic interactions between divalent anions and the positively charged metal hydroxide layers may stabilize higher oxidation states of Ni and Fe, which are widely regarded as the catalytically active species during OER[4]. Additionally, divalent anions may promote more favourable hydrogen-bonding networks and interlayer hydration, facilitating proton-coupled electron transfer processes[15].

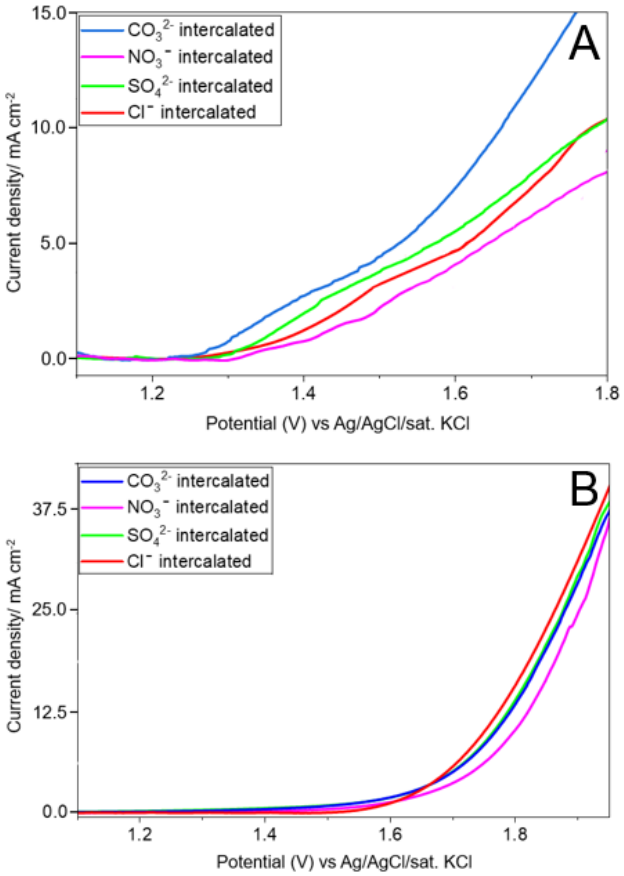

Fig 4. A) Linear sweep voltammograms (95% iR compensated) of Ni–Fe LDHs recorded in 0.1 M KOH, highlighting differences in OER onset behavior with respect to the interlayer anion and B) Linear sweep voltammograms measured in natural seawater, showing convergence of OER activity.

3.4 Electrocatalytic Performance in Seawater

The performance of the Ni–Fe LDHs was subsequently evaluated in natural seawater (B) to assess the relevance of interlayer anion engineering under realistic electrolyte conditions. In contrast to alkaline KOH, the distinct activity hierarchy observed previously became minimal[16]. Most of the catalysts exhibit similar onset potentials near 1.60 V vs Ag/AgCl/sat. KCl (approximately 1.84 V vs RHE), and their voltametric curves overlap substantially across the measured potential range.

Cyclic voltammograms obtained with natural sea water (**Error! Reference source not found.**) demonstrate the impact of the complex ionic environment on OER catalysis. All four samples display closely overlapping curves and reduced current generation compared to the results obtained with alkaline KOH. The CVs of the LDHs under sea water shows close overlap of curves. These results indicate that the intrinsic behavior demonstrated by different interlayer environment are suppressed in seawater[18]. The high concentration of chloride ions plays a central role in this behavior. Chloride ions can compete with hydroxide for adsorption at active sites and promote the chlorine evolution

reaction[7,19]. Further, the intercalated anions can exchange with the high concentrated Cl^- solution resulting similar electronic structure of the all LDH[19,17]. Therefore, noticeable effect of intercalated anions is diminished under sea water.

The effect of the morphology of LDH is reflected by the current densities. Similar to the trends observed in the KOH medium, the increase of current densities is lowest for the NO_3^- intercalated LDH under sea water. However, the difference between other morphologies is not significant. This may be due to the interfacial effects imparted by other ionic composition of sea water. Overall overpotential for all the samples were increased by 0.38 V compared to the overpotential of Cl^- intercalated LDH in KOH, indicating the significance of surface reactions apart from the effect of exchanging anion. Increased surface passivation surpasses any effect of the intercalated anion towards catalytic performance. Overall, the observation of all catalysts demonstrates that the improvements achieved through interlayer anion engineering in alkaline electrolytes show significant performance loss in complex, chloride-rich environments.

Overall, these results highlight the importance of evaluating electrocatalysts across electrolytes of increasing complexity. While interlayer anion chemistry provides a viable route to tuning intrinsic activity in alkaline systems, its influence becomes secondary when electrolyte effects dominate. For seawater electrolysis, corrosion studies on LDH surfaces may provide useful information towards designing active catalysts. Further implementation of strategies such as surface protection, selective ion transport, and electrolyte management would provide potential developments to preserve catalyst activity and suppress competing processes.

4. Conclusions

This study systematically synthesized Ni-Fe LDH with different intercalated anions and elucidated their role towards oxygen evolution reaction under electrolytes of high ionic activity. The formation of layers with the inclusion of different anions were characterized by XRD and FTIR spectroscopy. The synthesized LDHs with different anions were then subjected to electrocatalytic characterization under alkaline 0.1 M KOH conditions and with natural sea water as the electrolyte. The CO_3^{2-} intercalated LDH showed higher electrocatalytic performance owing to its ability of modify the electronic structure than others. Structural features such as well-developed, flower-like architectures composed of thin, radially oriented nanosheets which consists of edges and corners exposed to the electrolyte enhanced the charge transfer. LDHs intercalated with divalent oxyanions exhibited clearly enhanced intrinsic activity, with sulfate-intercalated and carbonate-intercalated samples showing lower OER onset potentials of between 1.26–1.30 V vs Ag/AgCl/sat. KCl compared to chloride- and nitrate-intercalated counterparts. These differences are attributed to stronger electrostatic interactions and more effective electron density modulation of the Ni–Fe hydroxide layers. Under natural seawater, all four catalysts displayed higher and mostly similar overpotential compared to that in alkaline medium indicating the effect of interlayer anion is largely suppressed. High chloride concentrations, competitive chlorine evolution[19], and complex interfacial effects dominate catalytic behavior under these conditions. Overall, these results show that the ionic environment improves catalytic property towards OER and the higher Cl^- concentration passivates the surface compromising its catalytic property. The findings emphasize the necessity of integrating catalyst design with electrolyte control, surface protection, and ion-selective strategies to achieve practical and efficient seawater-based hydrogen production.

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Competing Interests

The authors have no competing interests to declare

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