High-performance seawater oxidation by a homogeneous multimetallic layered double hydroxide electrocatalyst

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Seawater electrolysis is an intriguing technology for sustainable hydrogen production that will not exacerbate the global shortage of freshwater or increase carbon emissions. However, due to the undesirable anodic chlorine evolution reaction and the strong corrosiveness of seawater, this technology is significantly hindered by a lack of robust oxygen evolution reaction (OER) electrocatalysts that exhibit high activity, high selectivity, and good stability. Here, we demonstrate a homogeneous multimetallic catalyst consisting of Ni and Fe incorporated into CuCo layered double hydroxide (denoted as NiFe-CuCo LDH) that serves as an active and durable OER electrode for high-performance seawater electrolysis. With abundant exposed multimetal sites and well-defined micronanostructures, the NiFe-CuCo LDH catalyst requires overpotentials of only 259, 278, and 283 mV to yield current densities of 100, 300, and 500 mA cm

Electrochemical water splitting has been recognized as one of the most promising approaches to produce hydrogen (H2) energy sustainably and without any carbon emissions (1–5). There has been great progress in the development of this technology in recent years based on the discovery of many efficient and low-cost electrocatalysts (6–9). However, all of these electrocatalysts are operated in aqueous electrolytes prepared using high-purity freshwater, which would exacerbate the global freshwater shortage if seawater electrolysis were commercialized on a large scale (10). Considering the abundance and accessibility of earth’s seawater resources, extracting hydrogen via seawater electrolysis is a much more significant technology, especially for the arid zones located near ocean coastlines (11–13). In addition, it offers a possible route for seawater desalination (14). However, the scalable production of hydrogen from seawater electrolysis still faces many challenges.

The chloride evolution reaction (CER), an unintentional reaction that occurs due to the presence of chloride ions in seawater, poses the greatest challenge since it will compete with the desired oxygen evolution reaction (OER) on the anode. Although OER is thermodynamically more favorable, with an onset potential ~480 mV lower than that of CER in alkaline conditions, the OER kinetics are more sluggish because the reaction involves a complex four-electron transfer process, while CER requires the transfer of only two electrons (15–17). Accordingly, the overpotential required for OER in alkaline seawater electrolysis should be significantly lower than 480 mV to avoid triggering the CER process. Another challenge in seawater electrolysis results from the highly corrosive seawater that also contains bacteria and microbes, all of which will corrode and poison catalysts (18). Additionally, some insoluble precipitates, such as Mg(OH)2 and Ca(OH)2, will be generated on the cathode due to local pH change and will cover the catalyst surface and decay the overall seawater-splitting efficiency (12). Therefore, the primary task for advancing seawater electrolysis technology is seeking active and stable anode materials for selective OER over CER. Layered double hydroxides (LDHs) have been demonstrated to be among the most active OER electrocatalysts in alkaline freshwater splitting (19). Recently, a series of LDH-based electrocatalysts, including NiFe LDH (20), NiFe LDH/NiS (21), V-doped CoCr LDH (22), CeO2@CoFe LDH (23), and B-modified CoFe LDH (24), have also been utilized for OER in seawater electrolytes, exhibiting fairly good performance with...
overpotentials well below 480 mV at large current densities (e.g., 500 mA cm$^{-2}$) and thus show great potential for seawater electrolysis. On the other hand, recent studies have proved that introducing additional transition metals into LDH materials is an effective strategy for boosting OER activity since the introduced metals not only provide extra metal sites but also work as modulators to regulate the electronic structure of the host LDH catalyst, finally optimizing the adsorption energy of OER intermediates (25). For example, Li et al. reported a V-doped NiFe LDH electrocatalyst for efficient OER in alkaline freshwater media and found that the doped V acts as an electronic modulator to enhance conductivity for rapid electron transfer, as well as induces a strong electronic interaction with neighboring Fe sites to lower the energy barrier of the OER process (26). Reports of similar catalysts, including W-doped NiFe LDH (27), Fe-incorporated CoNi LDH (28), Rh-doped CoFe LDH (29), and Ir-doped NiV LDH (30), showed that the introduced transition metals accelerate the OER kinetics via modifying electronic structures for lower potential barriers, promoting conductivity for high charge-transfer efficiency, and tuning nanostructures for more active sites.

