Nitrate-coordinated FeNi(OH)\textsubscript{2} for hydrazine oxidation assisted seawater splitting at the industrial-level current density\textsuperscript{†}

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In this study, we developed a nitrate-coordinated iron-nickel hydroxide \([\text{NC–FeNi(OH)}\textsubscript{2}]\) catalyst for hydrazine oxidation-assisted seawater splitting. Replacement of \(O_2\) evolution by hydrazine oxidation in a two-electrode setup resulted in a cell voltage of 1.20 V at 100 mA cm\(^{-2}\). This represents a voltage reduction of 470 mV compared to conventional seawater splitting. Additionally, \(\text{NC–FeNi(OH)}\textsubscript{2}\) demonstrated remarkable stability over a period of 60 hours.

The pursuit of chlorine-free and energy-efficient seawater electrolysis represents a formidable challenge in realizing cost-effective hydrogen production.\textsuperscript{1,2} Therefore, substituting anodic side reactions such as chloride oxidation reaction (CIOR) with the hydrazine oxidation reaction (HzOR) in seawater electrolysis emerges as a noteworthy strategy to mitigate interference from side reactions and enhance the energy efficiency for overall seawater splitting.\textsuperscript{3} HzOR is a promising alternative to the OER due to its lower theoretical potential of \(-0.33\) V vs. RHE compared to OER's 1.23 V vs. RHE.\textsuperscript{3,4} Additionally, HzOR produces a safer mixture of \(H_2\) and \(N_2\), unlike the \(H_2\) and \(O_2\) from water splitting. Similar to OER, HzOR is also a four-electron transfer reaction in an alkaline medium (pH = 14). It proceeds through N-N bond breaking, forming \(*2NH_2\), which undergoes successive dehydrogenation to produce \(N_2\).\textsuperscript{3,4} Conversely, the OER involves the formation of O-O bonds through the high-valent \(M^{III}\)-OOH species formation. This reaction has a high thermodynamic potential, making it less favorable. In the context of HzOR, achieving industrial-level current density at a lower potential than the onset of OER/CIOR is crucial to ensure high faradaic efficiency.\textsuperscript{5,6}

Herein, we demonstrated a nitrate-coordinated iron-doped nickel hydroxide \([\text{NC–FeNi(OH)}\textsubscript{2}]\) catalyst and employed it for hydrazine oxidation-assisted seawater splitting (Fig. 1). Spectroscopic analysis unveiled that nitrate was coordinated to the nickel sites, thereby modulating the coordination properties of the catalyst. It was observed that the high-valent \(Ni^{IV}\) state was readily accessible in \(\text{NC–FeNi(OH)}\textsubscript{2}\) compared to the hydrothermally prepared nitrate intercalated iron-doped nickel hydroxide, \([\text{NI–FeNi(OH)}\textsubscript{2}]\). The \(\text{NC–FeNi(OH)}\textsubscript{2}\) displayed a current density of 100 mA cm\(^{-2}\) at 1.01 V vs. RHE for hydrazine oxidation, compared to OER (1.35 V) in seawater. Interestingly, substituting OER with hydrazine oxidation in real seawater led to the 1.20 V cell voltage at 100 mA cm\(^{-2}\) current density in a two-electrode system. In contrast, a cell voltage of 1.67 V was required without hydrazine. The \(\text{NC–FeNi(OH)}\textsubscript{2}\) also outperformed the Pt/C \(\|\) RuO\textsubscript{2} couple in overall seawater splitting with an excellent stability of 60 h. To date, this is one of the best performances in the literature in terms of potential demand for seawater.

The \(\text{NC–Ni(OH)}\textsubscript{2}\) and \(\text{NC–FeNi(OH)}\textsubscript{2}\) catalysts were synthesized using the molten salt technique on nickel foam. The Fe content was varied to produce \(\text{NC–FeNi(OH)}\textsubscript{2}-1\) and \(\text{NC–FeNi(OH)}\textsubscript{2}-2\).
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Patterns of N C–Ni(OH) 2 and N C–FeNi(OH) 2 showed the character-

Structural properties of the synthesized catalysts were examined using the powder X-ray diffraction (PXRD) technique. The PXRD patterns of N C–Ni(OH) 2 and N C–FeNi(OH) 2 showed the characteristic peaks of layered hydroxide nitrates Ni$_2$(NO$_3$)$_2$(OH)$_2$·2H$_2$O (JCPDF no. 27-0939) and hexagonal NiOOH species (JCPDF no. 06-0075) (Fig. 2a). The PXRD pattern of N C–FeNi(OH) 2 indicated a negative shift of 0.10° in two theta degrees compared to N C–Ni(OH) 2. This observation suggested the successful integration of Fe into the catalyst. 7

