Supporting Information

Brønsted base tuning the local reaction environment to enhance neutral water oxidation

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1. Experimental section

1.1 Reagents and materials

Nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$), Ferric nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$), Carbamide (CH_4N_2O), Potassium silicate (K_2SiO_3), Methanol (CH_3OH), Ethanol absolute (C_2H_6O) and Milli-Q ultrapure water (> 18 MΩ·cm).

1.2 Synthesis of catalysts

A piece of commercial nickel foam (2 cm × 3 cm) was cleaned with ethanol absolute and ultrapure water for 15 min, respectively. The 2.25mmol $Ni(NO_3)_2 \cdot 6H_2O$ and 0.75 mmol $Fe(NO_3)_3 \cdot 9H_2O$ were dissolved in 60 mL water, and the clean nickel foam was then immersed in this solution. Afterward, the mixture was transferred into a 100 mL Teflon-lined autoclave. The autoclave was sealed and heated at 120 °C for 10 h in an electric oven. The sample was washed with deionized water several times and dried in a vacuum drying oven (60°C, 2h). Through the above operations, pretreated NiFe$(OH)_x$ can be obtained. Electrochemical adsorption of SiO_3^{2-} experiments using a three-electrode system were carried out in a series of K_2SiO_3 solutions with varying concentrations (0.2 M, 0.5 M and 1.0 M). The NiFe$(OH)_x$ was used as the working electrode, platinum foil was used as the counter electrode, and Ag/AgCl was used as the reference electrode. The time and voltage were 120 s and 1V, respectively. The NiFe$(OH)_x$-SiO_3^{2-} sample was obtained after electrochemical adsorption. Based on the varying concentrations of the K_2SiO_3 electrolyte, the samples were sequentially labeled as NiFe$(OH)_x$-0.2SiO_3^{2-}, NiFe$(OH)_x$-0.5SiO_3^{2-} and NiFe$(OH)_x$-1.0SiO_3^{2-}.

1.3 Physicochemical characterization

The morphologies of the synthesized catalysts were characterized by field-emission scanning electron microscopy (SEM) (Hitachi S-4800) and transmission electron microscopy (TEM) (JEM-2100F). The crystal structure and elemental distribution were examined by powder X-ray diffraction (XRD) (Bruker D8) and energy-dispersive X-ray spectroscopy (EDS), respectively. The chemical states and surface composition information were analyzed by X-ray Photoelectron Spectroscopy (XPS) (AXIS SUPRA). The surface intermediates and phase changes during the reaction are detected by a Raman laser spectrometer (Renishaw inVia).

1.4 Electrochemical Measurements

The electrochemical experiments were carried out with the three-electrode system connected to the electrochemical workstation (Autolab PGSTAT302N). The working electrode was NiFe$(OH)_x$-SiO_3^{2-} (0.5 cm × 0.5 cm), the reference electrode was Ag/AgCl electrode, the counter electrode was Pt foil and the electrolyte was 0.5 M saturated $KHCO_3$. The linear sweep voltammetry (LSV) with a scan rate of 1 mV s^{-1} was used to evaluate the catalytic activity. All measured potentials were *vs* Ag/AgCl which are converted to a reversible hydrogen electrode (RHE) according to the Nernst equation ($E_{RHE} = E_{Ag/AgCl} + 0.059 \times pH + 0.197$). Tafel slopes were derived by plotting overpotential against log (current density) from the linear region of the LSV polarization curves. The value was calculated following the Tafel equation of $\eta = b \times \log j + a$, where η is the overpotential, b is the Tafel slope and j is the current density. The electrochemical impedance spectroscopy (EIS) measurements were carried out in a static solution at a potential of 1.7 V *vs.* RHE, with a frequency range from 0.1 Hz to 100 kHz. The long-term stability test is carried out by the chronopotentiometry method with a 0.025A setting current.

1.5 The in-situ Raman measurements

In-situ Raman spectra were collected using a three-electrode electrochemical system. The NiFe(OH)x-SiO_3^{2-} and control samples were used as the working electrodes (reaction area ~1 cm^2), with Pt foil as the counter electrode and Ag/AgCl as the reference electrode, and 0.5 M saturated $KHCO_3$ as the electrolyte. *In-situ* Raman measurements were conducted using a confocal Raman spectrometer (Alpha300, WITec) equipped with a 514 nm laser source. The surface intermediates formed during the reaction were detected using a Raman spectrometer (Renishaw inVia). Electrochemical experiments were performed using an electrochemical workstation (CHI760E) with a voltage scan range from 1.3 V to 2.1 V *vs.* RHE.

