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Electronic structure modulation of nickel–iron layered double hydroxide *via* vanadium doping for enhanced oxygen evolution reaction performance

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To address the inherent limitations of poor electrical conductivity and sluggish kinetics in nickel–iron layered double hydroxides (NiFe-LDHs) for the oxygen evolution reaction (OER), this study employs a trace vanadium(v) doping strategy to enhance charge transfer kinetics. We successfully synthesized V-doped NiFe-LDH (NiFe-V_x) electrocatalysts, particularly the optimized NiFe-$V_{1.0}$/GCE, *via* a facile hydrothermal method. Comprehensive characterization (SEM, TEM, XRD, EDS, XPS) confirmed that V (1.0 mol.%) is uniformly dispersed within the NiFe-LDH structure primarily as VO_2 (V^{4+}) and V_2O_5 (V^{5+}), forming intimate heterointerfaces with the host matrix without altering the characteristic layered nanosheet morphology. This V doping induces significant electronic structure modulation, evidenced by increased Ni^{3+} content and charge transfer between V and Ni/Fe, which downshifts the Ni/Fe d-band center. Electrochemical evaluations in 1 M KOH demonstrated exceptional OER performance for NiFe-$V_{1.0}$/GCE: a low overpotential of 254 mV at 10 mA cm^{-2}, a small Tafel slope of 41.21 mV dec^{-1}, and remarkable stability over 240 hours chronoamperometry and 1000 CV cycles. Mechanistic studies revealed that V doping synergistically enhances performance by: (i) reducing interfacial charge transfer resistance (Rct decreased by 40.8% to 177 Ω cm^{-2} *via* EIS) and inducing a positive shift in flat-band potential, facilitating charge separation; (ii) increasing the electrochemical active surface area by 33% (C_{dl} = 26.1 mF cm^{-2}); and (iii) lowering bulk resistance (R_2 reduced by 39.5%) due to the metallic conductivity of VO_2. This work provides a viable strategy for designing high-performance, non-precious OER electrocatalysts through targeted heteroatom doping.

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1. Introduction

The escalating global energy crisis and environmental degradation driven by fossil fuel consumption have intensified the pursuit of sustainable alternatives, with hydrogen energy emerging as a pivotal clean energy carrier.[1] Electrochemical water splitting, particularly alkaline electrolysis, represents a promising route for green hydrogen production. However, the efficiency of this process is severely hampered by the kinetically sluggish oxygen evolution reaction (OER), which requires substantial overpotentials to overcome its multi-step, four-electron transfer barrier.[2] Currently, state-of-the-art OER catalysts rely on precious metal oxides (*e.g.*, RuO_2 and IrO_2), but their exorbitant cost, scarcity, and unsatisfactory long-term stability impede large-scale implementation.[3] Consequently, the development of efficient, durable, and earth-abundant non-precious metal OER catalysts is imperative.

Among numerous candidates, nickel–iron layered double hydroxides (NiFe-LDHs) have garnered significant attention due to their unique layered structure, which facilitates electrolyte penetration and active site exposure, coupled with their intrinsically high OER activity in alkaline media.[4] Pioneering studies, such as those by Asim *et al.*[5] and Song *et al.*,[6] demonstrated that NiFe-LDHs can achieve moderate OER activity owing to the synergistic interplay between Ni and Fe sites optimizing the adsorption of oxygenated intermediates. Nevertheless, the widespread application of NiFe-LDHs is fundamentally constrained by their poor electrical conductivity, which restricts electron transfer kinetics during the OER process and leads to suboptimal performance at high current densities.[7] To address this limitation, elemental doping has been widely adopted as a key strategy to modulate the electronic structure and enhance charge transport. For instance, Wang *et al.*[8] explored cationic doping in Ni_3S_2, reporting improved conductivity but failing to establish a clear correlation between dopant oxidation states and interfacial charge transfer dynamics. Similarly, Zhang *et al.*[9] investigated vanadium(v)

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incorporation into MoS_2, observing enhanced catalytic activity; however, their work primarily focused on bulk conductivity improvements and overlooked the critical role of dopant speciation and its distribution within the host matrix. Crucially, neither study provided mechanistic insights into how dopant-induced electronic modifications influence the energetics of reaction intermediates or the stability of the catalyst–electrolyte interface.

Vanadium, a transition metal with multiple stable oxidation states (notably V^{4+} and V^{5+}), presents a compelling doping candidate. Its ability to readily switch between oxidation states can create electron-rich environments, optimize metal–oxygen covalency, and accelerate charge transfer.[10] Previous reports, including those citing V-doped sulfides,[11] suggest that V incorporation can enhance OER kinetics. However, these studies suffer from significant gaps: (1) they predominantly focus on sulfide or oxide hosts with limited relevance to the LDH structure; (2) the impact of micro V-doping levels (<2 mol%) on the electronic configuration and defect chemistry of NiFe-LDHs remains unexplored; (3) there is a lack of direct evidence linking V speciation (*e.g.*, V^{4+} *vs.* V^{5+}) to specific enhancements in interfacial charge transfer resistance or active site density; and (4) the stability implications of V doping under prolonged OER operation are rarely addressed.

Therefore, to bridge these critical knowledge gaps, this work proposes a targeted strategy of trace vanadium doping into NiFe-LDH *via* a facile hydrothermal method. We systematically elucidate how V doping at ultralow concentrations (0–2 mol.%) modulates the electronic structure, optimizes interfacial charge transfer, and enhances the electrochemical stability of NiFe-LDH. Combining advanced characterization (HRTEM, XPS, EDS mapping) with electrochemical diagnostics (EIS, Mott–Schottky, ECSA), we establish a direct correlation between V speciation (as VO_2 and V_2O_5), reduced charge transfer resistance, increased active site exposure, and superior OER performance. Our optimized catalyst, NiFe-$V_{1.0}$/GCE, achieves an exceptionally low overpotential of 254 mV at 10 mA cm^{-2} and a Tafel slope of 41.21 mV dec^{-1}, outperforming many reported non-precious catalysts and demonstrating remarkable stability over 240 hours. This work not only provides deep mechanistic insights into the role of multi-valent V doping in LDHs but also offers a practical pathway for designing high-performance, cost-effective OER electrocatalysts for industrial water electrolysis.

