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# Suppressing oxygen-vacancy-mediated chlorine corrosion for high-current stable seawater electrolysis

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NiFe layered double hydroxide (NiFe LDH) is an efficient seawater oxygen evolution reaction (OER) catalyst. However, its long-term stability is severely limited by  $\text{Cl}^-$ -induced corrosion. To address this issue, an innovative vanadate modification strategy is developed to mitigate  $\text{Cl}^-$  corrosion in NiFe LDH. The resulting  $\text{VO}_4^{3-}$ -NiFe LDH/ $\text{VO}_x$ /NF catalyst exhibits excellent activity and durability in alkaline seawater, maintaining a current density of  $1000 \text{ mA cm}^{-2}$  for 3500 h, which is significantly longer than the 300 h achieved by the single NiFe LDH. Through *in situ* characterization and theoretical studies, it is revealed that on the NiFe LDH,  $\text{Cl}^-$  preferentially adsorbs onto oxygen vacancies ( $\text{O}_v$ ) generated *via* the lattice oxygen mechanism. This adsorption induces M–Cl coordination and further accelerates the formation of  $\text{O}_v$ , thereby driving a self-reinforcing corrosion cycle. By contrast, the  $\text{VO}_x$  on the surface of  $\text{VO}_4^{3-}$ -NiFe LDH/ $\text{VO}_x$ /NF undergoes *in situ* conversion to  $\text{VO}_4^{3-}$ , combining with intercalated  $\text{VO}_4^{3-}$  to form a dynamically adaptive  $\text{VO}_4^{3-}$  species. These species generate a strong electrostatic field that repels  $\text{Cl}^-$ , while simultaneously stabilizing  $\text{OH}^-$  through a hydrogen-bonding network. As a result, it effectively suppresses metal–Cl coordination and optimizes the adsorption behavior of  $\text{OH}^-$ , thereby sustaining high catalytic activity and stability.

## Introduction

Seawater electrolysis provides a sustainable method for hydrogen production, conserving freshwater resources and contributing to global energy decarbonization.<sup>1–3</sup> Unfortunately, the four-electron oxygen evolution reaction (OER) at the anode suffers from inherently sluggish kinetics due to complex proton-coupled electron transfer steps, which limit the overall efficiency.<sup>4–6</sup> In addition, the high concentration of chloride ions ( $\text{Cl}^-$ ) in seawater competes with hydroxide ions ( $\text{OH}^-$ ) for adsorption on catalytically active sites. This competition weakens the participation of  $\text{OH}^-$  in OER and facilitates  $\text{Cl}^-$ -induced corrosion, thereby compromising both catalytic activity and structural stability under operational conditions.<sup>7</sup> To overcome these challenges, it is imperative to develop robust anode electrocatalysts capable of operating efficiently and stably in  $\text{Cl}^-$ -containing environments.<sup>8,9</sup>

Among various candidates, nickel-iron layered double hydroxides (NiFe LDH), have attracted substantial attention owing to their high catalytic activity and earth abundance.<sup>10,11</sup> Recent research studies have improved the OER activity of NiFe LDH in seawater electrolysis through doping and defect

engineering techniques, but the long-term stability remains unsatisfactory.<sup>12,13</sup> In particular, the atomic-scale origin of  $\text{Cl}^-$ -induced corrosion is still unclear. Most studies attribute degradation to surface coordination or ion exchange,<sup>14–16</sup> but such pathways cannot fully explain the rapid structural collapse observed during operation.

Furthermore, while introducing negatively charged anions is a common approach to electrostatically repel  $\text{Cl}^-$ , this also inhibits  $\text{OH}^-$  adsorption, reducing catalytic activity.<sup>17,18</sup> Reconciling these competing interactions remains a critical challenge. To address this, an ideal catalyst design should repel  $\text{Cl}^-$  *via* electrostatic exclusion while facilitating  $\text{OH}^-$  retention through directional hydrogen bonding.<sup>19</sup> Vanadate anions ( $\text{VO}_4^{3-}$ ) are ideal candidates for this dual function. Rich in highly electro-negative oxygen atoms, they provide ample hydrogen-bonding acceptor sites for  $\text{OH}^-$  and water molecules.<sup>20</sup> This induces the formation of a dynamic and stable hydrogen bond network at the catalyst/electrolyte interface, which in turn facilitates the transport and supply of  $\text{OH}^-$  without hindering its reactivity.

Thus, this study constructs the  $\text{VO}_4^{3-}$  intercalated-NiFe LDH/ $\text{VO}_x$ /NF catalyst by simple one-step immersion thermal treatment of NiFe LDH. The resulting catalyst demonstrates outstanding OER activity and durability in alkaline seawater, sustaining  $1000 \text{ mA cm}^{-2}$  for 3500 h and maintaining stability for 2500 h in a membrane electrode assembly. *In situ* spectroscopic characterization confirms  $\text{VO}_4^{3-}$  incorporation into NiFe LDH layers, while

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surface vanadium oxide ( $\text{VO}_x$ ) species dynamically convert to  $\text{VO}_4^{3-}$  at anodic potentials, forming hydrogen-bond networks that stabilize  $\text{OH}^-$  adsorption while inhibiting  $\text{Cl}^-$  adsorption. Theoretical calculations further elucidate the corrosion mechanism of NiFe LDH and the suppression mechanism of  $\text{VO}_4^{3-}$ . It is confirmed that oxygen vacancies ( $\text{O}_v$ ) generated during the OER process in NiFe LDH serve as active sites for preferential  $\text{Cl}^-$  adsorption, initiating a self-reinforcing corrosion cycle. Crucially, this study successfully interrupts this corrosion cycle *via*  $\text{VO}_4^{3-}$ . Interlayer  $\text{VO}_4^{3-}$  fundamentally blocks  $\text{Cl}^-$  intrusion through strong electrostatic repulsion, while surface  $\text{VO}_4^{3-}$  significantly enhances affinity for the key reaction intermediate  $\text{OH}^-$  by forming robust hydrogen-bond networks. This dual action not only addresses chloride corrosion at its source but also synergistically optimizes OER kinetics. This study provides a rational and generalizable framework for designing electrocatalysts with high activity, stability, and selectivity in complex electrolytic environments.