1.6 Electrochemical measurements in the AEM electrolyzers

The AEM electrolyzer is composed of bipolar plates with serpentine flow channels. The internal assembly includes a cathode electrode (Pt/C, loading mass of 1 mg cm^{-2}), an anode $NiFe(OH)_x$-SiO_3^{2-}

electrode, and an anion exchange membrane (Sustainion® X37-50). The assembly of the AEM electrolyzer does not require additional processes such as heating or pressing. For comparison, a commercial RuO_2 catalyst was coated onto nickel foam and used as the anode, with a loading mass of 1 mg cm^{-2}. The electrode area of the water electrolyzer is 0.25 cm^2. The electrolyte consists of 0.5 M saturated $KHCO_3$, which is circulated at a flow rate of 50 mL min^{-1} using a peristaltic pump. The performance of the AEM electrolyzer was studied in neutral electrolytes at temperatures of 25±2 °C and 60±2 °C. Polarization curves were measured using linear sweep voltammetry (LSV) at a scan rate of 10 mV s^{-1}, and durability tests were conducted using potentiostatic methods.

2. Supplementary Figures

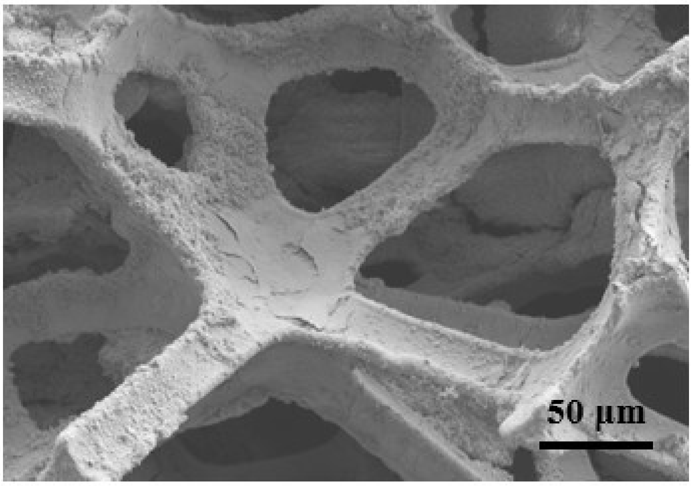

Fig. S1 The SEM image of the nickel foam surface with NiFe(OH)$_x$-SiO$_3^{2-}$.

