Supporting Information

Surface defect engineering of sub-2 nm NiFe layered double

hydroxide with multiple vacancies induced by alkaline ionic liquid

enabling enhanced water oxidation

1. Experimental section

1.1. Material Synthesis

The NiFe LDH/AIL-0.1 was prepared by an AIL-modified drastic nonequilibrium precipitation method. Firstly, Ni(NO₃)₂·6H₂O and Fe(NO₃)₃·9H₂O (0.05 M. 0.3 mL, with a mole ratio of Ni:Fe=2:1) were directly mixed with a methanol solution of 1-aminopropyl-3-methylimidazolum tetrafluoroborate (AIL, 0.1 mL, 50 mM) under vigorous stirring in methanol at room temperature, and then adding NaOH solution (3 mL, 1.0 M). Afterward, 30 mg Vulcan XC-72R carbon powders were added into the above solution for 4 h and then collected by centrifugation and washed three times with water and methanol, and finally freeze-dried to obtain the samples. For comparison, Other NiFe LDH/AIL-x catalysts were generated by a similar method with adding different AIL amounts (X= 0, 1, and 3 mL).

1.2. Physical characterization

High-Resolution Transmission Electron Microscope (TEM, Talos F200X G2, 200 kV) was adopted to characterize the morphologies of all materials. Powder X-ray diffractometer (XRD, SmartLab 9KW) was used to investigate the crystal structure of the samples. X-ray photoelectron (XPS, Thermo Scientific K-Alpha) was applied to characterize the valence state information of samples. Inductively coupled plasma optical emission spectroscopy (ICP-OES, PerkinElmer Optima 8300) was performed to detect the atomic ratios. Raman (Renishaw inVia) and Fourier transform infrared spectroscopy (FTIR, RT-DLaTGS) analysis was performed on the structure.

1.3. Electrochemical measurements

Electrochemical measurements were conducted by a 760E workstation in a 1.0 M KOH electrolyte solution. First, the 5 mg catalysts and 50 μ L 5 wt% Nafion solution were ultrasonically mixed with 950 μ L of isopropyl alcohol solution. Then 12 μ L of the homogeneous ink was added drop wisely onto a glass carbon electrode (5 mm in diameter) used as the working electrode in a three-electrode system by using Pt mesh and Hg/HgO electrodes as the counter and reference electrodes.

Before measurements, the potential of the Hg/HgO reference was calibrated to a reversible hydrogen electrode (RHE) by bubbling high-purity hydrogen over a freshly cleaned Pt mesh. So the conversion equation can be formulated as E(RHE) = E(Hg/HgO) + 0.919 V. After the cyclic voltammetry activation of the working electrodes, linear sweep voltammetry (LSV) curves at a scan rate of 5 mV s⁻¹ with 95% iR-correction was performed to evaluate the catalyst OER performances. In addition, electrochemical impedance spectroscopy (EIS) was performed over a frequency range from 10⁶ Hz to 0.1 Hz under 1.53 vs. RHE. Besides, the durability test was investigated via the chronopotentiometry method without iR compensation.

Meanwhile, the mass activity (MA) is calculated as follows: $MA = I/m_{metal}$, where I is the current at the overpotential of 0.3 V; m_{metal} is the mass of metal measured from ICP-OES.

The apparent activation energy (E_a) is calculated as follows:

$$\frac{d\ln(i_0)}{d(1/T)} = -\frac{E_a}{R}$$

where E_a is the apparent activation energy, R is the gas constant, T is the absolute temperature, and i_0 is the value of a current at zero-overpotential (E=1.23 V vs RHE).¹

1.4. DFT Calculations

Our computational analysis was carried out using the Materials Studio software package. The computational model utilized the (111) crystal plane of NiFe-LDH, consisting of two atomic layers, with a vacuum layer of 20 Å set. The calculations were performed using the GGA-PBE functional, with a plane-wave cutoff energy set to 400 eV.² A $2 \times 2 \times 1$ k-point grid was employed for structure optimization, while a $3 \times 3 \times 1$ k-point grid was used for calculating the density of states. Atomic positions were relaxed until the energy of each atom was less than 1×10^{-6} eV, and the absolute value of the Hellmann-Feynman forces on each atom was less than 0.01 eV/Å.



Fig. S1 HAADF-STEM image of the NiFe LDH/ AIL-0.



Fig. S2 EELS spectra of NiFe LDH/AIL-0.



Fig. S3 SAED pattern of NiFe LDH/ AIL-0.1.



Fig. S4 SAED pattern and SEM-EDS elemental mapping images of NiFe LDH/AIL-

0.1.



Fig. S5 a) Ni and b) Fe K-edge EXAFS oscillation function $k^3\chi(k)$ NiFe LDH/AIL-0.1, counter and reference samples.