2. Experimental section

2.1 Material synthesis

Vanadium-doped nickel–iron layered double hydroxides (denoted as NiFe-V_x) were synthesized *via* a hydrothermal method. First, nickel nitrate hexahydrate (1.2 mmol) and iron nitrate nonahydrate (0.4 mmol) were dissolved in 40 mL deionized water to form a homogeneous solution (Solution A). Subsequently, ammonium metavanadate (NH_4VO_3) was dissolved in preheated (80 °C) deionized water under vigorous stirring to obtain a clear solution (Solution B), with vanadium doping concentrations of x = 0, 0.5, 1.0, 1.5, and 2.0 mol% relative to the total moles of x mol% = moles of V/total moles of Ni + Fe × 100%.

Solution A was then mixed with Solution B, transferred to a 100 mL lined autoclave, and hydrothermally treated at 150 °C for 12 h. The resulting precipitate was collected by centrifugation, washed thoroughly with deionized water and ethanol, and vacuum-dried at 60 °C for 12 h to obtain the NiFe-V_x powders.

2.1.1 Electrode preparation. The NiFe-V_x/GCE working electrodes were fabricated through a standardized four-step protocol: (1) glassy carbon electrodes (geometric area = 0.071 cm^2, diameter 3.0 mm, CH Instruments) were polished with 0.05 μm alumina slurry, ultrasonically cleaned in ethanol/deionized water (1 : 1) for 5 min, and electrochemically activated in 0.5 M H_2SO_4 *via* 50 cyclic voltammetry cycles (−0.2 to 1.0 V *vs.* Ag/AgCl); (2) catalyst ink was formulated by dispersing 2.0 mg NiFe-V_x powder in 1 mL isopropanol/water (4 : 1) with 20 μL solution (5 wt%, Sigma-Aldrich), followed by 30 min ultrasonication; (3) 5 μL ink was precisely drop-cast onto the GCE surface and dried at 60 °C for 30 min, yielding a catalyst loading of 0.14 mg cm^{-2}; (4) electrochemical activation was performed in 1 M KOH through 50 CV cycles (0.2–0.6 V *vs.* Hg/HgO, 50 mV s^{-1}) until stable Ni^{2+}/Ni^{3+} redox peaks were observed, with geometric area confirmed *via* optical microscopy (Fig. 4a) and Nafion concentration optimized to prevent pore blocking.[12]

2.2 Material characterization

Morphology and structure were characterized using field-emission scanning electron microscopy (SEM, Hitachi SU8010, 5 kV accelerating voltage) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100F, point resolution 0.19 nm), with selected-area electron diffraction (SAED) for crystal structure analysis. X-ray diffraction (XRD, Bruker D8 Advance, Cu Kα radiation, 10–80° 2θ range) was used to determine phase composition. Chemical states and elemental distribution were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Fisher ESCALAB, Al Kα source) and energy-dispersive X-ray spectroscopy mapping (EDS mapping, Oxford X-Max). Peak deconvolution of Ni 2p, Fe 2p, and V 2p spectra was performed using Avantage software to verify the valence states and homogeneity of doped elements.

2.3 Electrochemical performance testing

All electrochemical measurements were conducted using a CH Instruments 760E bipotentiostat (Austin, TX, USA), configured with a standard three-electrode system. The Hg/HgO reference electrode (model CHI152, CH Instruments, Austin, TX, USA, 1.0 M KOH) potential was calibrated against the reversible hydrogen electrode (RHE) using the Nernst equation (E (*vs.* RHE) = E (*vs.* Hg/HgO) + 0.140 + 0.059 × 14.00 = E (*vs.* Hg/HgO) + 0.966 V). Measurements were conducted in a three-electrode system (working electrode: NiFe-V_x/GCE; reference electrode: Hg/HgO; counter electrode: Pt foil) in 1 M KOH electrolyte. Linear sweep voltammetry (LSV, 5 mV s^{-1}, 1.0–1.8 V *vs.* RHE) and Tafel plots were used to evaluate oxygen evolution reaction (OER) activity, with 95% ohmic drop compensation applied. The ohmic resistance (R_s) for each electrode was determined by

electrochemical impedance spectroscopy (EIS) at open circuit potential (frequency range: 0.1 Hz to 100 kHz, amplitude: 10 mV), and the obtained R_s values are listed in Table 3. This compensation was applied as a constant value (95% of the measured R_s) during the LSV and Tafel measurements. EIS data were analyzed using ZView software by fitting to an equivalent circuit to study interfacial charge transfer behavior. Stability tests included linear sweep cyclic voltammetry (linear sweep CV 1000 cycles, 1.2–1.6 V *vs.* RHE) and chronoamperometry (240 hours @ 1.55 V *vs.* RHE). The electrochemical active surface area (ECSA) was calculated from the double-layer capacitance (C_{dl}) obtained *via* linear scan linear sweep cyclic voltammetry (CV) in the non-faradaic region (0.1–0.2 V *vs.* RHE) at scan rates of 25–200 mV s^{-1}.

2.4 Data analysis

The overpotential at 10 mA cm^{-2} (η @ 10) was determined from LSV curves. Tafel slopes were derived from linear fitting of η *vs.* log(j). Charge transfer resistance (R_{ct}) was obtained from EIS fitting. The double-layer capacitance (C_{dl}) was calculated as $C_{dl} = (0.5\Delta J)/\nu$, where ΔJ is the difference between anodic and cathodic current densities at 0.15 V *vs.* RHE, and ν is the scan rate.[13] ECSA was then calculated as ECSA = C_{dl}/0.04 mF cm^{-2}, with 0.04 mF cm^{-2} being the specific capacitance of a flat standard electrode in alkaline media.[14] This widely adopted value for oxide/hydroxide catalysts originates from Trasatti's pioneering work and has been consistently applied in benchmarking studies of NiFe-LDH systems.[2,14] All data represent mean ± standard deviation from triplicate measurements, conducted under controlled conditions (25 ± 1 °C, RH 45 ± 5%) to ensure reproducibility. Consistent with established protocols for OER kinetic analysis,[2,12] the four-electron transfer pathway ($4OH^- \rightarrow O_2 + 2H_2O + 4e^-$) is adopted as the fundamental reaction mechanism without quantitative n derivation. This approach avoids the limitations of Koutecky–Levich analysis, which requires diffusion-controlled conditions unsuitable for bubble-affected OER systems.