## Results and discussion

### Material synthesis and characterization

The  $\text{VO}_4^{3-}$ -NiFe LDH/ $\text{VO}_x$ /NF is obtained by immersing hydrothermally synthesized NiFe LDH/NF into a  $\text{Na}_3\text{VO}_4$  solution (Fig. 1a).  $\text{VO}_4^{3-}$  anions intercalate into the LDH interlayers *via* ion exchange, while  $\text{VO}_x$  clusters form on the surface through spontaneous redox reactions. During alkaline seawater electrolysis, surface  $\text{VO}_x$  can dynamically transform into  $\text{VO}_4^{3-}$ .<sup>20,21</sup> X-ray diffraction (XRD) is employed to characterize the crystalline structure (Fig. 1b). The XRD pattern of the hydrothermally treated sample reveals characteristic peaks at  $12.32^\circ$  (003) and  $22.97^\circ$  (006), consistent with the lamellar structure of NiFe LDH (PDF #40-0215).<sup>22–24</sup> After immersion, a slight downshift in the (003) interlayer diffraction peak toward a lower  $2\theta$  angle is observed, which can be attributed to the expanded interlayer spacing of NiFe LDH due to the  $\text{VO}_4^{3-}$  intercalation.<sup>25,26</sup>

Raman analysis provides further evidence supporting the dual distribution of vanadium species in the  $\text{VO}_4^{3-}$ -NiFe LDH/ $\text{VO}_x$ /NF structure (Fig. 1c).<sup>26,27</sup> A pronounced Raman peak at  $900\text{ cm}^{-1}$ , assigned to the symmetric stretching vibration of  $\text{VO}_4^{3-}$ , confirms the successful intercalation of  $\text{VO}_4^{3-}$  into the interlayer spaces of NiFe LDH *via* ion exchange.<sup>28,29</sup> Fig. S1 reveals the lamellar array structure of NiFe LDH/NF. After  $\text{VO}_x$  modification, the nanosheet morphology of  $\text{VO}_4^{3-}$ -NiFe LDH/ $\text{VO}_x$ /NF remains unchanged (Fig. 1d), indicating that the surface  $\text{VO}_x$  clusters do not disrupt the layered architecture of NiFe LDH.<sup>30,31</sup> The microstructure of  $\text{VO}_4^{3-}$ -NiFe LDH/ $\text{VO}_x$ /NF is further characterized by transmission electron microscopy (TEM) (Fig. 1e and f). The clear lattice spacing of  $0.25\text{ nm}$  is attributed to the (012) plane of NiFe LDH. Moreover, amorphous  $\text{VO}_x$  clusters can be observed at the surface.<sup>32–34</sup> Elemental mapping provides a clearer visualization of the regional aggregation of  $\text{VO}_x$  clusters and the homogeneous distribution of  $\text{VO}_4^{3-}$ . Collectively, these above characterizations indicate that  $\text{VO}_4^{3-}$  is inserted into the interlayer of NiFe LDH through ion exchange, while  $\text{VO}_x$  is uniformly dispersed on

the surface of the nanosheet structure through interfacial bonding with NiFe LDH.

X-ray photoelectron spectroscopy (XPS) was conducted to further elucidate the surface compositions and chemical states of  $\text{VO}_4^{3-}$ -NiFe LDH/ $\text{VO}_x$ /NF. The survey spectrum (Fig. S2) clearly confirms the presence of V, Ni, Fe, and O elements. The V 2p spectrum displays multiple oxidation states ( $\text{V}^{3+}$ ,  $\text{V}^{4+}$  and  $\text{V}^{5+}$ ), indicating that partial reduction of  $\text{VO}_4^{3-}$  occurred during the immersion process, leading to the formation of surface  $\text{VO}_x$  species with mixed valence states (Fig. 1h).<sup>35,36</sup> Additionally, Ni 2p and Fe 2p peaks shift toward higher binding energies (Fig. 1i and j), reflecting the modulation of the metal oxidation states and suggesting altered electronic environments that may facilitate redox activation during catalysis.<sup>17,37</sup> These results validate the coexistence of interlayer  $\text{VO}_4^{3-}$  and surface  $\text{VO}_x$  species with distinct chemical states, thereby constructing a stable dual-modified interface.

### Electrocatalytic properties of catalysts

To assess whether the designed interfacial features improve practical performance as anticipated, the OER activity of  $\text{VO}_4^{3-}$ -NiFe LDH/ $\text{VO}_x$ /NF was evaluated in alkaline simulated seawater ( $1.0\text{ M KOH} + 0.6\text{ M NaCl}$ ). At a current density of  $100\text{ mA cm}^{-2}$ , the driving potential required for  $\text{VO}_4^{3-}$ -NiFe LDH/ $\text{VO}_x$ /NF ( $1.45\text{ V}_{\text{RHE}}$ ) is lower than that of NiFe LDH/NF ( $1.48\text{ V}_{\text{RHE}}$ ) and significantly lower than  $\text{RuO}_2$ /NF ( $1.60\text{ V}_{\text{RHE}}$ ). Notably, the potential to reach  $1000\text{ mA cm}^{-2}$  for  $\text{VO}_4^{3-}$ -NiFe LDH/ $\text{VO}_x$ /NF is reduced by  $329\text{ mV}$  compared to NiFe LDH/NF (Fig. 2a). The electrochemical surface areas (ECSA) of the as-prepared catalysts are determined by evaluating the electrochemical double-layer capacitances ( $C_{\text{dl}}$ ) within a non-faradaic potential range at different scan rates (Fig. S3). After normalization of the polarization curves by ECSA, the intrinsic OER activity of  $\text{VO}_4^{3-}$ -NiFe LDH/ $\text{VO}_x$ /NF surpasses that of NiFe LDH/NF (Fig. S4). This suggests that the observed performance enhancement may stem from the cooperative effects of interlayer and surface  $\text{VO}_4^{3-}$  species on interfacial ion regulation, rather than a simple increase in surface area. The turnover frequency (TOF) value of  $\text{VO}_4^{3-}$ -NiFe LDH/ $\text{VO}_x$ /NF is much higher than that of NiFe LDH/NF, further indicating that the introduction of the vanadium oxide species enhances the intrinsic activity (Fig. S5).

Consistent with this, Fig. 2b shows that the Tafel slope of  $\text{VO}_4^{3-}$ -NiFe LDH/ $\text{VO}_x$ /NF ( $48.5\text{ mV dec}^{-1}$ ) is significantly lower than that of NiFe LDH/NF ( $68.9\text{ mV dec}^{-1}$ ),  $\text{RuO}_2$ /NF ( $133.6\text{ mV dec}^{-1}$ ), and Ni foam ( $144.9\text{ mV dec}^{-1}$ ). This indicates faster reaction kinetics of  $\text{VO}_4^{3-}$ -NiFe LDH/ $\text{VO}_x$ /NF, which could be attributed to the surface  $\text{VO}_x$ -derived  $\text{VO}_4^{3-}$  species that enhance  $\text{OH}^-$  adsorption through hydrogen-bond networks. Electrochemical impedance spectroscopy (EIS) further reveals a much lower charge transfer resistance ( $R_{\text{ct}} = 1.01\text{ }\Omega$ ), supporting more efficient electron transport across the catalyst-electrolyte interface.

