Electronic Supplementary Information

Boosting electrocatalytic water oxidation by vanadium-iron-nickel

trimetal hydroxide catalysts through interphase ionic migration

method

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Supplementary calculation:

Physical characterization:

Scanning electron microscopy (SEM) images were obtained on Zeiss Sigma Scanning Electron Microscope. The high-resolution transmission electron microscopy (HRTEM), the corresponding selected area electron diffraction (SAED) and energy dispersive X-ray spectroscopy (EDX) results were measured on FEI Tecnai G2 F20 Field Emission Transmission Microscope. Powder X-ray diffraction(PXRD) measurements were performed by a Bruker D8 Advance X-ray diffractometer with a Cu K α radiation source (λ =0.15418 nm) from 5 to 80°at the scan rate of 5°/min. N₂ adsorption-desorption analysis was conducted on a Micromeritics ASAP 3020 instrument at 77 K. X-ray photoelectron spectroscopy (XPS) analyses were carried out by an X-ray photoelectron spectrometer (Thermo Fischer, ESCALAB Xi+) and the data was analyzed by CasaXPS Software version 2. 3. 19.

Electrochemical measurements:

All the electrochemical measurements were carried on a CHI-760E electrochemical workstation with a three-electrode system in 1M KOH, and the catalyst, Pt and Hg/HgO were chosen as working electrode, counter electrode and reference electrode, respectively. The catalyst ink was prepared by dispersing 3 mg catalyst and 1 mg XC-72 in 1 mL Nafion solution (0.1 wt%) after 30-minute ultrasonication. Before loading the catalyst, the surface of glassy carbon electrode (GCE, diameter = 5 mm) was polished with 500 nm and 50 nm α -Al₂O₃ successively. After washed by ultrapure water and ethanol, 12 µL ink was dripped on the clean surface and dried at room temperature. The mass loading of catalyst was calculated as 0.3 mg cm⁻².

To remove the unstable parts and activate the catalysts, 200 cyclic voltammetry scans (CVs) from the potential of 1.02 V to 1.82 V (vs. RHE) with a scan rate of 500 mV s⁻¹ were taken prior to the measurement. The OER cyclic voltammetry (CV) were measured from the potential of 1.12 V to 1.77 V (vs. RHE) at the scan rate of 5 mV s⁻¹, and the polarization curves were determined by the negatively scan part of CV, the

overpotentials (η) were obtained from: $\eta = E$ (vs. RHE) -1.23 V. All the curves were recorded without iR correction.

The Tafel plots of catalysts were depicted from their corresponding linear sweep voltammograms (LSV) data, which can be fitted based on the equation below:

 $\eta = a + b \times log(j)$

Where η is the overpotential, J is the steady-state current density to geometric area of working electrode. The durability test was performed using chronopotentiometry measurements, and carbon rod was used as counter electrode to avoid Pt migration.

The electrochemical surface area (ECSA) was evaluated by CV technique from low range from 1.17 to 1.27 V (vs. RHE) under different scan rates from 10 to 50 mV s⁻¹ to avoid the generation of Faradic current. The double-layer capacitance (C_{dl}) is linearly proportional to the ECSA, and it was estimated by plotting half of capacitive currents at 1.222 V (vs. RHE) ($\Delta J/2$, ΔJ is J_{anode} - J_{cathode}) against scan rate. Operando electrochemical impedance spectroscopy (EIS) measurements were performed from 0.01-1000000 Hz with the potential ranging from 1.495 to 1.595 V (vs. RHE).

EIS calculation:

The equivalent circuit is represented by R_s (R_fC_f) ($R_{ct}Q_{dl}$), with a good tuning capacity ($x^2 < 10^{-3}$), and is usually used to fit the impedance data for the OER electrocatalytic process. In the equivalent circuit, R_s represents the uncompensated solution resistance, R_f represents the film resistance of the electrocatalyst surface, and Cf represents the corresponding capacitance. The (RfCf) combination in parallel characterizes the physical responses of the electrocatalyst interface in the middle and high frequency regions. R_{ct} represents the corresponding capacitance. The ($R_{ct}Q_{dl}$) combination in parallel corresponds to the OER process in the low-frequency region.