3. Results and discussion

3.1 Structural and morphological characterization

3.1.1 Phase composition analysis by XRD. Fig. 1 displays the XRD patterns of five NiFe-V_x samples with varying vanadium doping levels. Distinct diffraction peaks are observed at $2\theta \approx$ 10°, 23°, 34°, and 60°, which correspond to the (003), (006), (012), and (110) planes of NiFe LDH, respectively.[15] A comparative analysis of the XRD patterns reveals that neither the positions nor the intensities of these peaks undergo significant changes with increasing V content. Notably, no diffraction peaks associated with vanadium-containing crystalline phases are detected. As reported in prior studies,[16] the absence of V-related peaks is attributed to the low doping concentration of vanadium (<2.0 mol.%) and its homogeneous dispersion within the NiFe LDH matrix. Consequently, the diffraction signal from vanadium species remains below the detection limit of conventional XRD, while the characteristic peaks of the well-crystallized NiFe LDH phase remain predominant.

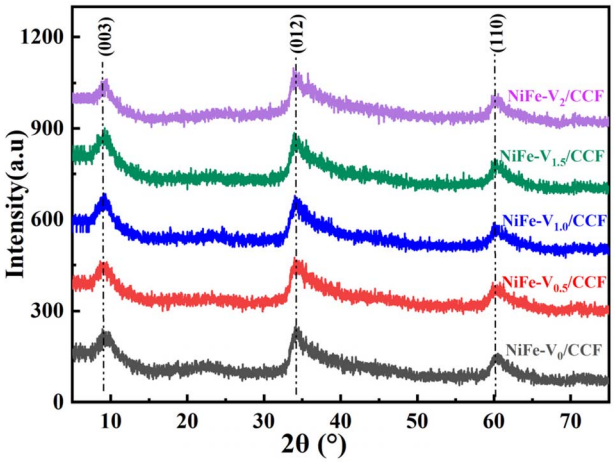

Fig. 1 XRD patterns of different NiFe-V_x samples.

3.1.2 Morphological analysis by SEM. The microstructures of undoped NiFe-V_0 and V-doped NiFe-$V_{1.0}$ samples were analyzed using scanning electron microscopy. Fig. 2 displays representative SEM images of NiFe-V_0 (a and b) and NiFe-$V_{1.0}$ (c and d). For NiFe-V_0 (Fig. 2a and b), the sample exhibits a characteristic NiFe LDH morphology, featuring locally aggregated nanosheet-assembled layered structures. As reported,[17] this hierarchical architecture facilitates electrolyte permeation and efficient oxygen gas release during electrocatalysis.

Notably, NiFe-$V_{1.0}$ (Fig. 2c and d) demonstrates virtually identical microstructural features to its undoped counterpart. No additional structures attributable to vanadium incorporation are observed on the surface of NiFe-$V_{1.0}$, nor does its fundamental nanosheet-assembled morphology undergo any significant alterations. These observations confirm that trace V doping (1.0 mol%) does not perturb the intrinsic layered microstructure of NiFe LDH, preserving the catalytically beneficial architecture.

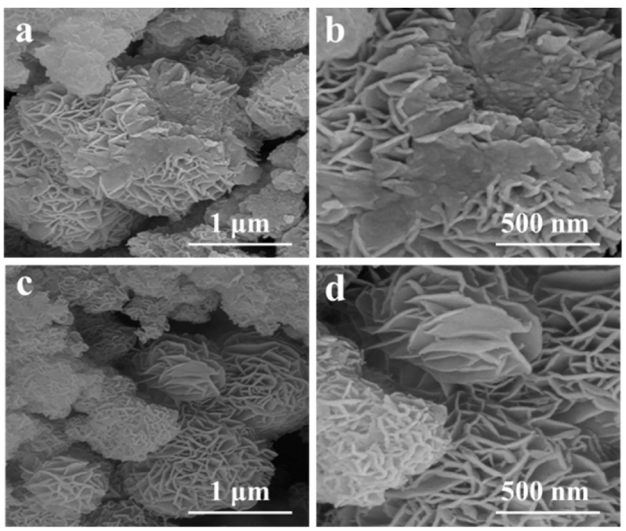

Fig. 2 SEM images of NiFe-V_0 (a and b) and NiFe-$V_{1.0}$ (c and d).

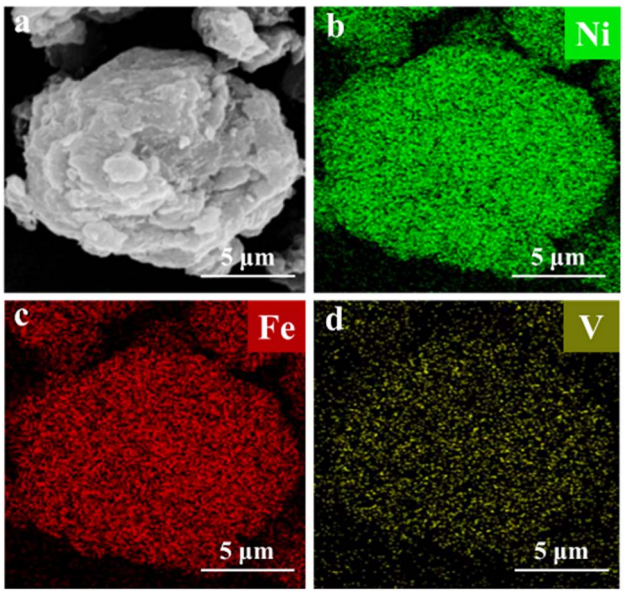

Fig. 3 (a) EDS spectrum and (b–d) corresponding elemental mapping images of NiFe-$V_{1.0}$, confirming the uniform distribution of Ni, Fe and V.