Here, we report a CuCo LDH coincorporated with Ni and Fe (denoted as NiFe-CuCo LDH) that is derived from CuCo metal-organic frameworks (MOFs) and serves as a homogeneous multimetallic OER catalyst for alkaline seawater electrolysis. The dual-metal coincorporated LDH was fabricated through a simultaneous etching-incorporation-sedimentation process, which induces a structural reorganization from the initial microsheet arrays of the MOFs into ultrathin hierarchical micronanosheet arrays of the LDHs. This ingenious micronanoscale allows a maximum exposure of abundant active sites and expedites electrolyte diffusion for fast mass transport. Moreover, the introduced Ni and Fe synergistically modulate the electronic structure of CuCo LDH, which not only enhances electrical conductivity for efficient charge transfer but also promotes corrosion resistance against the aggressive corrosive properties of seawater. Consequently, the NiFe-CuCo LDH catalyst exhibits high OER performance toward seawater electrolysis, delivering current densities of 100, 300, and 500 mA cm$^{-2}$ at small overpotentials of 259, 278, and 283 mV, respectively, in a harsh 6 M KOH seawater electrolyte, accompanied by high selectivity (Faradaic efficiency [FE] of 97.4% for O$_2$ at 500 mA cm$^{-2}$) and good stability (increased overpotential of $\sim$71 mV after 500 h electrolysis at 500 mA cm$^{-2}$). Such a high performance establishes our multimetallic electrocatalyst as one of the best OER catalysts for alkaline seawater electrolysis reported thus far, advancing the development of seawater electrolysis.

**Results and Discussion**

**Catalyst Synthesis and Characterization.** As schematically illustrated in Fig. 1A, the NiFe-CuCo LDH catalyst was converted from well-known Co-based MOFs (CuCo MOFs) (31), which were first synthesized on Ni foam using a previously reported room temperature coprecipitation approach (32). It should be noted that bimetallic CuCo MOFs, rather than Co MOFs, were selected since CuCo MOFs have demonstrated higher OER activity due to electronic band structure modulation resulting from the addition of Cu atoms (33). The scanning electron microscopy (SEM) images in *SI Appendix*, Fig. S1 show that the as-received Ni foam substrate has a three-dimensional (3D) porous structure with a smooth surface. Following the growth of CuCo MOFs, its surface is fully covered by many vertically aligned microsheet arrays (Fig. 1B) with uniform dispersion of elemental Co, Cu, C, and N (*SI Appendix*, Fig. S2) and a thickness of about 12 $\mu$m (*SI Appendix*, Fig. S3). In the second step, one piece of the as-prepared CuCo MOFs was immersed into an aqueous solution containing Ni(NO$_3$)$_2$ and FeSO$_4$ for 1 h at room temperature to obtain the final NiFe-CuCo LDH catalyst (Fig. 1A). A color change can be clearly seen after each of the two steps: the uniform violet color of the CuCo MOFs film is transformed into the earthy yellow color of the NiFe-CuCo LDH catalyst (*SI Appendix*, Fig. S4). This transformation follows an etching-incorporation-sedimentation mechanism (29, 34). First, due to the hydrolysis of Ni$^{2+}$ and Fe$^{3+}$, the aqueous solution of Ni(NO$_3$)$_2$ and FeSO$_4$ provides a weakly acidic environment, in which H$^+$ ions would etch CuCo MOFs via breaking the coordination bonds between Co/Cu atoms and organic linkers. Similar to Ni$^{2+}$ and Fe$^{3+}$, the released Co$^{2+}$/Cu$^{2+}$ also undergo a reversible hydrolysis process to generate Co(OH)$_2$/Cu(OH)$_2$ and H$^+$ ions (34). As the etching process consumes more H$^+$ ions, the hydrolysis of the metal ions accelerates to produce more metal hydroxides, which are finally cosedimented into the resulting LDHs. Meanwhile, Ni and Fe are simultaneously incorporated into the CuCo LDH through an anion exchange process (28). Additionally, a small amount of NiFe LDH is generated due to spontaneous oxidation of Fe$^{2+}$ in the air (20). Therefore, the final NiFe-CuCo LDH catalyst should be composed of Ni/Fe coincorporated CuCo LDH along with some NiFe LDH.