Fig. S6 FTIR spectra of NiFe LDH/AIL-0.1 and pure AIL.



Fig. S7 FTIR of NiFe LDH/AIL-0.1 and pure AIL.



Fig. S8 CV curves of NiFe LDH/AIL-x (x=0, 0.1, 1, 3 mL) catalysts at different scan

rates in a non-faradaic region.



Fig. S9 Corresponding C_{dl} values of these catalysts were calculated from Fig. S8.



Fig. S10 ECSA normalized OER LSV curves of NiFe LDH/ AIL-x catalysts.



Fig. S11 Mass normalized OER activity of NiFe LDH/ AIL-x catalysts.



Fig. S12 Comparison of oxygen volume (red dots) and faradic efficiency (green dots) for NiFe LDH/AIL-0.1 electrode and its theoretical value (solid line) calculated based on the amount of consumed charges over the course of electrolysis.



Fig. S13 XPS spectra for a) Ni 2p, b) Fe 2p, c) O 1s, and d) N 1s of NiFe LDH/ AIL-

0.1 after the OER reaction.



Fig. S14 Amplified XRD pattern of NiFe LDH/ AIL-x catalysts.



Fig. S15 Differential pulse voltammetry (DPV) curves of NiFe LDH/ AIL-x catalysts in 1.0 M KOH.



Fig. S16 Top view of NiFe LDH/AIL-0, where blue, brown, indigo, red, and grey balls represent Ni, Fe, N, O, and H atoms, respectively.

Samples	Path	CN	R(Å)	$\triangle E_0(eV)$	R factor
NiFe LDH/AI L-0.1	Ni-O	5.7 ± 0.5	2.06 ± 0.01	17 1 2	0.009
	Ni-M	5.4 ± 0.2	3.09 ± 0.01	1.7 ± 1.3	
	Fe-O	5.8 ± 0.5	2.00 ± 0.01	2.0 + 1.7	0.004
	Fe-M	5.7 ± 0.7	3.08 ± 0.01	2.0 ± 1.7	0.004
NiFe LDH/AI L-0	Ni-O	6.0 ± 0.4	2.06 ± 0.01	10 1 1 4	0.009
	Ni-M	5.9± 0.3	3.08 ± 0.01	1.9 ± 1.4	
	Fe-O	5.9 ± 0.4	1.99 ± 0.01		0.007
	Fe-M	6.0 ± 0.6	3.07 ± 0.01	3.3±1.3	0.007

Table S1 Local structure parameters of NiFe LDH/AIL-0 and NiFe LDH/AIL-0.1estimated by EXAFS analysis.

Note: CN, coordination number; R, distance between absorber and backscatter atoms; σ^2 , Debye Waller factor to account for both thermal and structural disorders; ΔE_0 , inner potential correction; R factor (%) indicates the goodness of the fit.

Samples (<i>wt</i> %)	Ni	Fe
NiFe LDH/ AIL-0	1.74	0.98
NiFe LDH/AIL-0.1	2.02	1.02

Table S2 ICP-OES determination of metal element ratio in obtained catalysts.

Table S3 The calculated difference value of free energies (units in eV) of OER intermediates on the active sites at the potential of U = 0 V vs. RHE.

Samples (eV)	ΔG_1	ΔG_2	ΔG_3	ΔG_4
NiFe LDH/ AIL-0	0.23	1.85	2.19	0.65
NiFe LDH/ AIL-0.1	1.37	1.39	1.41	0.75

Catalysts	Loading (mg cm ⁻²)	Overpotential at 10 mA cm ⁻² (mV)	Tafel slope (mV dec ⁻¹)	Mass activity at (A g ⁻¹)	Ref.
NiFe LDH/ AIL-0.1	0.01	273	38	3296	This
NiFe LDH/ AIL-0	~0.01	286	43	2188	work
23% Fe- doped chiral cobalt oxide	l -	314	34	1730	[3]
NiFeO _x H _y	-	414	37	1280	[4]
CoO _X (OH) _Y - nm	9 0.003	385	43	20	[5]
Ni-Fe LDH hollow nanoprisms	0.16	280	49	375	[6]
Ir ₁ /Ni LDH-7	Г -	228	41	330	[7]
Ni _{0.8} Fe _{0.2} O _x H	y 0.005	/	37	140	[8]
IrOx/Zr ₂ ON	₂ 0.4	225	48	849	[9]
50Ni50Co- SURMOFD 10 cycles	0.00022	/	/	2530	[10]
Ru-Co/ELCO	D 1.0	247	49	1000	[11]

Table S4 Summary of the catalytic performance of recently representative OERcatalysts in a 1.0 M KOH electrolyte.

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