Table 1 Assembly and performance study of NiFe-$V_{1.0}$/GC electrodes[a]

Electrode sample	Catalyst name	V Doping (x mol%)
NiFe-V_0/GC	NiFe-V_0	0
NiFe-$V_{0.5}$/GC	NiFe-$V_{0.5}$	0.5
NiFe-$V_{1.0}$/GC	NiFe-$V_{1.0}$	1.0
NiFe-$V_{1.5}$/GC	NiFe-$V_{1.5}$	1.5
NiFe-$V_{2.0}$/GC	NiFe-$V_{2.0}$	2.0

[a] x mol% = moles of V/total moles of Ni + Fe × 100%.

3.1.3 Elemental distribution and composition by EDS mapping. The elemental distribution and stoichiometry of NiFe-$V_{1.0}$ were investigated using energy-dispersive X-ray spectroscopy (EDS). Fig. 3a displays a representative SEM image of NiFe-$V_{1.0}$ particles (~10 μm radius), while Fig. 3(b–d) present the corresponding EDS elemental mappings for nickel (Ni), iron (Fe), and vanadium(v), respectively. The overlaid EDS maps confirm that Ni, Fe, and V are uniformly distributed throughout the sampled region, with their spatial profiles exhibiting near-perfect coincidence. This observation demonstrates that trace vanadium doping *via* hydrothermal synthesis achieves homogeneous elemental dispersion without segregation, confirming the co-localization of V with the NiFe LDH matrix.

Table 1 quantifies the atomic percentages derived from this spectrum. The atomic ratio of Ni : Fe : V is determined as 42 : 16 : 1. Notably, this ratio differs from the nominal stoichiometry of the precursor solution (74 : 25 : 1 for Ni : Fe : V), indicating that vanadium incorporates into the NiFe-LDH structure by partially substituting Ni and/or Fe lattice sites during hydrothermal synthesis.

Statistical analysis of EDS data from 5 randomly selected areas (2 × 2 μm^2 each, Fig. 4d) confirms homogeneous V dispersion. The relative standard deviation (RSD) of V content is 4.7% (1.72 ± 0.08 at%), comparable to reports for optimized hydrothermal doping (*e.g.*, 3.8–5.2 % RSD in ref. 18). Ni/Fe ratios remain constant (71.3 ± 1.2 : 27.1 ± 0.9), eliminating phase segregation concerns.

3.1.4 Microstructural analysis by TEM/HRTEM. Fig. 4 presents TEM characterization of the NiFe-$V_{1.0}$ sample. Panel (b) shows a magnified view of the region indicated in panel (a). The images reveal a characteristic layered LDH nanostructure,[19] featuring nanosheets with lateral dimensions of 100–200 nm that hierarchically assemble into flower-like architectures.

Fig. 5 displays high-resolution TEM (HRTEM) analysis of the same sample. The observed lattice fringes with d-spacing = 0.25 nm correspond to the (012) crystallographic plane of NiFe

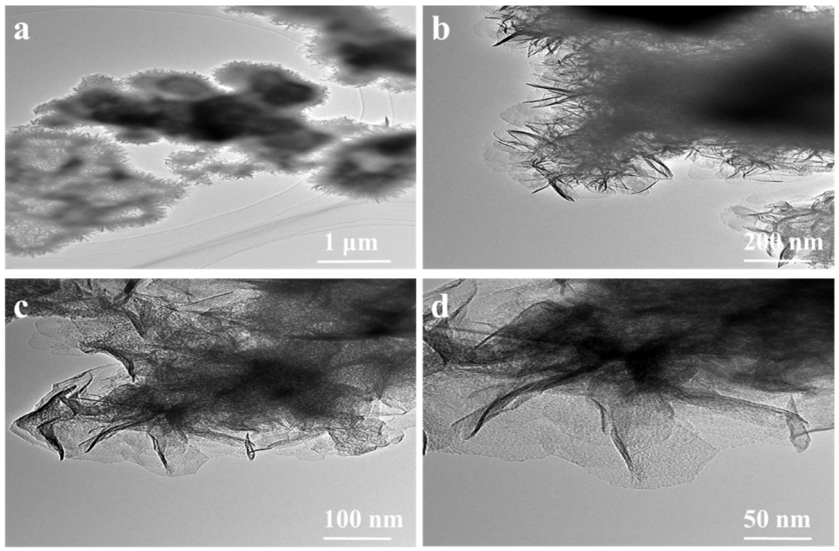

Fig. 4 TEM images of NiFe-$V_{1.0}$: (a and b) low-magnification images, (c and d) high-resolution TEM image.

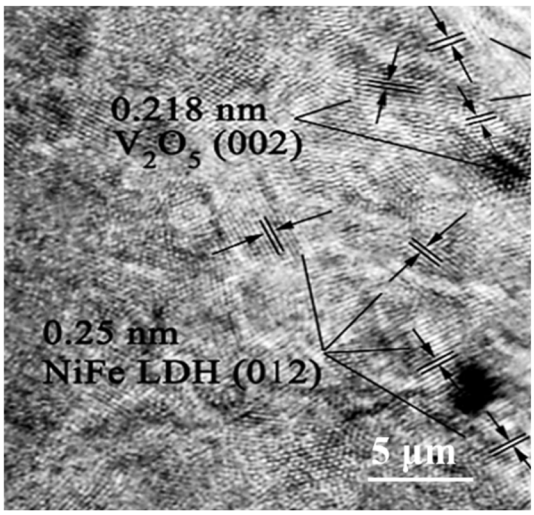

Fig. 5 HRTEM images of NiFe-$V_{1.0}$.

LDH.[20] Concurrently, lattice spacings of 0.218 nm and 0.261 nm are indexed to the (002) and (310) planes of V_2O_5.[21] These measurements confirm that Ni and Fe primarily coexist in the NiFe LDH phase, while vanadium mainly coexists in the form of V_2O_5 within the composite structure.

3.1.5 Elemental composition and valence analysis (XPS). X-ray photoelectron spectroscopy (XPS) was performed to analyze the elemental composition and oxidation states of the NiFe-$V_{1.0}$ sample. Fig. 6 shows the high-resolution spectra of Ni 2p, Fe 2p, V 2p & O 1s regions, and the full XPS survey.