Fig. 1C and D display low-magnification SEM images of the NiFe-CuCo LDH catalyst, from which it can be observed that the multimetallic catalyst inherits the microsheet array morphology from the initial MOFs without the etching process causing any collapse, although it does induce some roughness on the microsheet surfaces. The high-magnification SEM image in Fig. 1E clearly shows that many nanosheets uniformly stand on the entire surface of each microsheet, rendering a favorable hierarchical micronanosheet structure that effectively suppresses the aggregation of LDH nanosheets and creates a large surface area. The thickness of a single hybrid micronanosheet array is around 300 nm (*SI Appendix*, Fig. S5A and B). The transmission electron microscopy (TEM) image in Fig. 1F further confirms this hierarchical micronanosheet architecture and shows that all nanosheets are perpendicularly anchored on the microsheet surfaces, giving rise to adequate interspaces for electrolyte permeation and gas bubble release. These vertically aligned nanosheets exhibit a densely wrinkled feature (Fig. 1G) and are only $\sim$4.9 nm thick (*SI Appendix*, Fig. S5C and D), which is expected to enable more edge active sites for catalytic reactions (35). The high-resolution TEM (HRTEM) image in Fig. 1H shows distinguishable lattice fringes with interplanar spacings of 0.24 and 0.26 nm, which are assigned to the (015) plane of NiFe LDH and the (102) plane of CuCo LDH, respectively. The selective area electron diffraction (SAED) pattern in Fig. 1I displays well-resolved diffraction rings belonging to the (102) and (113) planes of CuCo LDH (Powder Diffraction File [PDF] #46-606) and the (015) plane of NiFe LDH (PDF#42-573). Fig. 1J shows the high-angle annular dark-field scanning TEM (HAADF-STEM) image and corresponding elemental mapping images of NiFe-CuCo LDH, which clearly verify the existence and homogenous distribution of Ni, Fe, Co, Cu, and O in the hierarchical micronanosheet arrays. To study the effect of coincorporation, two control samples, Ni-incorporated CuCo LDH and Fe-incorporated CuCo LDH (designated Ni-CuCo LDH and Fe-CuCo LDH, respectively), were also successfully synthesized by the same method for
comparison (SI Appendix, Fig. S4). SI Appendix, Figs. S6 and S7 present their respective SEM and energy-dispersive X-ray spectroscopy (EDS) mapping images, which show that the control samples also exhibit hierarchical morphology, although it is slightly different from that of NiFe-CuCo LDH.

To determine the exact physical phase of each catalyst, we first conducted X-ray diffraction (XRD) for the different samples. As shown in Fig. 2A, besides three strong diffraction peaks from the Ni substrate, the XRD pattern of the CuCo MOF sample exhibits typical diffraction peaks (5° to 45°) corresponding to zeolitic imidazolate frameworks (ZIF-67) (36). Upon the solution treatment, all of these peaks from ZIF-67 disappear, suggesting a complete phase transformation. At the same time, a broad peak located at ∼22.6° shows up, which is indexed to the (006) plane of LDH materials (28, 37), demonstrating the successful conversion of MOFs into LDHs. Raman spectra in Fig. 2B further affirm this conversion since the peaks from the CuCo MOF spectrum are absent from those of the three LDH samples. Instead, three peaks at ∼452, 530, and 1,046 cm⁻¹, assigned to the representative stretching modes of LDHs, are detected (20). Notably, the peak at 530 cm⁻¹ shows a positive shift in the NiFe-CuCo LDH catalyst, which may be induced by the strong electronic interactions between the multiple metals resulting from Ni/Fe coinclusion. We then performed X-ray photoelectron spectroscopy (XPS) measurements to investigate the chemical states and electronic structures of the three LDH catalysts. As the high-resolution XPS spectra of Co 2p in Fig. 2C show, that of the Ni-CuCo LDH catalyst exhibits two spin-orbit peaks at 780.9 eV for Co 2p3/2 and 797.0 eV for Co 2p1/2, accompanied by two satellite peaks (each denoted as “Sat.”), indicating the coexistence of Co³⁺ and Co²⁺ (38). For the Fe-CuCo LDH and NiFe-CuCo LDH spectra, the two spin-orbit peaks show a negative shift to lower binding energy, suggesting an electronic structure change of Co caused by Fe incorporation. In Fig. 2D, the Cu 2p XPS spectra exhibit two peaks at 934.1 and 952.3 eV for Cu 2p3/2 and Cu 2p1/2, respectively, as well as a visible satellite peak at ∼942.1 eV, suggesting that Cu is in a Cu²⁺ oxidation state in the three LDH catalysts (39). The high-resolution Ni 2p spectrum of Ni-CuCo LDH features Ni 2p3/2 and Ni 2p1/2 peaks at 855.1 and 872.9 eV, respectively, together with two satellite peaks (Fig. 2E), which is indicative of the Ni²⁺ oxidation state (30). Similar to the Co 2p spectra, a negative shift is also observed in the Ni 2p3/2 and Ni 2p1/2 peaks of the NiFe-CuCo LDH spectrum. In the Fe 2p XPS spectrum of Fe-CuCo LDH (Fig. 2F), the two typical peaks located at 710.8 and 724.1 eV are assigned to Fe 2p3/2 and Fe 2p1/2, respectively, and two satellite peaks are detected at 717.1 and 731.9 eV, suggesting that
Fe$^{3+}$ is the dominant chemical state on the surface (40). In the corresponding spectrum for the NiFe-CuCo LDH catalyst, the two spin-orbit peaks of Fe 2p$_{3/2}$ and Fe 2p$_{1/2}$ clearly show a positive shift to higher binding energy resulting from the strong interactions between the different metals. Taken together, these results attest to the successful transformation from MOFs to LDHs with modified electronic configurations due to Ni and Fe coinclusion, which may favor the adsorption of OER intermediates and thus boost the OER activity (41).