Considering the nonhomogeneity of the electrode surface, a constant phase element (CPE) is employed instead of the capacitive element (Q_{dl}), and the CPE impedance was represented by Equation:

$$Z_{CPE} = \frac{1}{Qdl(jw)^n}$$

where Q_{dl} is the CPE constant, n is the corresponding dispersion coefficient (accounting for the deviation from the ideal behavior, the value being 1 for the perfect capacitors), and w is the angular frequency

DFT calculation:

In this work, first-principles calculations were carried out using density functional theory (DFT) with generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) implemented in the Vienna Ab-Initio Simulation Package (VASP). The valence electronic states were expanded on the basis of plane waves with the corevalence interaction represented using the projector augmented plane wave (PAW) approach and a cutoff of 520 eV. A Γ -centered k-mesh of 3 × 3 × 1 was used for the surface calculations. Convergence is achieved when the forces acting on ions become smaller than 0.03 eV/Å. The Vanderbilt ultrasoft pseudopotential was used with a cutoff energy of 450 eV. Geometric convergence tolerances were set for maximum force of 0.03 eV/Ű, maximum energy change of 10-5 eV/atom, maximum displacement of 0.001 A° and maximum stress of 0.5 GPa. Density mixing electronic minimisation was implemented and the self-consistent field (SCF) tolerance was set to "fine" with high accuracy of 10-6 eV/atom for energy convergence.

The reaction steps of alkaline OER:

According to a previous study on the OER pathway in alkaline media, the OER pathway was described as the adsorption of successive intermediate species on the catalyst and the relevant reaction energies were as follows (*Eq.* $1 \sim Eq.$ 4):

(1) $OH^- + M \rightarrow M^*OH^- + e^-$

- (2) $M*OH + OH \rightarrow M*O + H_2O + e^-$
- (3) $M*O + OH \rightarrow M*OOH + e^{-}$
- (4) $M*OOH + OH \rightarrow O_2\uparrow + H2O + e^-$

The "M" represented the active metal site in catalyst when OER occurred. The "M*OH", "M*O", "M*OOH" represented the intermediate oxygen-containing species adsorbed on the active metal sites. In order to evaluate OER activity, we calculated the free energy ($\Delta G1 \sim \Delta G4$) using the computational standard hydrogen electrode model. The free energy calculation could be obtained as follows:

- (1) $\Delta G1 = G_{M*OH} G_M GH_2O + 1/2GH_2 eU + KBTln10 \cdot pH$
- (2) $\Delta G2 = G_{M*O} G_{M*OH} + 1/2GH_2 eU + KBTln10 \cdot pH$
- (3) $\Delta G3 = G_{M*OOH} G_{M*O} GH_2O + 1/2GH_2 eU + KBTln10 \cdot pH$
- (4) $\Delta G4 = 4.92 \Delta G1 \Delta G2 \Delta G3$

It should be noted that -eU represented the free energy changes for one electron transfer where U was electrode potential respect to the standard hydrogen electrode. For pH \neq 0, pH effected on free energy could be defined as -KBTLn10·pH, where KB was Boltzman constant. Δ G4 was calculated by 4.92 - Δ G1 - Δ G2 - Δ G3 to avoid calculating the O2 adsorption and desorption.

Supplementary Images:



Figure S1. SEM images of (a-b) VO(OH)₂ nanorods, (c-d) VFeNi/VO(OH)₂-2



Figure S2. (a) LSV plots normalized by the BET surface area, and (b) Pore size distribution curve corresponding to specific surface area of VO(OH)₂ nanorods and VFeNi/VO(OH)₂-2.



Figure S3. XRD patterns of the FeNi-OH, VO(OH) $_2$ nanorods and VFeNi/VO(OH) $_2$ -2 .



Figure S4. SEM images of VFeNi hydroxides supported on $VO(OH)_2$ nanorods prepared with different reaction times: (a) 2, (b) 6, (c) 12, (d) 24 h. Scale bars: a-d 500 nm.