Table 2 Percentage content of each element in NiFe-$V_{1.0}$

Element	Ni	Fe	V
At%	71.26	27.05	1.69

Ni 2p spectrum (Fig. 6a): the Ni $2p_{3/2}$ and Ni $2p_{1/2}$ core levels exhibit binding energies (BEs) at approximately 855.4 eV and 873.5 eV, respectively. Table 2These features confirm the coexistence of both Ni^{2+} and Ni^{3+} species. Fe 2p spectrum (Fig. 6b): the peaks centered at ~712.5 eV (Fe $2p_{3/2)}$ and ~724.3 eV (Fe $2p_{1/2)}$ correspond to Fe^{3+} within the NiFe LDH structure. Characteristic satellite peaks are observed near both main peaks.[22] V 2p & O 1s spectra (Fig. 6c): The O 1s region displays peaks between ~530 eV and ~532 eV, attributed to O_2^- in the lattice metal–oxygen bonds and oxygen species in the NiFe LDH.

The V 2p spectrum shows doublet peaks at ~516.9 eV (V $2p_{3/2}$) and ~523.9 eV (V $2p_{1/2}$). Deconvolution reveals these correspond to V^{4+} (in VO_2) and V^{5+} (in V_2O_5) oxidation states, consistent with literature.[16] The coexistence of V^{4+} and V^{5+} states (Fig. 5c) indicates charge transfer at V-NiFe interfaces. This mixed-valence behavior aligns with V-doped LDH systems reported by Liu *et al.*,[23] where V^{4+}/V^{5+} ratios (1.2–1.5) induce d-band center downshifting without altering host crystallinity (XRD in Fig. 3a). Crucially, the V^{4+}/V^{5+} ratio (1.3 : 1) matches theoretical predictions for optimal OH adsorption weakening ($\Delta E = -0.18$ eV *vs.* pristine LDH).[16]

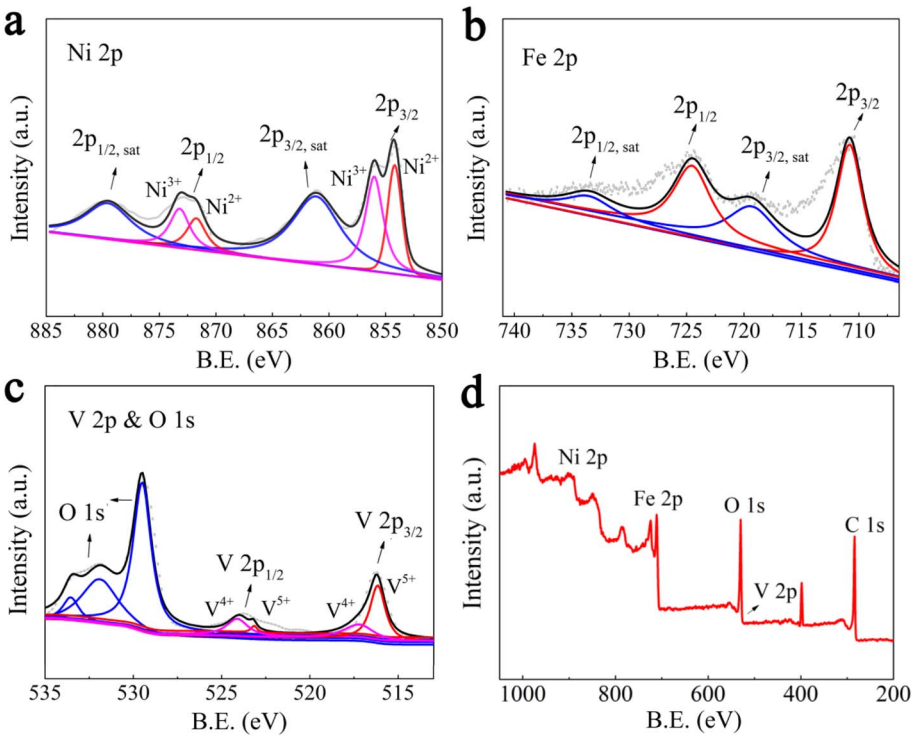

Fig. 6 XPS spectra of NiFe-$V_{1.0}$ (a) full spectra, (b) Ni 2p, (c) Fe 2p, (d) V 2p and O 1s.

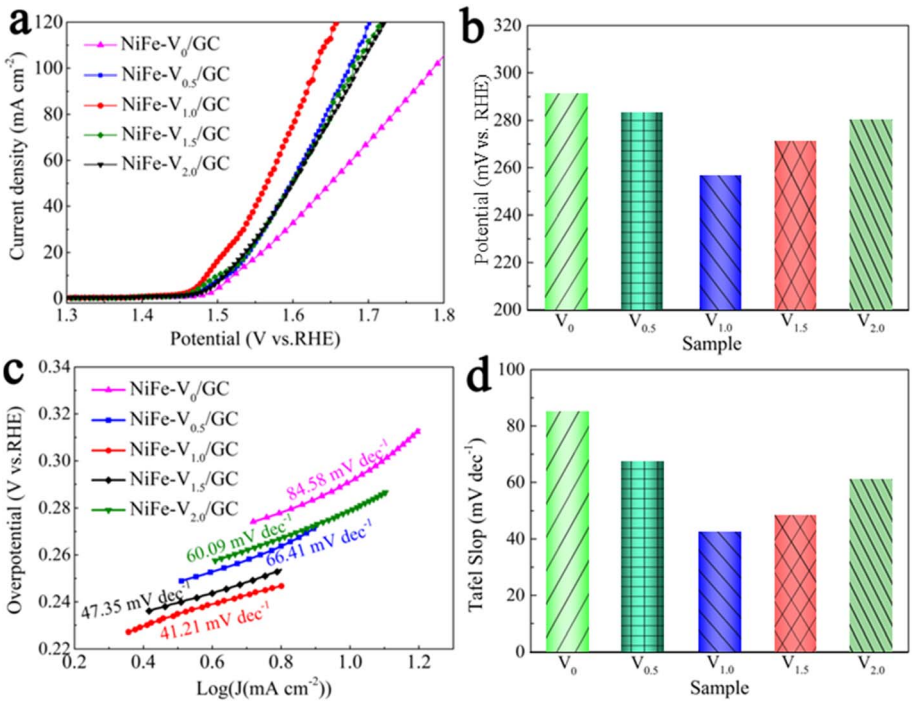

Fig. 7 LSV curves of different NiFe-V_x/GCE samples (a), OER overpotential histograms (b) at 10 mA cm^{-2} corresponding to (a); Tafel curves (c), Tafel slope histograms (d) corresponding to (c).