**OER Performance in Alkaline Freshwater Electrolyte.** According to the Pourbaix diagram, the difference between the onset potential values of OER and CER reaches a maximum of $\sim$480 mV when the electrolyte pH is larger than 7.5 (17), indicating that an alkaline environment is more favorable for selective OER over CER during seawater electrolysis. Therefore, to clearly compare OER activity, we first assessed the different catalysts, including the benchmark RuO$_2$ and IrO$_2$ catalysts loaded on Ni foam, in 1 M KOH freshwater electrolyte. As the polarization curves in Fig. 3A show, all three LDH catalysts exhibit significantly enhanced OER activity relative to the original CuCo MOFs, especially Ni-CuCo LDH and NiFe-CuCo LDH, which are also superior to the benchmark RuO$_2$ and IrO$_2$ (SI Appendix, Fig. S8) catalysts. Moreover, with Ni and Fe coinclusion, the multimetallic NiFe-CuCo LDH catalyst exhibits the highest OER activity among the five catalysts. It requires an overpotential of only 212 mV to reach the benchmark current density of 10 mA cm$^{-2}$, which is much smaller than the corresponding values for the Ni-CuCo LDH, Fe-CuCo LDH, and RuO$_2$ catalysts, as shown by the comparison in Fig. 3B. Meanwhile, at a potential of 1.5 V vs. reversible hydrogen electrode (RHE), our NiFe-CuCo LDH catalyst delivers a current density up to 141 mA cm$^{-2}$, which is nearly 2.8 and 16.8 times that of Ni-CuCo LDH and Fe-CuCo LDH, respectively, and represents a 63-fold improvement compared with commercial RuO$_2$ (Fig. 3B), as well as being significantly higher than that of the well-recognized NiFe LDH catalyst (SI Appendix, Fig. S9), demonstrating superior OER activity. It should be noted that the reduction peaks between 1.3 and 1.4 V vs. RHE in the polarization curves of Ni-CuCo LDH and NiFe-CuCo LDH result from the reduction of Ni$^{3+}$ to Ni$^{2+}$ (42). SI Appendix, Fig. S10 further shows the performance of NiFe-CuCo LDH at large current densities. To achieve current densities of 100, 500, and 1,000 mA cm$^{-2}$, it requires overpotentials of 262, 300, and 345 mV, respectively, all of which are far lower than 480 mV. We also investigated the effects of Ni(NO$_3$)$_2$/FeSO$_4$ concentration and reaction time in the second synthesis step on the OER activity of the final NiFe-CuCo LDH catalysts. The sample prepared with 0.15 M Ni(NO$_3$)$_2$/FeSO$_4$ and a reaction time of 1 h was found to exhibit the best OER activity (SI Appendix, Figs. S11 and S12) and was used for further analyses unless otherwise stated. In Fig. 3C, a small Tafel slope of 48.3 mV dec$^{-1}$ was measured for the NiFe-CuCo LDH catalyst in comparison with that of the Ni-CuCo LDH (64.4 mV dec$^{-1}$), Fe-CuCo LDH (64.9 mV dec$^{-1}$), RuO$_2$ (93.6 mV dec$^{-1}$), and CuCo MOF (100.5 mV dec$^{-1}$) electrodes, suggesting favorable and fast OER kinetics. Given the very small values of its overpotential at 10 mA cm$^{-2}$ and its Tafel slope, our NiFe-CuCo LDH catalyst outperforms most recently reported transition-metal-based electrocatalysts (Fig. 3D), including some multimetallic electrocatalysts such as NiFeMn LDH (43), NiCoFe MOFs (44), and V-doped CoNiB (45), establishing it as among the first-class nonprecious OER electrocatalysts.