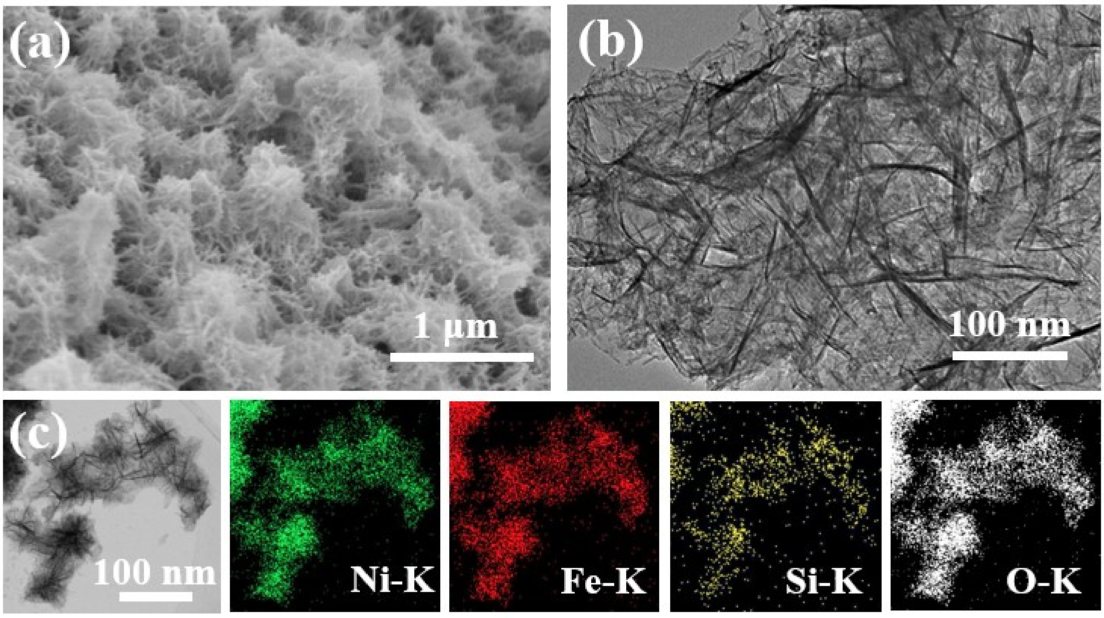

Fig. S2 (a) The SEM, (b) TEM and (c) STEM images and the corresponding EDS elemental mapping of Ni, Fe, Si, O for NiFe(OH)$_x$-SiO$_3^{2-}$ after OER.