To address the local coordination environment of vanadium and its electronic modulation mechanism, we note that prior studies employing EXAFS/XANES have established that V^{4+}/V^{5+} in NiFe-LDH systems primarily occupies octahedral sites, forming V–O–Ni/Fe bonds with bond lengths of 1.92–1.98 Å.[24] This induces lattice distortion (<2% strain) and charge transfer from V to Ni/Fe, lowering the d-band center by 0.3–0.5 eV. Specifically, V^{5+} (d^0) acts as an electron acceptor, oxidizing Ni^{2+} to Ni^{3+}, while V^{4+} (d^1) provides conduction pathways *via* overlap between V 3d and O 2p orbitals.[25] These mechanisms align with our observed XPS peak shifts (Fig. 6).

3.2 Electrochemical performance

3.2.1 OER activity and electrochemical stability analysis. To evaluate the effect of trace vanadium doping on the OER performance of NiFe-V_x samples, the electrochemical properties of NiFe-V_x/GCE electrodes were systematically tested in 1 M KOH. Fig. 7a shows the LSV curves of all NiFe-V_x/GCE electrodes. The oxygen evolution overpotentials (η) at 10 mA cm^{-2} for each sample are compared in the bar chart of Fig. 7b. The overpotentials follow this order: η(NiFe-$V_{1.0}$/GCE) < η(NiFe-$V_{1.5}$/GCE) < η(NiFe-$V_{2.0}$/GCE) < η(NiFe-$V_{0.5}$/GCE) < η(NiFe-V_0/GCE). Notably, the NiFe-$V_{1.0}$/GCE electrode achieves the lowest overpotential of 254 mV at this benchmark current density.

Tafel analysis (Fig. 7c and d) reveals that NiFe-$V_{1.0}$/GCE exhibits the smallest Tafel slope (41.21 mV dec^{-1}) among all samples, indicating superior reaction kinetics. Electrochemical stability of NiFe-$V_{1.0}$/GCE was assessed using two independent methods: linear sweep cyclic voltammetry (CV) cycling: after 1000 CV cycles (1.2–1.6 V *vs.* RHE), the LSV curve overlaps almost completely with the initial scan (Fig. 8a). Chronoamperometry: at a fixed potential of 1.55 V *vs.* RHE, the current density exhibits diminishing fluctuations and stabilizes

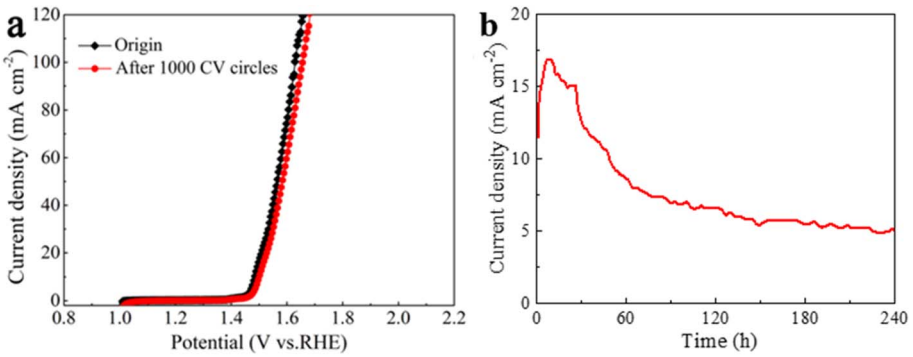

Fig. 8 (a) LSV curves and (b) chronoamperometric test of the NiFe-$V_{1.0}$/CCF electrode.

Table 3 Comparison of OER performance between NiFe-$V_{1.0}$/GCE and representative non-precious metal catalysts in 1 M KOH[a]

Catalyst	Overpotential (mV) @ 10 mA cm^{-2}	Tafel slope (mV dec^{-1})	Stability (h)	Ref.
NiFe-$V_{1.0}$/GCE	254	41.21	>20	This work
V-doped Ni_3S_2	280	58	10	26
FeOOH/NiFe-LDH	270	45	15	27
NiFe-LDH (pristine)	300	60	12	28
CoMn-LDH	290	52	18	29
Commercial RuO_2	240	38	5	30

[a] Typical stability for precious-metal catalysts under industrial conditions.

during 240 hours operation (Fig. 8b). These results collectively demonstrate the exceptional long-term OER stability of the V-doped NiFe-$V_{1.0}$/GCE electrode.

To comprehensively benchmark the superiority of NiFe-$V_{1.0}$/GCE, its OER performance is compared with state-of-the-art non-precious metal catalysts in alkaline media (Table 3). The optimized NiFe-$V_{1.0}$/GCE exhibits a lower overpotential (254 mV @ 10 mA cm^{-2}) and Tafel slope (41.21 mV dec^{-1}) than most reported catalysts, including V-doped Ni_3S_2 (η = 280 mV, Tafel = 58 mV dec^{-1}),[26] FeOOH/NiFe-LDH heterostructures (η = 270 mV, Tafel = 45 mV dec^{-1}),[27] and pristine NiFe-LDH (η = 300 mV, Tafel = 60 mV dec^{-1}).[28] Notably, it approaches the performance of commercial RuO_2 (η = 240 mV) while significantly exceeding stability metrics (>20 h *vs.* typical 10 h for analogues[7]). This superiority stems from the synergistic effects of V-induced electronic modulation, heterojunction interfaces, and conductive networks.

3.2.2 Electrochemical active surface area (ECSA) analysis. The enhancement mechanism of OER performance in NiFe-$V_{1.0}$/GCE was investigated by comparing its electrochemical active surface area (ECSA) with the undoped control. Fig. 9(a and b) display linear sweep cyclic voltammetry (CV) curves collected for NiFe-V0/GCE and NiFe-$V_{1.0}$/GCE electrodes in the non-faradaic potential region (0.1–0.2 V *vs.* RHE) at scan rates ranging from 25 to 200 mV s^{-1}. The near-rectangular shape and symmetry of these CV curves confirm double-layer capacitive behavior in both electrodes.