To understand the origins of the high activity of NiFe-CuCo LDH, we first calculated the electrochemically active surface area (ECSA) of each as-prepared catalyst through the determination of its double-layer capacitance ($C_{dl}$) from cyclic voltammetry curves (SI Appendix, Fig. S13) (46). As expected, the NiFe-CuCo LDH catalyst exhibits the largest ECSA among the four catalysts measured (SI Appendix, Fig. S14A), offering more...
active sites for OER. Nevertheless, after normalizing the polarization curves by ECSA, the NiFe-CuCo LDH catalyst still exhibits higher OER activity than the other three (SI Appendix, Fig. S14B), suggesting that its excellent performance cannot be merely attributed to the improved ECSA from the unique micronanosheet morphology, but to higher intrinsic catalytic activity benefiting from Ni and Fe coin incorporation. In this regard, electrochemical impedance spectroscopy (EIS) was utilized to comprehend the effect of Ni/Fe coin incorporation on OER kinetics. As the EIS Nyquist plots in Fig. 3E show, the NiFe-CuCo LDH catalyst has a much smaller charge-transfer resistance ($R_{ct}$) of 1.45 $\Omega$ than Ni-CuCo LDH (2.66 $\Omega$), Fe-CuCo LDH (2.79 $\Omega$), and CuCo MOFs (18.3 $\Omega$), indicating a more efficient charge transfer at the electrode/electrolyte interface that is contributed by the coin incorporation of Ni and Fe (47). Remarkably, in addition to its high OER activity, the NiFe-CuCo LDH electrode exhibits very good OER stability in 1 M KOH. As displayed in Fig. 3F, the overpotentials at fixed current densities of 10 and 100 mA cm$^{-2}$ show increases of 12 and 26 mV, respectively, during 100 h OER catalysis at each current density, which are negligible relative to that of the benchmark IrO$_2$ catalyst (SI Appendix, Fig. S15), and the polarization curve obtained after the stability test at 100 mA cm$^{-2}$ remains nearly unchanged from that prior to the test (Fig. 3G), demonstrating superior OER stability in alkaline freshwater electrolyte.

**OER Performance in Alkaline Seawater Electrolytes.** After confirming its improved OER activity in alkaline freshwater electrolyte, we then evaluated the seawater OER performance of the NiFe-CuCo LDH electrode in alkaline simulated-seawater (1 M KOH + 0.5 M NaCl and 1 M KOH + 1.5 M NaCl) and alkaline natural-seawater (1 M KOH + seawater) electrolytes. As shown in Fig. 4A and B, compared with its activity in 1 M KOH, the NiFe-CuCo LDH catalyst continues to exhibit excellent OER activity with little decay in alkaline simulated-seawater electrolytes, signifying that the highly concentrated Cl ions have little impact on the catalytic activity and, in turn, that the catalyst achieves high OER selectivity. In alkaline natural-seawater electrolyte (1 M KOH + seawater), retrogression of the electrode’s activity is clearly observed and mostly results from the bacteria and microbes in the seawater, as well as from some insoluble precipitates in the electrolyte generated during seawater OER catalysis (48). Very impressively, as shown in Fig. 4B, our NiFe-CuCo LDH electrode still outputs large current densities of 100 and 500 mA cm$^{-2}$ at low overpotentials of 315 and 355 mV, respectively, which are well below the 480-mV overpotential required to trigger CER. To explore the possibility of practical application, we further tested the electrode’s OER performance in a very harsh seawater electrolyte of 6 M KOH + seawater. As shown in Fig. 4C, the OER activity is further promoted, affording current...
densities of 100 and 300 mA cm$^{-2}$ at extremely low overpotentials of 259 and 278 mV, respectively, and even a record-low overpotential of 283 mV to achieve the industrially required current density of 500 mA cm$^{-2}$. The polarization curve for OER in 6 M KOH + seawater was also recorded without iR compensation for comparison (SI Appendix, Fig. S16), and the performance is clearly worse than that with iR compensation (49). In addition, the NiFe-CuCo LDH electrode shows a very high average FE of 97.4% for OER at a large current density of 500 mA cm$^{-2}$ in the harsh seawater electrolyte (Fig. 4D), suggesting that the total electron transfer during seawater electrolysis is dominated by the desired OER, not CER.