Figure S5. LSV curves in OER of NiFeV hydroxides supported on $VO(OH)_2$ nanorods prepared with different reaction times: (a) 2, (b) 6, (c) 12, (d) 24 h. Scale bars: a-d 500 nm.



Figure S6. LSV curves in OER of samples with different Fe/Ni irons ratios ranging from 1:2 to 1:8.

Figure S7. SEM images of samples : (a) VFeNi/VO(OH)₂ nanorods , (b) FeNi-OH, (c) VNi/VO(OH)₂ nanorods, (d) VFe/VO(OH)₂ nanorods. Scale bars: a-d 1 μ m.

Figure S8. SEM images of samples after a 24h constant current OER test at 10 mA cm^{-2} : (a) VFeNi/VO(OH)₂ nanorods, scale bars: 500 nm, (b) FeNi-OH, (c) VNi/VO(OH)₂ nanorods, (d) VFe/VO(OH)₂ nanorods. Scale bars: a-d 1 μ m.

Figure S9. XPS spectra for: (a) Ni 2p, (b) Fe 2p, (c) V 2p of VFeNi/VO(OH)₂-2 before and after a 24h constant current OER test at 10 mA cm⁻².

sample	V	Ni	Fe
VFeNi/VO(OH) ₂ -2	25.50	13.06	4.03
VO(OH) ₂	43.01		
FeNi-OH		30.58	7.24

 Table S1. The metal elements composition (%) of samples determined by ICP.

sample	V	Ni	Fe	0
VFeNi/VO(OH) ₂ -2	5.52	20.22	3.07	36.75
VO(OH) ₂	20.37			66.31
FeNi-OH		27.24	4.7	45.26

Table S2. The surface atomic composition (%) of samples determined by XPS.

Figure S10. XPS spectra for: (a) Ni 2p of VFeNi/VO(OH)₂-2 and VNi/VO(OH)₂, (b) Fe 2p of VFeNi/VO(OH)₂-2 and VFe/VO(OH)₂.

Figure S11. LSV curves in OER of VFeNi/VO(OH)₂-2 and bear VO(OH)₂ nanorods.

Figure S12. The top view and the side view of FeNi LDH (001) surface and the water dissociation and H adsorption.

Figure S13. The top view and the side view of VFeNi/VO(OH)₂ (001) surface and the water dissociation and O adsorption.

Catalyst	$\eta_{10}(mA)$	Tafel slope (mV dec ⁻¹)	Stability	Reference
VFeNi/VO(OH)2-2	251	51	150 h at 10mA cm ⁻¹	This work
NiFe@NCNT	330	74	14 h at 20mA cm ⁻¹	[1]
NaBH ₄ -NiFe LDH	280	56	5 h at 50mA cm ⁻¹	[2]
/NF	280			
NiO/C@Ni	200	45	5 h -+ 10 m A	[3]
Fe-LDH	299	45	$5 \text{ h at 10mA cm}^{-1}$	[2]
VOOH-NF	270	68	50 h at 50mA cm ⁻¹	[4]
IrO ₂ @ SL-NiFe	270	50	251 (10) 1	[5]
LDHs	270	59	35 h at 10mA cm ⁻¹	
Ni ₃ Fe@NC	260	79	11 h at 10mA cm ⁻¹	[6]
NiFe LDH	270	63	24 h at 10mA cm ⁻¹	[7]
NFO/3DGN-10	270	64	25 h at 10mA cm ⁻¹	[8]
FeNi ₃ @NCNT	264	58.5	40 h at 40mA cm ⁻¹	[9]
NiFe@C@Co CNFs	336	62	48 h at 0.5V	[10]
MoS ₂ /NiFe LDH	257	59	25 h at 50mA cm ⁻¹	[11]
[MFe(tda)(H ₂ O)]n	254	54	24 h at 10mA cm ⁻¹	[12]
CVN/CC	263	64.1	100h at 10mA cm-1	[13]
F _{0.2} -V-Co ₃ O ₄	320	75.9	4000r	[14]
NiVP	253	78	24 h at 50mA cm-1	[15]

Table S3. Comparison of OER activity of VFeNi/VO(OH)2-2 nanorod in this workwith other reported electrocatalysts in 1 M alkaline solution.

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