$\text{VO}_4^{3-}$ -NiFe LDH/ $\text{VO}_x$ /NF also delivers excellent OER performance under real seawater conditions, achieving a low overpotential of  $368\text{ mV}$  at  $1000\text{ mA cm}^{-2}$  (Fig. S6 and Table S2), while maintaining nearly 100% faradaic efficiency (FE) for  $\text{O}_2$



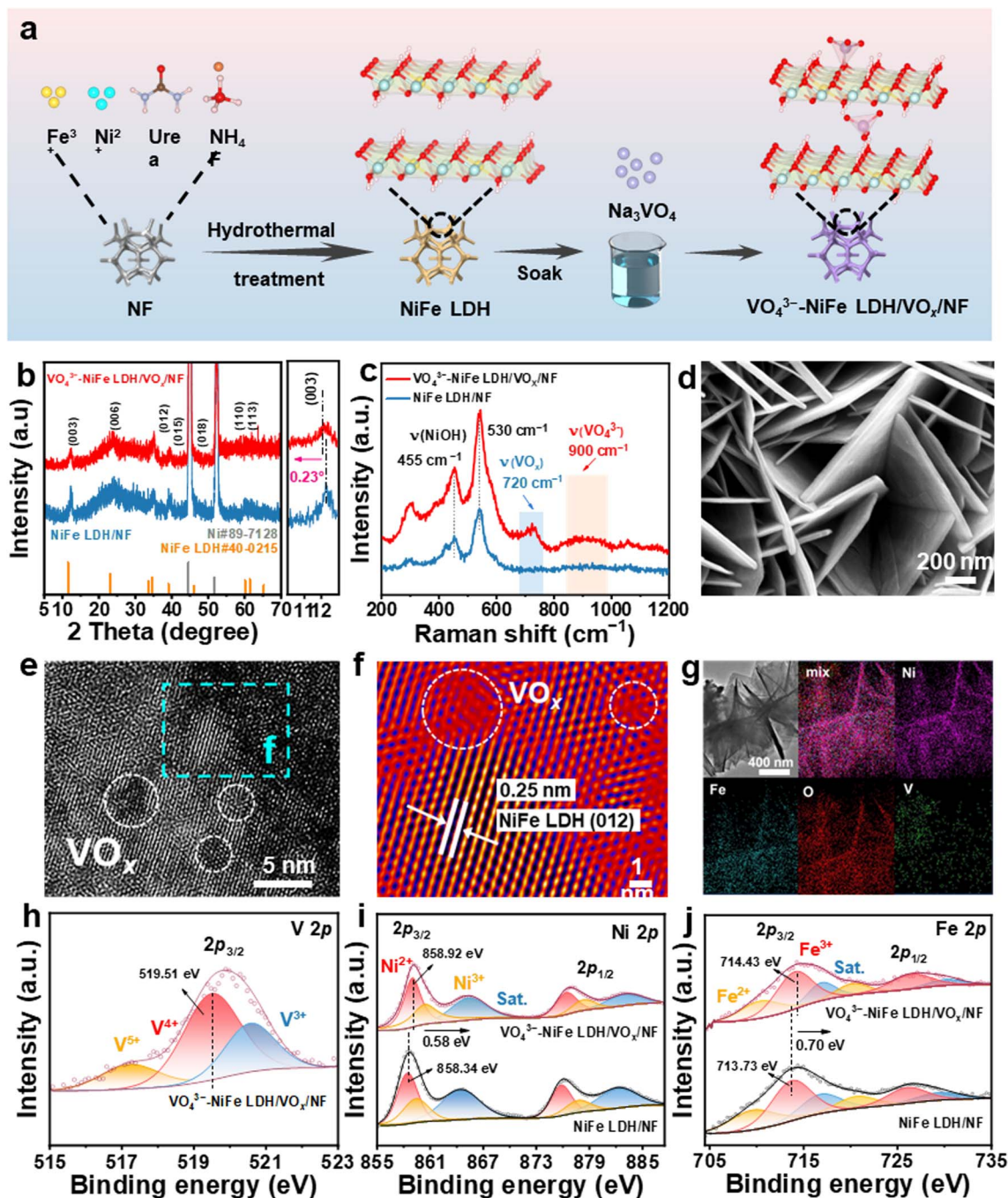


Fig. 1 Material characterization. (a) Schematic illustration of the synthesis process; (b) XRD patterns of  $\text{VO}_4^{3-}\text{-NiFe LDH/VO}_x\text{/NF}$  and  $\text{NiFe LDH}$ ; (c) Raman spectra; (d) SEM images of the  $\text{VO}_4^{3-}\text{-NiFe LDH/VO}_x\text{/NF}$ ; (e) TEM picture; (f) HRTEM image; (g) TEM image and corresponding elemental distributions; (h–j) HRXPS spectra of V 2p, Ni 2p, and Fe 2p.

generation throughout extended operation (Fig. S7). Post-electrolysis analysis using KI-starch test paper (Fig. S8) reveals no color change, confirming its exceptional selectivity.

More importantly, the catalyst exhibits remarkable long-term durability in alkaline simulated seawater. As shown in Fig. 2d and S9,  $\text{VO}_4^{3-}\text{-NiFe LDH/VO}_x\text{/NF}$  maintains stable operation at  $1000 \text{ mA cm}^{-2}$  for 3500 h, significantly longer than  $\text{NiFe LDH/NF}$  (300 h). This exceptional stability under constant current is further corroborated by accelerated electrochemical

cycling tests. CV cycling (Fig. S10) reveals that the activity of unmodified  $\text{NiFe LDH/NF}$  rapidly declines with increasing cycle number, suffering a noticeable current density drop after only 50 cycles. In contrast,  $\text{VO}_4^{3-}\text{-NiFe LDH/VO}_x\text{/NF}$  exhibits an initial increase in current density during the first 300 cycles, attributed to the gradual transformation of  $\text{VO}_x$  species to  $\text{VO}_4^{3-}$ . This stability surpasses many reported catalysts in alkaline seawater electrolysis (Fig. 2e and Table S1). Post-test analyses show that the  $\text{VO}_4^{3-}\text{-NiFe LDH/VO}_x\text{/NF}$  retains its