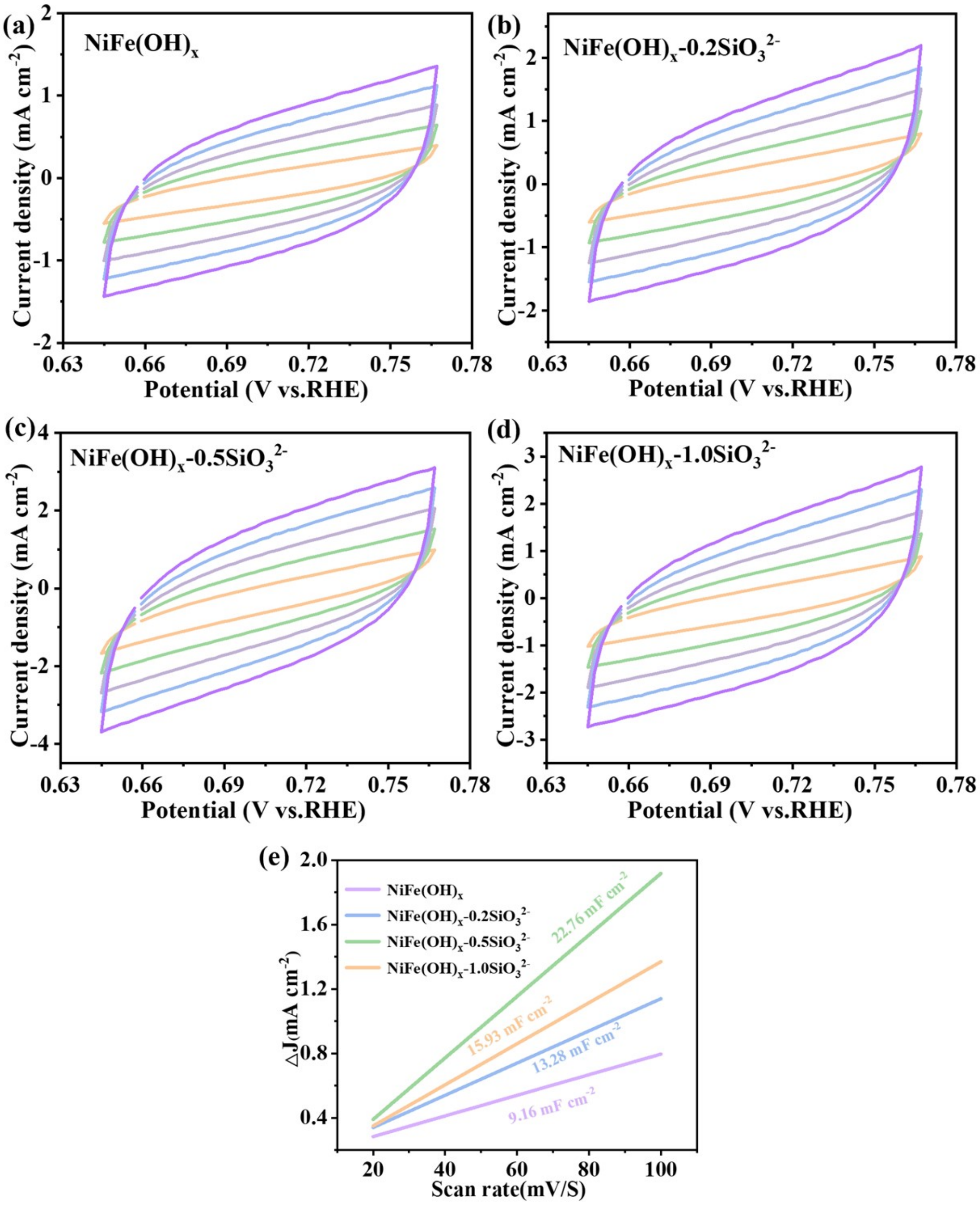

Fig. S3 Cyclic voltammograms at various scan rates of 20, 40, 60,80 and 100 mV s^{-1} for (a) $NiFe(OH)_x$ (b) $NiFe(OH)_x$-0.2SiO_3^{2-} (c) $NiFe(OH)_x$-0.5SiO_3^{2-} and (d) $NiFe(OH)_x$-1.0SiO_3^{2-}. (e) The differences between capacitive currents at the center of selected potential window as a function of scan rate for catalysts.

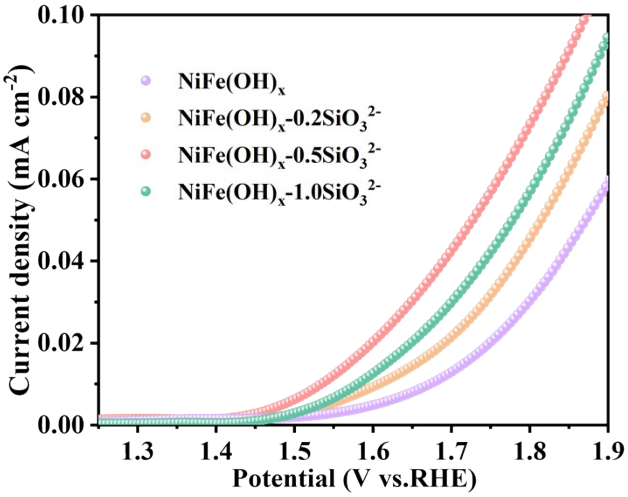

Fig. S4 The polarization curves normalized to the electrochemical active surface area (ECSA) of NiFe(OH)$_x$, NiFe(OH)$_x$-0.2SiO$_3^{2-}$, NiFe(OH)$_x$-0.5SiO$_3^{2-}$ and NiFe(OH)$_x$-1.0SiO$_3^{2-}$.

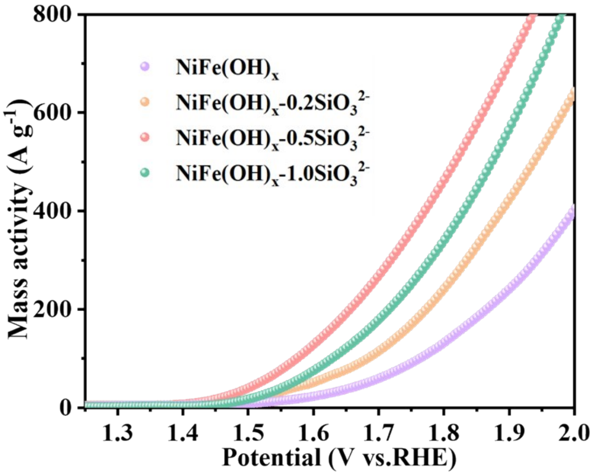

Fig. S5 The linear sweep voltammetry (LSV) polarization curves normalized to the catalyst mass of NiFe(OH)$_x$, NiFe(OH)$_x$-0.2SiO$_3^{2-}$, NiFe(OH)$_x$-0.5SiO$_3^{2-}$ and NiFe(OH)$_x$-1.0SiO$_3^{2-}$.