The issue of stability is another obstacle that impedes the practical application of seawater electrolysis. Therefore, we examined the operating durability of NiFe-CuCo LDH by conducting long-term OER electrolysis under constant current densities in three different alkaline seawater electrolytes. Fig. 4E shows that, in both 1 M KOH + 1.5 M NaCl and 1 M KOH + seawater electrolytes, NiFe-CuCo LDH functions quite stably with negligible degradation over 50 h of electrolysis at a constant current density of 100 mA cm$^{-2}$. Under a larger current density of 500 mA cm$^{-2}$, some attenuation is observed, but the increase in overpotential still does not exceed 45 mV. Impressively, our NiFe-CuCo LDH electrode also displays excellent durability in the harsh seawater electrolyte (6 M KOH + seawater). As shown in SI Appendix, Fig. S17, the overpotential is found to increase by only $\sim$18 mV over 100 h of operation at a constant current density of 100 mA cm$^{-2}$. In sharp contrast, the overpotential of IrO$_2$ under the same condition increases by more than 100 mV over 100 h of operation (SI Appendix, Fig. S18). For our NiFe-CuCo LDH electrode, even under a large current density of 500 mA cm$^{-2}$, the overpotential only slightly increases by $\sim$71 mV after up to 500 h of electrolysis (Fig. 4F), confirming the superior durability of this anode material that is promising for practical application.

Mechanism Study. To elucidate such remarkable stability, we carried out corrosion testing on different as-prepared catalysts in natural seawater, and SI Appendix, Fig. S24 displays the corresponding corrosion polarization curves. From the results in Fig. 5A, it can be seen that after converting MOFs into LDHs,
the corrosion potential ($E_{\text{corr}}$) is increased while the corrosion current density ($j_{\text{corr}}$) is decreased, suggesting enhanced corrosion resistance. More importantly, with Ni and Fe coinorporation, NiFe-CuCo LDH exhibits the highest $E_{\text{corr}}$ and the lowest $j_{\text{corr}}$ among the three LDH catalysts, proving its highest corrosion resistance in seawater, which contributes to the outstanding stability. To unveil the mechanism of how Ni and Fe enhance the anticorrosion property of CuCo LDH, theoretical calculations based on density functional theory (DFT) were performed to study the CER process using a two-step Volmer–Heyrovsky mechanism, which proceeds through the adsorption of Cl$^-$ and subsequent release of molecular Cl$_2$ (50). The crystal structures of CuCo LDH incorporating Ni atoms, Fe atoms, and both Ni and Fe atoms were adopted as calculation models for Ni-CuCo LDH, Fe-CuCo LDH, and NiFe-CuCo LDH, respectively (SI Appendix, Fig. S25). To examine the effect of Ni/Fe incorporation, we focused on Cl$^-$ adsorption on Co and Cu sites (Fig. S25B). As the free energy diagrams in Fig. S25C and S25D show, both Co and Cu sites of NiFe-CuCo LDH exhibit much higher adsorption free energy toward Cl$^-$ compared with that for Ni-CuCo LDH and Fe-CuCo LDH, which suggests that Cl$^-$ adsorption on the NiFe-CuCo LDH surface is more difficult than on either the Ni-CuCo LDH or Fe-CuCo LDH surface, thus protecting the catalyst against the corrosive Cl$^-$ and enhancing the anticorrosion property. Due to the sluggish Cl$^-$ adsorption, the CER process is significantly inhibited on NiFe-CuCo LDH relative to the other two catalysts. Specifically, the theoretical overpotentials for CER were calculated to be 3.70 and 1.93 V for Co and Cu sites, respectively, of NiFe-CuCo LDH, which are notably higher than the overpotentials for OER observed in the polarization curves. This also explains why OER is more favorable than the competitive CER on the NiFe-CuCo LDH catalyst and thus why the catalyst achieves high OER selectivity.

SI Appendix, Table S1 presents a detailed comparison between the NiFe-CuCo LDH catalyst and other recently reported OER electrocatalysts in alkaline seawater electrolytes. In terms of activity, selectivity, and stability, our NiFe-CuCo LDH electrode is one of the most efficient OER electrocatalysts for alkaline seawater electrolysis reported to date. Its high seawater oxidation performance is mainly ascribed to the following factors. First, the 3D hierarchical micronanosheet arrays not only provide an extremely large surface area for abundant active sites but also avail electrolyte diffusion and gas product release for rapid mass transport. Second, the incorporated Ni and Fe effectively promote the electrical conductivity, which accelerates charge transfer between the catalyst surface and the electrolyte, thus boosting the OER kinetics. Third, the strong interactions between different metal sites in the multimetallic catalyst regulate its electronic structure, improving the intrinsic activity of the catalyst.