The PXRD pattern of N C–FeNi(OH) 2 revealed peaks corresponding to α-Ni(OH)$_2$, matching with JCPDS No.38-0175 (Fig. 2a). It should be noted that the crystal phases of N C–FeNi(OH)$_2$ and N C–FeNi(OH)$_2$ are different. The N C–FeNi(OH)$_2$ with the layered hydroxide nitrate Ni$_2$(NO$_3$)$_2$(OH)$_2$·2H$_2$O phase exhibited nitrate-coordinated Ni sites where some of the octahedrally coordinated hydroxyl ions were replaced with nitrate ions. 8–10 In contrast, N C–FeNi(OH)$_2$, with brucite α-Ni(OH)$_2$ phase, possessed intercalated nitrate ions between the hydroxide layers. 8–10 The coordination of nitrate, compared to intercalation, modulates the coordination and electronic properties of the catalyst. 8–10

The coordination of nitrate in N C–Ni(OH)$_2$ and N C–FeNi(OH)$_2$ was evidenced by Fourier transform infrared (FTIR) and Raman spectroscopy. The FTIR spectrum of N C–FeNi(OH)$_2$ showed 1640 cm$^{-1}$ and 1396 cm$^{-1}$ bands attributed to the monodentate NO$_3^-$ vibrations (Fig. 2b). 8–11 These IR peaks indicated that nitrate ions possessed C$_{3v}$ symmetry and were coordinated with Ni sites. In contrast, the IR spectrum of N C–FeNi(OH)$_2$ revealed a band at 1350 cm$^{-1}$ (Fig. 2b). 8–10 The appearance of the 1350 cm$^{-1}$ band was consistent with nitrate anions being in D$_{3h}$ symmetry, intercalated between the layers of alpha-phase hydroxides. 8–10 Therefore, PXRD and IR data underscore the formation of nitrate-coordinated N C–FeNi(OH)$_2$ and nitrate intercalated N C–FeNi(OH)$_2$. Furthermore, the Raman spectra of N C–Ni(OH)$_2$ and N C–FeNi(OH)$_2$ identified the bands at 1295, 1044, and 995 cm$^{-1}$, which were attributed to the monodentate coordination of nitrate with nickel (Fig. S1, ESI†). 11

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were performed to examine the morphological features of the catalysts. The SEM images revealed the nanowire morphology of N C–Ni(OH)$_2$ (Fig. S2, ESI†), while after Fe$^{3+}$-introduction, the morphology was changed to nanosheets (Fig. S3, ESI†). The TEM image corroborated the nanosheet morphology of N C–FeNi(OH)$_2$ (Fig. 2c). The high-resolution TEM (HRTEM) image manifested a d-spacing value of 0.23 nm for the (101) plane of Ni$_2$(NO$_3$)$_2$(OH)$_2$·2H$_2$O (Fig. 2d). Further, fast Fourier transform (FFT) and inverse FFT also supported the HRTEM analysis. The selected area electron diffraction (SAED) pattern was indexed for 0.25 nm d-spacing for the (111) plane (Fig. 2d inset). Energy dispersive X-ray (EDX) spectroscopy identified the presence of Ni, Fe, O, and N elements in N C–FeNi(OH)$_2$ and Ni, O, and N elements in N C–Ni(OH)$_2$ (Fig. S4 and S5, ESI†). The composition of N C–FeNi(OH)$_2$ and N C–Ni(OH)$_2$ with Ni and Fe ratios was also determined using EDX studies (Table S1, ESI†).

X-ray photoelectron spectroscopy (XPS) was conducted to elucidate the modulation of the electronic properties. The Ni 2p XPS spectrum of N C–FeNi(OH)$_2$ displayed two primary peaks at 856.38 eV and 873.96 eV, corresponding to Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$, respectively (Fig. S6, ESI†). 11,12 Further deconvolution of these peaks indicated the presence of Ni$^{2+}$ and Ni$^{3+}$ peaks at 855.79 eV and 857.30 eV, respectively. The Ni 2p$_{3/2}$ XPS peak in N C–FeNi(OH)$_2$ was shifted towards positive binding energy by 0.46 eV compared to the N C–Ni(OH)$_2$ (Fig. S6, ESI†). 11,12 The peak area intensity ratio of Ni$^{3+}$/Ni$^{2+}$ in N C–FeNi(OH)$_2$ was significantly larger (1.48) compared to the N C–Ni(OH)$_2$ (1.23). These results evidenced the larger amount of high valent Ni in N C–FeNi(OH)$_2$ compared to N C–Ni(OH)$_2$. The Lewis acid behaviour of Fe$^{3+}$ led to the transfer of electrons from Ni$^{2+}$ to Fe$^{3+}$, making Ni sites more electrophilic. 11,12