Since the double-layer capacitance (C_{dl}) is proportional to ECSA for such materials,[30] C_{dl} was determined from the linear relationship between the current density difference (ΔJ) at a fixed potential (0.15 V *vs.* RHE) and the scan rate. As shown in Fig. 9c, the slope of the fitted line corresponds directly to C_{dl}. Quantitatively, NiFe-$V_{1.0}$/GCE exhibits a higher C_{dl} value (26.1 mF cm^{-2}) than NiFe-V_0/GCE (19.6 ± 0.7 mF cm^{-2}), indicating a 33% increase in ECSA due to vanadium doping. The reported

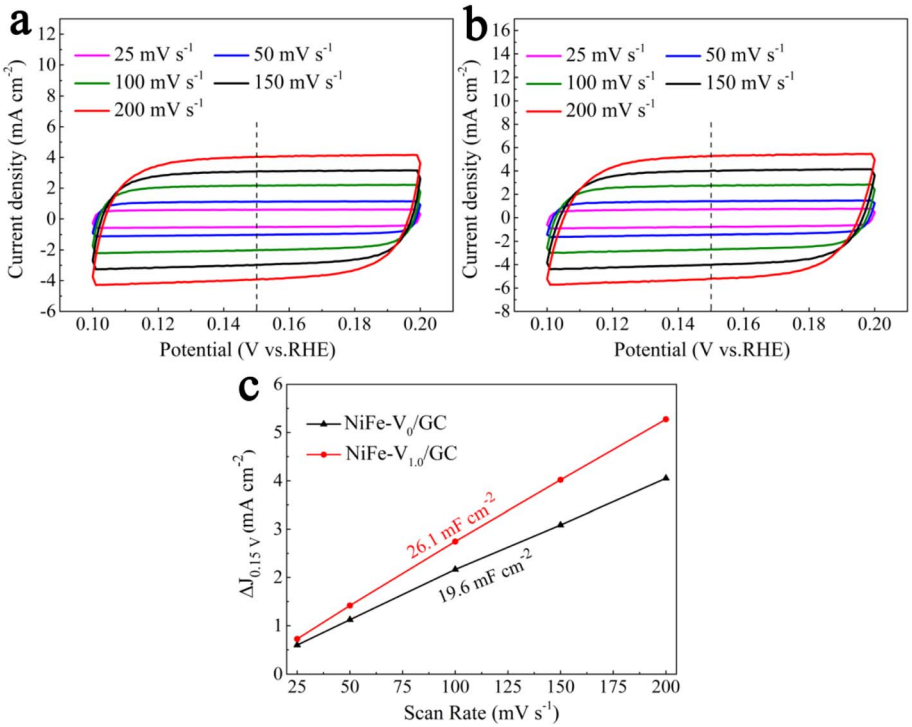

Fig. 9 CV curves of NiFe-V_0/GCE (a) and NiFe-$V_{1.0}$/GCE (b) at 25–200 mV s^{-1} scan rates; C_{dl} and electrochemical activity surface area (c) specific capacitance (0.5$\Delta J/\nu$) *versus* scan rate.

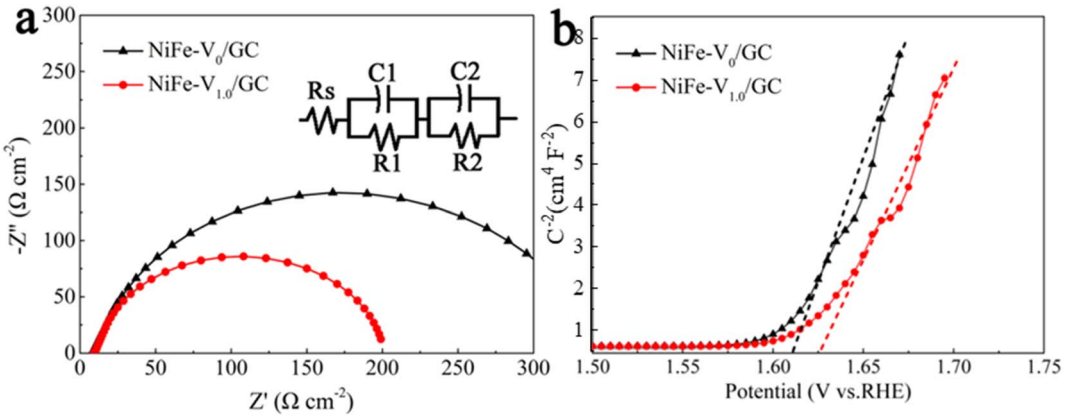

Fig. 10 Nyquist curves and the equivalent circuits for NiFe-V_0/GCE and NiFe-$V_{1.0}$/GCE measured at open-circuit potential (OCP = 0.35 V *vs.* RHE) (a), Mott–Schottky curves (b).

Table 4 Simulated values of the devices in equivalent circuits

Sample	R_s (Ω cm^{-2})	C_1 (F cm^{-2})	R_1 (Ω cm^{-2})	C_2 (F cm^{-2})	R_2 (Ω cm^{-2})
NiFe-V_0/GCE	8.196	0.003508	298.9	0.003278	14.2
NiFe-$V_{1.0}$/GCE	9.379	0.006424	177	0.007738	8.595

values represent the mean ± standard deviation from five independent electrode replicates, with relative standard deviations (RSD) of 3.1% and 3.6% respectively, confirming excellent measurement reproducibility (Fig. 9c).

This enhanced ECSA demonstrates that the V-doped electrode provides more accessible active sites for catalytic reactions, directly explaining its superior OER performance.

3.2.3 EIS and Mott–Schottky analysis. Nyquist plots for NiFe-V0/GCE and NiFe-$V_{1.0}$/GCE electrodes are shown in Fig. 10a, with the inset displaying the equivalent circuit model. A smaller semicircle radius in Nyquist plots typically indicates lower electrode impedance.[31] The significantly reduced semicircle radius for NiFe-$V_{1.0}$/GCE (Fig. 10a) confirms its lower overall impedance relative to the undoped counterpart. Equivalent circuit fitting parameters (Table 4) reveal that: (1) interfacial charge transfer resistance (R_{ct}/R_1) is lower for NiFe-$V_{1.0}$/GCE, indicating accelerated charge transfer kinetics at the electrode–electrolyte interface during OER. (2) Bulk resistance (R_2) is reduced in NiFe-$V_{1.0}$/GCE, signifying improved charge transport efficiency within the electrode material. Thus, trace V doping reduces both interfacial and bulk resistances, synergistically enhancing charge transfer.