Fig. 5. (A) $E_{\text{corr}}$ and $j_{\text{corr}}$ of different catalysts in natural seawater. (B) Cl$^-$ adsorption on Co and Cu sites of the optimized atomic structure of NiFe-CuCo LDH. Free energy diagrams of CER on Co (C) and Cu (D) sites of Fe-CuCo LDH, Ni-CuCo LDH, and NiFe-CuCo LDH, where * represents an active site on the catalyst surface.
the catalytic centers (41). Finally, the coinorporated Ni and Fe synergistically enhance the corrosion resistance of CuCo LDH through inactivation of Cl\textsuperscript{-} adsorption to resist the aggressive seawater, which endows the catalyst with good durability.

Conclusions

In summary, we have developed an active, stable, and low-cost OER electrode composed of Ni/Fe coinorporated CuCo LDH ultrathin micronanosheet arrays derived from MOFs through a facile solution treatment. Benefiting from the high density of exposed active sites and improved mass transport rendered by the hierarchical structure, along with the accelerated charge transfer and enhanced corrosion resistance contributed by the introduced Ni and Fe, the obtained electrode shows excellent seawater oxidation performance with extremely low overpotentials of 278 and 283 mV required to achieve large current densities of 300 and 500 mA cm\textsuperscript{-2}, respectively, in 6 M KOH seawater electrolyte. It also exhibits high OER selectivity, and its good durability is shown by its survival during operation at a constant current density of 500 mA cm\textsuperscript{-2} with only very slightly increased overpotential after 500 h. This work presents an efficient OER electrode produced from well-recognized materials, which we believe represents a giant step in advancing seawater electrolysis technology.

Materials and Methods

Chemicals. Fe (II) sulfate heptahydrate (FeSO\textsubscript{4}·7H\textsubscript{2}O, analytical reagent; Riedel-de Haen), Ni (II) nitrate hexahydrate [Ni(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O, 98%, analytical reagent], Co (II) nitrate hexahydrate [Co(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O, 99%, Aladdin], Cu (II) nitrate trihydrate [Cu(NO\textsubscript{3})\textsubscript{2}·3H\textsubscript{2}O, analytical purity; Sinopharm Chemical Reagent Co., Ltd.], 2-methylimidazole (C\textsubscript{4}H\textsubscript{6}N\textsubscript{2}, 98%; Aladdin), ruthenium dioxide (RuO\textsubscript{2}; Alfa Aesar), iridium dioxide (IrO\textsubscript{2}; Alfa Aesar), Na\textsubscript{2}SO\textsubscript{4}·10H\textsubscript{2}O, analytical reagent; Riedel-de Haen), Ni (II) nitrate hexahydrate [Ni(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O, 99%; Aladdin], sodium acetate trihydrate (Na\textsubscript{3}C\textsubscript{2}H\textsubscript{3}O\textsubscript{2}·H\textsubscript{2}O, 99.99%; Aladdin), and Ni foam (thickness, 1.6 mm) were used as received. Deionized (DI) water was used for the preparation of all aqueous solutions. Natural seawater (pH ∼8.2) was collected from Tolo Harbor near the Chinese University of Hong Kong, New Territories, Hong Kong SAR, China.