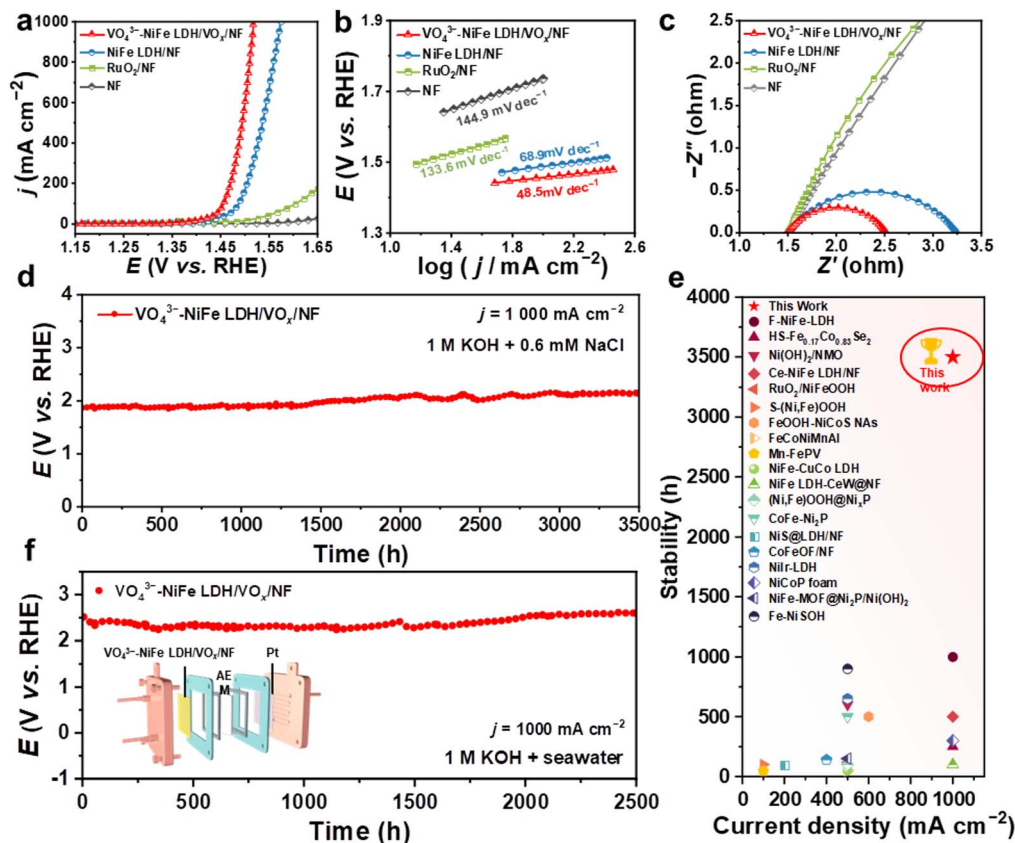


Fig. 2 (a) OER polarization curves of all catalysts in 1.0 M KOH + 0.6 M NaCl; (b) Tafel plots; (c) EIS Scheme; (d) durability evaluation by the chronopotentiometry at  $1000 \text{ mA cm}^{-2}$ ; (e) comparison of stability with other works; (f) durability evaluation using electrolysis membrane electrode assembly.

nanosheet morphology, while unmodified NiFe LDH/NF suffers severe structural collapse (Fig. S11). Further characterization confirms the structural and chemical stability of the modified catalyst. XRD analysis reveals that the  $\text{VO}_4^{3-}$ -NiFe LDH/ $\text{VO}_x$ /NF composite maintains its crystalline phase structure after stability testing (Fig. S12a). Raman spectroscopy indicates a decrease in the intensity of the characteristic  $\text{VO}_x$  peak and an increase in the  $\text{VO}_4^{3-}$  peak intensity, suggesting the conversion of  $\text{VO}_x$  to  $\text{VO}_4^{3-}$  during operation (Fig. S12b). This transformation is likely key to conferring the observed high stability. Inductively coupled plasma mass spectrometry (ICP-MS) reveals continuously increasing dissolved Ni and Fe concentrations from NiFe LDH/NF, indicating progressive corrosion. In contrast,  $\text{VO}_4^{3-}$ -NiFe LDH/ $\text{VO}_x$ /NF shows low initial metal ion release, suggesting  $\text{VO}_4^{3-}$  incorporation effectively suppressed leaching (Fig. S13). Furthermore,  $\text{VO}_4^{3-}$ -NiFe LDH/ $\text{VO}_x$ /NF demonstrates superior corrosion resistance (0.337 V vs. Hg/HgO) and lower corrosion current density ( $0.017 \text{ mA cm}^{-2}$ , Fig. S14) than NiFe-LDH/NF, confirming its enhanced  $\text{Cl}^-$  corrosion resistance.

To demonstrate practical applicability, Pt|| $\text{VO}_4^{3-}$ -NiFe LDH/ $\text{VO}_x$ /NF was integrated into a membrane electrode assembly (MEA)-based alkaline anion exchange membrane water electrolyzer (AEMWE) (Fig. 2f and S15). The full cell achieves an industrially relevant current density of  $1000 \text{ mA cm}^{-2}$  at only

2.38 V in 1.0 M KOH seawater solution. Impressively, the AEM electrolyzer maintains stable operation for over 2500 hours at  $1000 \text{ mA cm}^{-2}$  with minimal voltage increase, representing state-of-the-art durability among reported AEM-based seawater electrolyzer (Table S3). These results collectively demonstrate that the combined contributions of interlayer and surface  $\text{VO}_4^{3-}$  species enhance the intrinsic OER activity. More importantly, they also provide robust structural and electrochemical stability under highly corrosive seawater conditions, enabling long-term operation that surpasses conventional NiFe LDH-based catalysts.