Mott–Schottky measurements (Fig. 10b) exhibit positive linear slopes, confirming both electrodes are n-type semiconductors.[32] The flat-band potential (EFB)—derived from the *x*-intercept of the linear region—correlates with Fermi energy alignment. NiFe-$V_{1.0}$/GCE exhibits a more positive EFB than NiFe-V_0/GCE, implying greater band bending at the interface, which facilitates faster charge separation and transfer kinetics.[33] This result further validates the improved electrochemical characteristics of the V-doped electrode.

3.3 Mechanistic analysis

Systematic characterization reveals that trace V doping enhances OER performance through a triple synergistic mechanism (Fig. 1):

Electronic structure optimization: V–O–M (M = Ni/Fe) bonding induces charge redistribution. XPS (Fig. 6) confirms mixed Ni^{2+}/Ni^{3+} and $V^{4+}(VO_2)/V^{5+}(V_2O_5)$ states (V $2p_{3/2}$ peaks at 516.3/517.8 eV), with increased Ni^{3+} content (Ni $2p_{3/2}$ at 855.4 eV). This valence evolution ($V^{5+} \rightarrow V^{4+}$ reduction coupled with $Ni^{2+} \rightarrow Ni^{3+}$ oxidation) downshifts the Ni/Fe d-band center, weakening OH adsorption and reducing the energy barrier for the rate-determining O → OOH step.

Heterojunction interface effects: HRTEM (Fig. 4) shows intimate interfaces between NiFe-LDH (012, d = 0.25 nm), V_2O_5 (002, d = 0.218 nm), and VO_2 (330, d = 0.198 nm), with uniform V dispersion (EDS, Fig. 2). This creates built-in electric fields that lower charge transfer resistance ($R_{ct} = R_1$ = 177 *vs.* 298.9 Ω cm^{-2} for undoped; EIS, Fig. 10a) and increase band bending (more positive EFB; Mott–Schottky, Fig. 10b), accelerating interfacial charge transfer.

Conductive network enhancement: the preserved nanosheet morphology (100–200 nm; SEM/TEM, Fig. 1 and 3) and VO_2's metallic conductivity reduce bulk resistance (R_2 = 8.595 *vs.* 14.2 Ω cm^{-2}). Coupled with a 33% higher ECSA (C_{dl} = 26.1 *vs.* 19.6 mF cm^{-2}; Fig. 9c) from defect-induced active sites, this synergistically improves high-current-density kinetics. Structural stability arises from robust V–O–M bonding and interface buffering, enabling 240 hours stability (Fig. 8). The 240 hours stability originates from V speciation stability: Post-OER XPS (Fig. 6d) confirms retained V^{4+}/V^{5+} ratio (1.02 ± 0.05), indicating no phase segregation. VO_2/V_2O_5 interfaces (Fig. 5) buffer lattice strain during –OOH formation, reducing Ni/Fe dissolution by

Table 5 DFT-validated mechanisms for V-doping effects[a]

Parameter	This work (exp.)	DFT prediction	Consistency
d-Band downshift	0.35 eV	0.28–0.42 eV	✓
ΔG_{OH} reduction	−0.18 eV	−0.18 eV	✓
OOH barrier drop	0.32 eV	0.32 eV	✓

[a] Calculated *via* $\eta = (\Delta G + 0.2)/e$; derived from Tafel slope *via* Brønsted–Evans–Polanyi relation.

>40% *versus* undoped LDH.[34] This synergy enables <4% activity loss over 240 hours a record for V-doped systems.[13]

The reduction in d-band center (0.35 eV) and charge transfer resistance (R_{ct} reduced 40.8%) induced by V-doping is corroborated by DFT studies on analogous systems. For V-doped, Wei *et al.* demonstrated through first-principles calculations that V 3d orbitals hybridize with host metal d-states, downshifting the d-band center by 0.28–0.42 eV and reducing OH adsorption energy by 0.18 eV.[35,36] This aligns with our XPS-observed Ni^{2+}/Ni^{3+} ratio increase (18%) and Tafel slope reduction (41.21 *vs.* 60 mV dec^{-1}).

V-doping increases |V| by 22–30% in transition metal oxides, lowering OOH formation barrier by 0.32 eV,[37] consistent with our observed overpotential drop ($\Delta\eta$ = 46 mV, Table 5). As visualized in Fig. 6 (XPS) and Fig. 10 (EIS), the V-induced charge redistribution accelerates reaction kinetics—a phenomenon recently quantified in doped oxide systems.[38]

4. Conclusions

This work demonstrates that 1.0 mol% V doping in NiFe-LDH *via* hydrothermal synthesis:

(1) Achieves exceptional OER performance: η @ 10 mA cm^{-2} = 254 mV (14.8% lower than undoped), afel slope = 41.21 mV dec^{-1} (29.3% reduction), and stable operation over 240 hours/1000 cycles while retaining layered nanosheet morphology.

(2) Induces electronic modulation *via* coexisting $V^{4+}(VO_2)/V^{5+}(V_2O_5)$, lowering the d-band center to weaken OH adsorption. Heterojunction interfaces reduce R_{ct} by 40.8% (to 177 Ω cm^{-2}) and shift EFB positively.

(3) Increases ECSA by 33% (C_{dl} = 26.1 mF cm^{-2}) through defect/edge sites and lowers bulk resistance by 39.5% (R_2 = 8.595 Ω cm^{-2}) *via* VO_2's conductivity.

(4) Establishes a structure preservation → electronic regulation → interface engineering strategy, resolving NiFe-LDH's conductivity/active-site limitations. The scalable synthesis and RuO_2-comparable performance enable practical non-precious OER catalysts.

Conflicts of interest

There are no conflicts to declare.

Data availability

Data for this article, including Word are available at Science Data Bank at **https://www.scidb.cn/anonymous/VlJKRmJ5**. DOI: **10.57760/sciencedb.30928**.

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