The Fe 2p XPS analysis of N C–FeNi(OH)$_2$ revealed two prominent peaks at 711.11 eV and 723.97 eV for Fe 2p$_{1/2}$ and Fe 2p$_{3/2}$, respectively (Fig. S7, ESI†). 13,14 The Fe 2p$_{3/2}$ peak was further fitted into two peaks at 709.53 eV and 711.04 eV for the Fe$^{2+}$ and Fe$^{3+}$ species, respectively. The N 1s XPS of N C–FeNi(OH)$_2$ showed a single peak (407.32 eV) assigned to the metal–nitrate bond (Fig. S8, ESI†). 13,14 The N 1s XPS of N C–FeNi(OH)$_2$ showed a positive shift in N 1s (0.11 eV) and O 1s (1.20 eV) towards higher binding energy compared to N C–Ni(OH)$_2$ catalyst (Fig. S10 and S11, ESI†). 13,14 The surface composition of the catalysts was close to the bulk composition as determined from EDX (Table S1, ESI†). The comparison of XPS of N C–FeNi(OH)$_2$ and N C–FeNi(OH)$_2$ manifested the 2.00 eV positive shift in Ni 2p$_{3/2}$ peak (Fig. S12, ESI†) and 3.42 eV positive shift in Fe 2p$_{3/2}$ peak (Fig. S13, ESI†) of N C–FeNi(OH)$_2$ suggesting the higher oxidation state of Ni and Fe in N C–FeNi(OH)$_2$ compared to N C–FeNi(OH)$_2$. 13,15 The N 1s XPS revealed two peaks at 404.98 eV and 405.82 eV corresponding to NO$_3^-$ and N–O bond, respectively (Fig. S14, ESI†). The O 1s XPS of N C–FeNi(OH)$_2$ showed two peaks
Following the spectroscopic and microscopic analyses, we proceeded with cyclic voltammetry (CV) to assess the oxidation process of metal sites. The CV profile of N$_C$–FeNi(OH)$_2$ showed two prominent oxidation waves at 1.37 and 1.45 V vs. RHE corresponding to Ni$^{2+}$/Ni$^{3+}$ and Ni$^{3+}$/Ni$^{4+}$ (Fig. 3a), respectively. Notably, the oxidation wave of N$_C$–FeNi(OH)$_2$ appeared at a lower potential compared to that of N$_C$–Ni(OH)$_2$, suggesting a facile oxidation process of Ni$^{2+}$ to Ni$^{4+}$ due to the incorporation of Fe (Fig. 3a). Conversely, the CV profile of N$_C$–FeNi(OH)$_2$ displayed oxidation waves of Ni$^{2+}$/Ni$^{3+}$ and Ni$^{3+}$/Ni$^{4+}$ at higher potential (1.38 V and 1.48 V vs. RHE) compared to N$_C$–FeNi(OH)$_2$ (Fig. 3a). These findings suggested that the nitrate coordination in N$_C$–FeNi(OH)$_2$ facilitates easier access of Ni$^{4+}$ to promote O–O bond formation compared to nitrate-intercalated N$_C$–FeNi(OH)$_2$ catalyst.

The electrochemical performance of the catalysts was investigated in real seawater with or without 0.1 M hydrazine. The linear sweep voltammetry (LSV) profile depicted that N$_C$–FeNi(OH)$_2$ reached 100 mA cm$^{-2}$ current density at 1.35 V vs. RHE potential for seawater OER (Fig. 3b). After the addition of 0.1 M hydrazine, the required potential was reduced to 1.01 V vs. RHE to deliver the same current density (Fig. 3b). In contrast, N$_C$–Ni(OH)$_2$ demanded 1.10 V and 1.50 V vs. RHE potential for hydrazine oxidation and OER, respectively (Fig. 3b).