### Anti-corrosion property of $\text{VO}_4^{3-}$ -NiFe LDH/ $\text{VO}_x$ /NF

Although experimental results demonstrate that  $\text{VO}_4^{3-}$ -NiFe LDH/ $\text{VO}_x$ /NF exhibit outstanding corrosion resistance, the corrosion mechanism of NiFe LDH remains to be fully elucidated. To clarify the corrosion pathway involving  $\text{Cl}^-$  adsorption, a series of spectroscopic characterizations is conducted under operating conditions. Electron paramagnetic resonance (EPR) spectroscopy was first employed to monitor the evolution of  $\text{O}_v$  before and after the oxygen evolution reaction (OER). As shown in Fig. 3a, both NiFe LDH/NF and  $\text{VO}_4^{3-}$ -NiFe LDH/ $\text{VO}_x$ /NF exhibit asymmetric signal peaks centered at  $g = 2.003$ , which correspond to the  $\text{O}_v$ .<sup>38,39</sup> After long-term OER operation, the  $\text{O}_v$



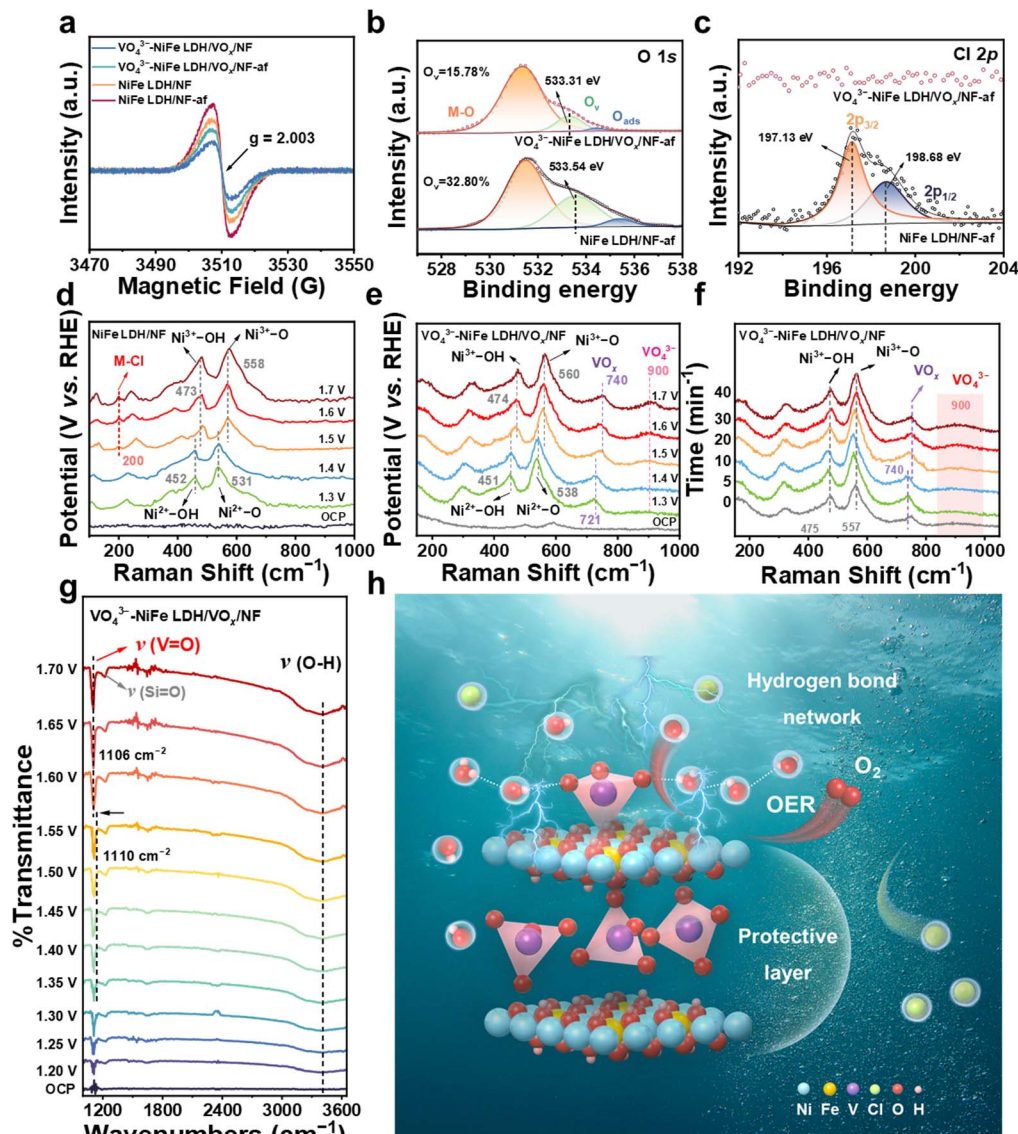


Fig. 3 Anti-corrosion property of  $\text{VO}_4^{3-}$ -NiFe LDH/ $\text{VO}_x$ /NF. (a) EPR spectra; (b and c) HRXPS spectra after stability testing; (d and e) potential-dependent Raman spectra; (f) time-dependent Raman spectra; (g) *In situ* FTIR spectra; (h) schematic diagram of the anti-corrosion mechanism.

concentration increases in both materials, consistent with the occurrence of lattice oxygen mechanism (LOM) pathway.<sup>40</sup> Additionally, XPS further reveals the chemical environment of post-electrolysis samples (Fig. S16). Notably, NiFe LDH/NF-af shows a higher concentration of  $\text{O}_v$  and the emergence of Cl 2p signals attributed to M-Cl coordination bonds (Fig. 3b and c). Since  $\text{Cl}^-$  exhibits lower nucleophilicity than  $\text{OH}^-$ , it is difficult to replace  $\text{OH}^-$  and break the M-OH bond. Therefore,  $\text{Cl}^-$  may adsorb onto the  $\text{O}_v$  generated during the LOM process, leading to corrosion of the NiFe LDH. In contrast,  $\text{VO}_4^{3-}$ -NiFe LDH/ $\text{VO}_x$ /NF-af shows neither excessive  $\text{O}_v$  accumulation nor detectable Cl 2p signals. This confirms that  $\text{VO}_4^{3-}$  species suppress  $\text{Cl}^-$  adsorption at  $\text{O}_v$  sites, preventing the formation of structurally disruptive M-Cl bonds.<sup>41,42</sup>

*In situ* Raman spectroscopy was employed to investigate the structural changes in  $\text{VO}_4^{3-}$ -NiFe LDH/ $\text{VO}_x$ /NF and NiFe LDH/