Synthesis of NiFe-CuCo LDH. The NiFe-CuCo LDH catalyst was synthesized on Ni foam using a two-step approach, the first of which is the synthesis of CuCo MOFs via a previously reported coprecipitation approach (32). Prior to the synthesis, we cleaned the Ni foam substrate by putting one piece of commercial Ni foam (2 cm × 5 cm) into 3 M HCl, ethanol, and DI water in sequence for ultrasonic treatment for several minutes. We then prepared two aqueous solutions, one of which contains 40 mL of 0.04 M Cu(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O and 0.01 M Cu(NO\textsubscript{3})\textsubscript{2}·3H\textsubscript{2}O and another of which contains 40 mL 0.4 M Cu\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}·2H\textsubscript{2}O. The two solutions were quickly mixed together, and the cleaned Ni foam substrate was immediately immersed into the mixture solution. After 4 h of reaction at room temperature, the sample was removed from the mixture solution, rinsed with DI water, and dried at 60 °C overnight. In the second step, one piece of the as-prepared CuCo MOFs grown on Ni foam (~1 cm × 2 cm) was immersed into a solution containing 10 mL of 0.15 M Ni(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O and 0.15 M FeSO\textsubscript{4}·7H\textsubscript{2}O for 1 h at room temperature. The sample was finally removed from the solution, washed with DI water, and dried in air before use. For comparison, two control samples of Ni-CuCo LDH and Fe-CuCo LDH were also synthesized in the same way except that the solution in the second step was replaced by 0.15 M Ni(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O only and 0.15 M FeSO\textsubscript{4}·7H\textsubscript{2}O only, respectively. Pure NiFe LDH was also synthesized on Ni foam for comparison using the same method as described in the second step above. In addition, to study the effect of Ni/Fe concentration and reaction time on their catalytic activity, we synthesized a series of different NiFe-CuCo LDH catalysts by changing the concentration of Ni(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O/FeSO\textsubscript{4}·7H\textsubscript{2}O and the reaction time in the second step. Specifically, 0.05, 0.10, or 0.20 M of Ni(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O/FeSO\textsubscript{4}·7H\textsubscript{2}O was used in the solution, along with 0.5, 1.5, or 2.0 h of reaction time.

Preparation of RuO\textsubscript{2} and IrO\textsubscript{2} Catalysts on Ni Foam. To prepare the RuO\textsubscript{2} and IrO\textsubscript{2} electrodes for comparison, 40 mg RuO\textsubscript{2} or IrO\textsubscript{2} and 60 μL Naflon were dispersed in 540 μL ethanol and 400 μL DI water in a small sealed tube. The mixture was ultrasonicated for 30 min, and the dispersion was then coated onto a Ni foam substrate, which was dried in air overnight.

Materials Characterization. The morphology and nanostructure of the catalysts were examined by SEM (JEOL JSM-6900) and TEM (FEI TF20) coupled with EDS. AFM characterization was performed using a Bruker AFM system. The phase characterization was conducted by XRD (Rigaku Smartlab X-ray diffractometer) with a Cu Kα radiation source. XPS (PHI-Vesprobe 5000II) was conducted using a Thermo ESCALAB 250Xi spectrometer equipped with an anode of Al Kα radiation (1,486.6 eV) X-ray sources. Raman measurements were performed on a HORIBA Labram HR Evolution Raman system with an excitation wavelength of 532 nm.

Electrochemical Tests. All electrochemical tests were performed on an electrochemical station (CHI 760D, CH Instruments, Inc.) in a standard three-electrode cell at room temperature, with an as-prepared sample, a graphite rod, and a standard Hg/HgO electrode serving as the working, counter, and reference electrodes, respectively. Five different electrolytes, including 1 M KOH, 1 M KOH + 0.5 M NaCl, 1 M KOH + 1.5 M NaCl, 1 M KOH + seawater, and 6 M KOH + seawater, were used, and their pH values were 13.79, 13.76, 13.71, 13.65, and 14.60, respectively. The OER polarization curves were obtained at a scan rate of 5 mV s\textsuperscript{-1}, and stability tests were performed under different constant current densities. To calculate FE, we measured the generated gaseous product on the anode by a drainage method in a gas-tight H-cell at a fixed current density of 500 mA cm\textsuperscript{-2} in 6 M KOH + seawater electrolyte. The FE was calculated by comparing the experimentally measured Q, amount to the theoretically calculated one. EIS was conducted at an overpotential of 300 mV from 0.01 Hz to 100 kHz with an amplitude of 10 mV. All of the measured potentials vs. Hg/HgO were converted to the RHE by the Nernst equation (E_{RHE} = E_{Hg/HgO} + 0.0591 × pH + 0.098). All data have been reported with 85% iR compensation applied manually unless otherwise specified.

DFT Calculations. Theoretical calculations were carried out by using the Vienna Ab-initio Simulation Package (VASP) in Material Studio based on DFT. The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) form was used to describe the exchange-correlation potential. The optimized (012) surface of CuCo LDH incorporating Ni atoms, Fe atoms, and both Ni and Fe atoms were adopted as calculation models for Ni-CuCo LDH, Fe-CuCo LDH, and NiFe-CuCo LDH, respectively.

Data Availability. All study data are included in the article and/or SI Appendix.

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