It is noteworthy that N$_C$–FeNi(OH)$_2$ attained the industrial current density (400 mA cm$^{-2}$) at 1.07 V vs. RHE, lower than the onset of OER and CIOR, avoiding interference of side reactions (Fig. 3b). The catalytic performance of N$_C$–FeNi(OH)$_2$ was far better than that of N$_I$–FeNi(OH)$_2$, N$_C$–FeNi(OH)$_2$-1 and N$_C$–FeNi(OH)$_2$-2 (Fig. 3b and Fig. S16, ESI†). The N$_C$–FeNi(OH)$_2$ outperformed the literature reported catalysts in seawater OER performance (Table S2, ESI†).

The catalytic performance of the synthesized catalysts was also investigated in freshwater (1.0 M KOH) with or without hydrazine. The N$_C$–FeNi(OH)$_2$ manifested 100 mA cm$^{-2}$ current density for OER (1.34 V vs. RHE) and HzOR (0.99 V vs. RHE), far better than that of N$_C$–Ni(OH)$_2$ (Fig. S17, ESI†). However, compared to the seawater, a decrease of 20 mV potential was observed for hydrazine oxidation with N$_C$–FeNi(OH)$_2$ in freshwater.

Notably, the superior performance of N$_C$–FeNi(OH)$_2$ was attributed to the modulated electronic properties of Ni sites due to nitrate coordination. The nitrate coordination provided a higher current density at 1.35 V and 1.45 V vs. RHE compared to the freshwater (Fig. S18 and S19, ESI†). After the addition of hydrazine, the Tafel slope values were decreased to 40 mV dec$^{-1}$ and 77 mV dec$^{-1}$ for N$_C$–FeNi(OH)$_2$ and N$_C$–Ni(OH)$_2$, respectively (Fig. S18, ESI†). A similar trend of reaction kinetics was also observed in the case of freshwater OER and HzOR (Fig. S19, ESI†). However, the Tafel slopes in seawater were observed to be higher compared to the freshwater (Fig. S18 and S19, ESI†).

Further, we constructed a two-electrode water electrolyzer by employing N$_C$–FeNi(OH)$_2$ at the anode and cathode. In real seawater, the overall water splitting was achieved at 1.67 V cell voltage to deliver 100 mA cm$^{-2}$ current density (Fig. 3c). After the addition of hydrazine, the cell voltage was reduced to 1.20 V affording the same current density (Fig. 3c). The N$_C$–FeNi(OH)$_2$ || N$_C$–FeNi(OH)$_2$ couple also outperformed the Pt/C || RuO$_2$ system (Fig. S20, ESI†) and N$_C$–FeNi(OH)$_2$ || N$_C$–FeNi(OH)$_2$ couple (Fig. 3c) in real seawater splitting.

In freshwater, N$_C$–FeNi(OH)$_2$ || N$_C$–FeNi(OH)$_2$ couple delivered 100 mA cm$^{-2}$ current density at 1.57 V cell voltage, which was decreased to 1.16 V after the addition of hydrazine (Fig. S21, ESI†). The anodic hydrazine oxidation led to a significant reduction in cell voltage, avoiding interference from OER in freshwater and CIOR in seawater. The N$_C$–FeNi(OH)$_2$ || N$_C$–FeNi(OH)$_2$ manifested an impressive stability of 60 h in a two-electrode system (Fig. 3d). Interestingly, the hydrogen production was increased by 3.2 times during hydrazine oxidation compared to OER in seawater (Fig. S22, ESI†). The increase in the production of H$_2$ is ascribed to the enhanced H$_2$ evolution efficiency. It is noteworthy that HzOR leads to the formation of N$_2$ and H$_2$O molecules rather than H$^+$ in alkaline medium. The creation of H$^+$ from hydrazine do not contribute to enhanced H$_2$ production because H$^+$ can be generated only in acidic medium.2–4

Further, faradaic efficiency (FE) was measured in fresh water as well as seawater to verify the interference from side reactions. The FE was determined to be 98.7% and 98.2% in fresh water and seawater, respectively (Fig. S23 and S24, ESI†). The excellent FE suggested that no side reaction was occurred at the
anode. To verify the ClOR interference, we performed the o-tolidine test followed by UV-vis spectroscopy. The peak for oxidized o-tolidine ($I_{\text{max}} = 437$ nm) was not detected in the UV-vis spectrum (Fig. S25, ESI†). The UV-vis spectra of seawater, taken before and after anodic chronocoulometry, showed no differences suggesting the absence of ClOR interference at the anode.