NF during OER testing. The peak positions at  $452\text{ cm}^{-1}$  and  $531\text{ cm}^{-1}$  in Fig. 3d, and those at  $451\text{ cm}^{-1}$  and  $538\text{ cm}^{-1}$  in Fig. 3e, correspond to the Ni-O(H) and Ni-O bonds in NiFe LDH/NF and  $\text{VO}_4^{3-}$ -NiFe LDH/ $\text{VO}_x$ /NF, respectively.<sup>43</sup> As the potential increases, these peaks begin to disappear at approximately 1.5 V for NiFe LDH/NF and 1.4 V for  $\text{VO}_4^{3-}$ -NiFe LDH/ $\text{VO}_x$ /NF. Two new peaks at 474 and  $560\text{ cm}^{-1}$  in Fig. 3e confirm the formation of Ni-OOH, indicating that NiFeOOH is the true active material.<sup>44</sup> Importantly, during the OER, a characteristic M-Cl vibrational mode ( $270\text{ cm}^{-1}$ ) was clearly observed in the NiFe LDH/NF material, whereas this mode was absent in the  $\text{VO}_4^{3-}$ -NiFe LDH/ $\text{VO}_x$ /NF material. This indicates that the  $\text{VO}_4^{3-}$ -derived surface layer effectively blocks  $\text{Cl}^-$  coordination.<sup>45</sup> Beyond  $\text{Cl}^-$  inhibition, time-resolved Raman spectra (Fig. 3f) reveal a gradual evolution of surface vanadium species during electrolysis. Specifically, the intensity of the peak at

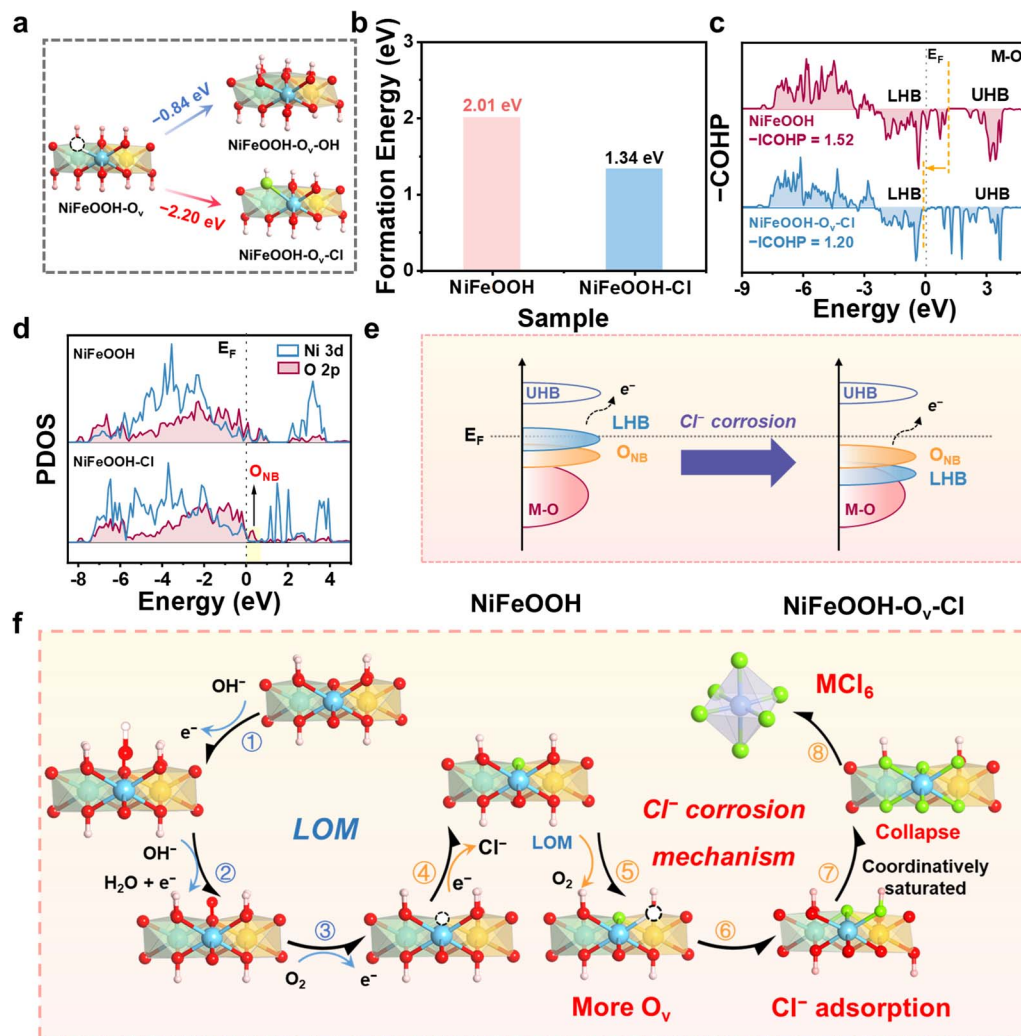


Fig. 4 Elucidation of the corrosion mechanism of NiFe LDH. (a) Comparison of the calculated adsorption energies of  $\text{Cl}^-$  and  $\text{OH}^-$  on the  $\text{O}_v$  of NiFeOOH; (b) calculated formation energy of  $\text{O}_v$ ; (c) -COHP analysis; (d) PDOS of NiFeOOH and NiFeOOH-Cl; (e) schematic energy bands of NiFeOOH and NiFeOOH- $\text{O}_v$ -Cl; (f) comprehensive schematic illustrating the self-reinforcing corrosion cycle perpetuated by the preferential adsorption of  $\text{Cl}^-$ , which ultimately leads to the rapid degradation of the NiFe LDH structure.

900  $\text{cm}^{-1}$ , attributed to the symmetric stretching vibration of  $\text{VO}_4^{3-}$ , increases over time, accompanied by a corresponding decrease in the  $\text{VO}_x$ -associated peak at approximately 720  $\text{cm}^{-1}$ . This spectral evolution indicates a progressive oxidation and conversion of surface  $\text{VO}_x$  into  $\text{VO}_4^{3-}$  species under anodic potentials. This transformation enhances electrostatic repulsion against  $\text{Cl}^-$ , further reinforcing corrosion resistance. However, despite these findings, its impact on interfacial hydroxide behavior remains unclear.

Therefore, *in situ* Fourier-transform infrared (FTIR) spectroscopy was conducted to probe the interfacial processes under operating conditions. As shown in Fig. 3g, upon applying increasing potentials, the  $\nu(\text{V}=\text{O})$  stretching vibration initially located near 1110  $\text{cm}^{-1}$  undergoes a red shift to 1106  $\text{cm}^{-1}$  along with intensity enhancement. This indicating the protonation of  $\text{VO}_4^{3-}$  into  $\text{HVO}_4^{2-}$  species, which could promote stronger interactions between terminal vanadium oxygens and surrounding  $\text{OH}^-$  or  $\text{H}_2\text{O}$ .<sup>46</sup> Concurrently, the broadening and

enhanced intensity of the O-H stretching band in the range of 3000–3600  $\text{cm}^{-1}$  reflect the establishment of an extended hydrogen-bond network at the catalyst-electrolyte interface (Fig. S17), which facilitates the stabilization and adsorption of interfacial  $\text{OH}^-$  and thereby improves the OER kinetics.<sup>47,48</sup> The above results corroborate the synergistic role of surface and interlayer  $\text{VO}_4^{3-}$  in simultaneously enhancing  $\text{OH}^-$  adsorption and suppressing  $\text{Cl}^-$  intrusion, thereby significantly enhancing corrosion resistance (Fig. 3h).

#### Elucidation of the corrosion mechanism of NiFe LDH

To gain a deeper insight into the fundamental mechanisms at the atomic scale about how chloride ions adsorb onto  $\text{O}_v$  and trigger structural degradation, a series of density functional theory (DFT) calculations were conducted.<sup>49–51</sup> Based on the actual catalytic active species NiFeOOH, a corresponding theoretical model was constructed. To investigate the interactions between  $\text{Cl}^-$  and the catalyst in depth, a NiFeOOH model





Fig. 5 Theoretical investigation into the dual regulation mechanism of  $\text{VO}_4^{3-}$ -modified catalyst. (a) Adsorption energy comparison of  $\text{Cl}^-$  with and without interlayer  $\text{VO}_4^{3-}$  species. (b) Charge density of  $\text{NiFeOOH-V}_I$  in the Z direction; (c) charge density difference of  $\text{NiFeOOH-V}_I$ ; (d and e) diffusion path models and energy barriers of  $\text{V}_S/\text{NiFeOOH}$  and  $\text{NiFeOOH}$ ; (f) electrostatic potential of  $\text{V}_S/\text{NiFeOOH}$ ; (g) representative side-view snapshots of the electrode surfaces; (h) hydrogen bond number density distribution of  $\text{V}_S/\text{NiFeOOH}$ ; (i) radial distribution function  $g(r)$  of Ni-Cl and the concentration of  $\text{Cl}^-$   $c(r)$  as a function of the distance from electrode.

adsorbing  $\text{Cl}^-$  ( $\text{NiFeOOH-O}_v\text{-Cl}$ ) was further developed to simulate the corrosion process (Fig. S18). The calculations reveal that the adsorption of  $\text{Cl}^-$  to  $\text{O}_v$  in  $\text{NiFeOOH}$  is significantly stronger ( $-2.20$  eV) compared to  $\text{OH}^-$  ( $-0.84$  eV), resulting in the formation of M-Cl coordination bonds (Fig. 4a). This strong adsorption subsequently reduces the energy barrier for the formation of more  $\text{O}_v$  from 2.01 eV to 1.34 eV, which establishes a self-reinforcing corrosion cycle that further exacerbates catalyst corrosion (Fig. 4b).

To elucidate how  $\text{Cl}^-$  adsorption alters the electronic structure of the catalyst, Bader charge analysis was performed. Fig. S19 shows that  $\text{Cl}^-$  occupies the  $\text{O}_v$  and bonds with the adjacent Ni, increasing the Bader charges of both Ni (from  $8.72e^-$  to  $9.76e^-$ ) and O (from  $7.04e^-$  to  $7.10e^-$ ). This indicates that  $\text{Cl}^-$  adsorption enhances the electron density near the Ni-O bond. The upper d-band edge is considered by J. K. Nørskov to be a more accurate descriptor for the d-band model.<sup>52</sup> Therefore, a crystal orbital Hamiltonian population (COHP) analysis and density of states (DOS) analysis were performed.<sup>53</sup> COHP results reveal that compared to  $\text{NiFeOOH}$ , the upper edge of the lower Habert band (LHB) d-band shifts downward from 1.12 eV to 0.08 eV upon chloride ion lattice insertion. This suggests

chloride adsorption increases electron occupation in the LHB of M-O bonds, causing this band to shift downward. The density of states (DOS) analysis indicates that this downward shift exposes the oxygen nonbonding orbital ( $\text{O}_{\text{NB}}$ ) (Fig. 4d), making it susceptible to electron loss. This further promotes the formation of the  $\text{O}_v$ , continuously exacerbating structural degradation.<sup>54</sup> Quantitative assessment of M-O bond strength *via* integral COHP analysis (-ICOHP) reveals that the Ni-O bond strength in  $\text{NiFeOOH-O}_v\text{-Cl}$  (1.20) is significantly lower than that in pristine  $\text{NiFeOOH}$  (1.52). This confirms that  $\text{Cl}^-$  doping weakens the M-O bond, accelerating structural degradation and forming a self-reinforcing corrosion cycle (Fig. 4e and f).<sup>55</sup>

#### Theoretical investigation into the dual regulation mechanism of $\text{VO}_4^{3-}$ -modified NiFe LDH

To further investigate the intrinsic regulatory mechanism underlying the exceptional corrosion resistance and activity of  $\text{VO}_4^{3-}$ -NiFe LDH/ $\text{VO}_x/\text{NF}$ , DFT calculations and *ab initio* molecular dynamics (AIMD) simulations were performed.<sup>56</sup> Four distinct structures ( $\text{NiFeOOH}$ ,  $\text{V}_S/\text{NiFeOOH}$ ,  $\text{NiFeOOH-V}_I$ , and  $\text{V}_S/\text{NiFeOOH-V}_I$ ) are systematically constructed to



independently assess the effects of surface  $\text{VO}_4^{3-}$  ( $V_s$ ) and interlayer  $\text{VO}_4^{3-}$  ( $V_l$ ) species (Fig. S20). The adsorption behaviors of  $\text{Cl}^-$  on  $\text{NiFeOOH-V}_l$  are first examined (Fig. 5a and S21). Compared with  $\text{NiFeOOH}$  ( $-1.29$  eV),  $\text{NiFeOOH-V}_l$  exhibits positive adsorption energy for  $\text{Cl}^-$  ( $0.14$  eV), suggesting that  $V_l$  weakens the binding ability of  $\text{Cl}^-$  on the catalyst surface. This reduction stems from the strong electrostatic field created by interlayer  $\text{VO}_4^{3-}$ , which increases the electron density on the  $\text{NiFeOOH}$  surface and repels negatively charged  $\text{Cl}^-$  (Fig. 5b), thereby reducing the mutual electron interaction between  $\text{Cl}^-$  and  $\text{NiFeOOH}$  (Fig. 5c and S22). Furthermore,  $\text{Cl}^-$  diffusion is significantly hindered in the  $\text{VO}_4^{3-}$ -intercalated structure, with the energy barrier rising from  $0.31$  eV to  $0.77$  eV (Fig. 5d and e). These results demonstrate that  $V_l$  builds an internal electrostatic barrier that blocks  $\text{Cl}^-$  infiltration. While this strong repulsion effectively prevents  $\text{Cl}^-$  intrusion, it also makes it harder for  $\text{OH}^-$  to adsorb onto the surface ( $-0.28$  eV), potentially reducing the catalytic activity for OER.<sup>10</sup>