The outstanding electrochemical performance of NC–FeNi(OH)$_2$ was attributed to the partial electron transfer between the metals, which optimizes the redistribution of the electrons and stabilized the high valent metal (Fig. S26, ESI†). The electrochemical impedance spectroscopy (EIS) of the catalysts was conducted to study the charge transfer properties. The lower charge-transfer resistance ($R_{ct}$) was determined for NC–FeNi(OH)$_2$ (0.90 Ω) compared to NC–Ni(OH)$_2$ (2.00 Ω), and N$_2$–FeNi(OH)$_2$ (1.23 Ω) (Fig. S27, ESI†). The lower $R_{ct}$ value indicates improved charge transfer properties in NC–FeNi(OH)$_2$ due to the introduction of iron. Furthermore, the double layer capacitance ($C_{dl}$) of NC–FeNi(OH)$_2$ was measured to be $5.33 \times 10^{18}$ F cm$^{-2}$, which is higher compared to NC–Ni(OH)$_2$ ($3.91 \times 10^{18}$ F cm$^{-2}$) and N$_2$–FeNi(OH)$_2$ ($3.54 \times 10^{18}$ F cm$^{-2}$) (Fig. S28, ESI†). The larger $C_{dl}$ value suggested the improved surface area of NC–FeNi(OH)$_2$. Additionally, the reduction peak area of CV profiles was also integrated to determine the number of active Ni sites (Fig. S29, ESI†). The number of Ni sites was determined to be $7.55 \times 10^{18}$ for NC–FeNi(OH)$_2$, higher than that of NC–Ni(OH)$_2$ ($6.17 \times 10^{18}$) and N$_2$–FeNi(OH)$_2$ ($5.79 \times 10^{18}$) (eqn (S1), ESI†).

Post-catalytic characterization was conducted to investigate the morphological and electronic features of the catalysts. The Ni 2p XPS studies of NC–FeNi(OH)$_2$ and NC–Ni(OH)$_2$ compared to their fresh catalysts, confirmed a positive shift of 0.54 and 0.77 eV in the Ni 2p$_{3/2}$ peak, respectively (Fig. S30 and S31, ESI†). This suggests the presence of a significant amount of Ni$^{3+}$ after catalysis due to anodic oxidation. Similarly, the Fe 2p XPS of NC–FeNi(OH)$_2$ revealed a positive shift of the Fe 2p$_{3/2}$ peak compared to fresh NC–FeNi(OH)$_2$ catalyst (Fig. S32, ESI†). The N 1s XPS of NC–FeNi(OH)$_2$ showed evidence of nitrate bonding. However, a lower intensity was observed after catalysis compared to the fresh sample (Fig. S33 and S34, ESI†). This indicates that some nitrate ions leached out and adsorbed onto the catalyst’s surface during catalysis, enhancing catalytic performance. Consequently, the surface composition suggested a higher nitrogen content on the surface of NC–FeNi(OH)$_2$ after catalysis compared to the fresh sample (Table S1, ESI†). The O 1s XPS of NC–FeNi(OH)$_2$ and NC–Ni(OH)$_2$ showed three peaks with a slight negative shift compared to their corresponding fresh catalysts (Fig. S35 and S36, ESI†). TEM studies indicated slight agglomeration of nanosheets after hydrazine oxidation (Fig. S37a, ESI†). The HRTEM image evidenced the lattice spacing of 0.23 nm for the (101) plane of Ni$_2$(NO$_3$)$_3$(OH)$_2$·2H$_2$O (Fig. S37b, ESI†). The post-catalytic characterization revealed the generation of more amounts of high valent Ni$^{3+}$ and Fe$^{3+}$ with the retained morphology.

In summary, we have developed a facile molten salt method to synthesize nitrate-coordinated iron-doped nickel hydroxide for hydrazine oxidation-assisted seawater splitting. The NC–FeNi(OH)$_2$ delivered a current density of 100 mA cm$^{-2}$ at 1.01 V vs. RHE for H$_2$OR, whereas OER required 1.35 V vs. RHE in seawater. Additionally, a cell voltage of 1.20 V vs. RHE was required to attain 100 mA cm$^{-2}$ current density in a two-electrode system with hydrazine in seawater. Therefore, our work provides a rational design of nitrate-coordinated metal hydroxide with efficient seawater splitting activity.

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Data availability

The data supporting this article have been included as part of the ESL†.

Conflicts of interest

There are no conflicts to declare.

Notes and references