Meanwhile, the surface  $\text{VO}_4^{3-}$  species contribute to interfacial activation by enhancing  $\text{OH}^-$  affinity. Specifically,  $V_s/\text{NiFeOOH}$  exhibits a significantly stronger affinity toward  $\text{OH}^-$ , with a more negative adsorption energy ( $-0.96$  eV) than that of  $\text{NiFeOOH}$  ( $-0.84$  eV). This enhanced likely arises from the formation of directional hydrogen bonds between  $\text{OH}^-$  and the highly electronegative oxygen atoms in the  $V_s$ . Electrostatic potential mapping (Fig. 5f) corroborates this mechanism, revealing localized negative potential sites within the  $V_s$  region that facilitate hydrogen bonding with both  $\text{OH}^-$  and  $\text{H}_2\text{O}$ .<sup>29</sup> Although  $\text{Cl}^-$  adsorption is also weakened on  $V_s/\text{NiFeOOH}$  ( $-0.73$  eV), the surface  $\text{VO}_4^{3-}$  species mainly contribute to enhancing  $\text{OH}^-$  retention through hydrogen bonding and localized electrostatic interactions. As a result, the adsorption energy of  $\text{Cl}^-$  ( $0.53$  eV) on  $V_s/\text{NiFeOOH-V}_l$  is the most positive, while that of  $\text{OH}^-$  ( $-1.69$  eV) is the most negative, suggesting that the combined presence of  $V_s$  and  $V_l$  provides the most favorable selectivity for  $\text{OH}^-$  adsorption while effectively suppressing  $\text{Cl}^-$  binding.

To elucidate the synergistic mechanism of surface and interlayer  $\text{VO}_4^{3-}$  species in modulating the electrolyte-catalyst interface, AIMD simulations were performed (Fig. 5g). The results reveal that  $\text{OH}^-$  and  $\text{H}_2\text{O}$  molecules in  $V_s/\text{NiFeOOH-V}_l$  maintain prolonged proximity to the catalyst surface, indicating that  $\text{VO}_4^{3-}$  groups promote sustained interfacial interactions *via* hydrogen bonding.<sup>19</sup> Conversely,  $\text{Cl}^-$  ions in  $\text{NiFeOOH}$  are observed at short distances from the surface, suggesting a higher propensity for  $\text{Cl}^-$  intrusion and potential corrosion initiation. This comparison underscores the ability of  $V_s/\text{NiFeOOH-V}_l$  to create a more selective electrocatalytic interface that suppresses  $\text{Cl}^-$  access while promoting  $\text{OH}^-$  stabilization. The hydrogen bond number density distribution (Fig. 5h) visually demonstrates that  $V_s/\text{NiFeOOH-V}_l$  exhibits a significantly denser hydrogen-bonding network at the electrolyte-catalyst interface compared to  $\text{NiFeOOH}$ . These bonds primarily formed between the electronegative oxygen atoms of surface  $\text{VO}_4^{3-}$  and surrounding  $\text{OH}^-$  or  $\text{H}_2\text{O}$ , contributing to a highly ordered and hydrophilic interfacial environment, conducive to retaining  $\text{OH}^-$  near the active site.<sup>57,58</sup> Radial distribution

functions  $[g(r)]$  and concentration gradient  $[c(r)]$  of  $\text{Cl}^-$  (Fig. 5i) further illustrate that  $\text{Cl}^-$  accumulation near Ni sites is significantly suppressed in  $V_s/\text{NiFeOOH-V}_l$ . In  $\text{NiFeOOH}$ ,  $g(r)$  shows a distinct peak at  $2.5\text{--}3.5$  Å, indicating  $\text{Cl}^-$  accumulation near Ni sites, while the  $c(r)$  curve rapidly rises within  $3.7\text{--}6.0$  Å. In contrast,  $V_s/\text{NiFeOOH-V}_l$  exhibits a flatter  $g(r)$  and a delayed  $c(r)$  increase, demonstrating that  $\text{VO}_4^{3-}$ , effectively repels  $\text{Cl}^-$  from the active zone.<sup>19</sup>

Collectively, surface  $\text{VO}_4^{3-}$  facilitates  $\text{OH}^-$  retention through hydrogen bonding, whereas interlayer  $\text{VO}_4^{3-}$  establishes the electrostatic field required to exclude  $\text{Cl}^-$ . The integration of these two effects creates a selective interfacial environment that simultaneously enhances corrosion resistance and catalytic activity, providing a rational design framework for seawater OER catalysts.

## Conclusion

In summary, a  $\text{VO}_4^{3-}$ - $\text{NiFe LDH}/\text{VO}_x/\text{NF}$  catalyst was developed that achieves efficient and durable alkaline seawater electrolysis, delivering  $1000\text{ mA cm}^{-2}$  for  $3500$  h and maintaining stability for  $2500$  h in an MEA electrolyzer. The synergistic action of interlayer  $\text{VO}_4^{3-}$ , which electrostatically excludes  $\text{Cl}^-$ , and surface  $\text{VO}_x$ , and dynamically converts to  $\text{VO}_4^{3-}$  to stabilize interfacial  $\text{OH}^-$ , underpins its outstanding stability. Mechanistic investigations further uncover a previously unidentified chloride corrosion pathway in which oxygen vacancies act as corrosion-active sites that initiate a self-reinforcing cycle of  $\text{Cl}^-$  adsorption and lattice degradation. This work not only provides an atomic-scale understanding of the corrosion mechanism but also establishes interfacial species engineering as a general strategy to tackle corrosion issues. By precisely modulating interfacial species to simultaneously repel corrosive ions and stabilize reactive species, this approach offers a new paradigm for designing highly durable catalysts.

## Author contributions

S. Y. designed the work, planned the experiments, conducted the theoretical calculations, and drafted the initial manuscript. Z. Z. conducted the theoretical calculations. F. G., Z. N., Z. S., J. W., W. J. and L. L. carried out the characterization experiments. S. Y. supervised the research and contributed to the review and editing of the manuscript. All authors participated in discussions and revised the manuscript.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

All data included in this study are available upon request by contact with the corresponding author.

Supplementary information is available. See DOI: <https://doi.org/10.1039/d5sc07816d>.



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