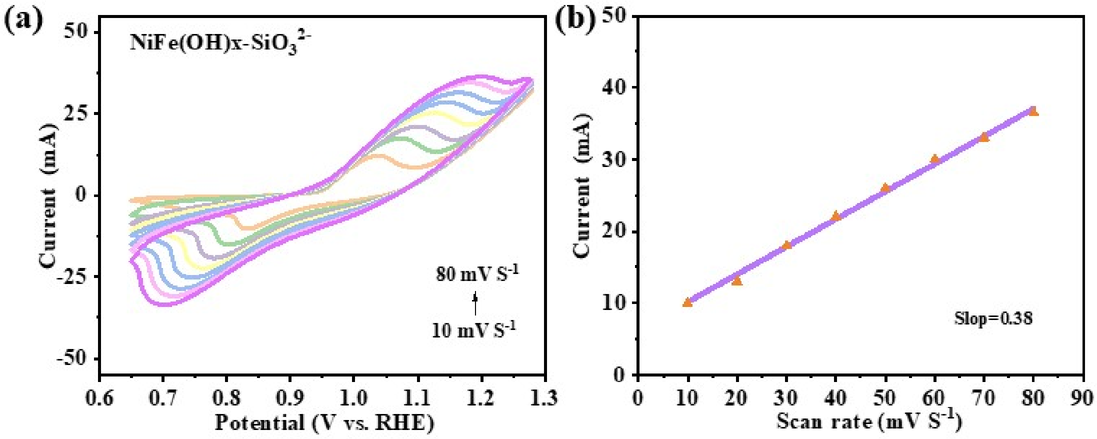

Fig. S6 (a) CVs of NiFe(OH)$_x$-SiO$_3^{2-}$ at different scan rates increasing from 10 to 80 mV s^{-1}. (b) Oxidation peak current versus scan rate plot of NiFe(OH)$_x$-SiO$_3^{2-}$.

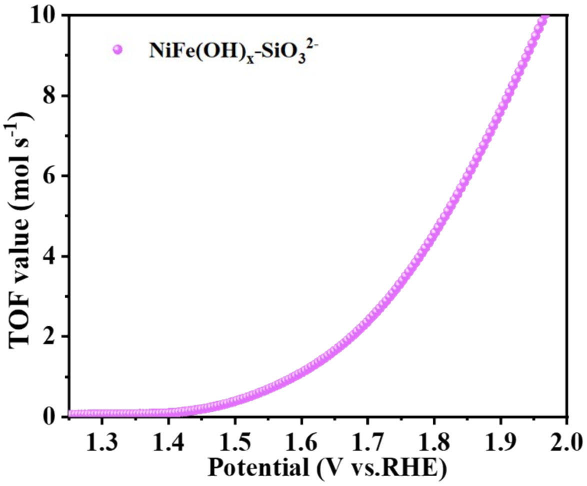

Fig. S7 Plot of turnover frequency (TOF) *vs.* overpotential for NiFe(OH)$_x$-SiO$_3^{2-}$.

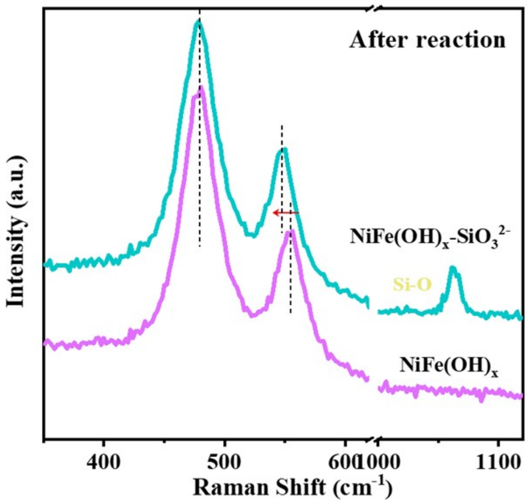

Fig. S8 High-resolution Raman of $NiFe(OH)_x$ and $NiFe(OH)_x$-SiO_3^{2-} after the reaction.

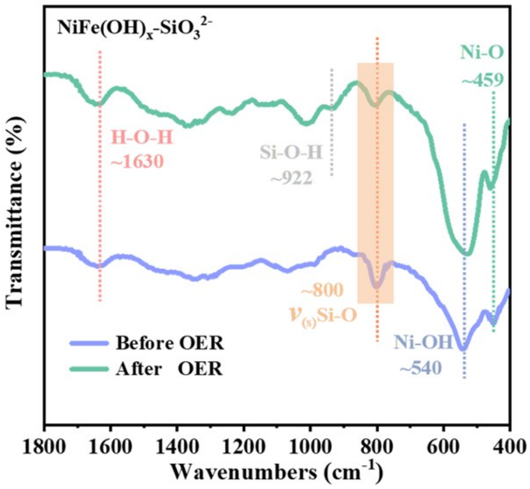

Fig. S9 The FTIR spectra of $NiFe(OH)_x$-SiO_3^{2-} before and after OER.

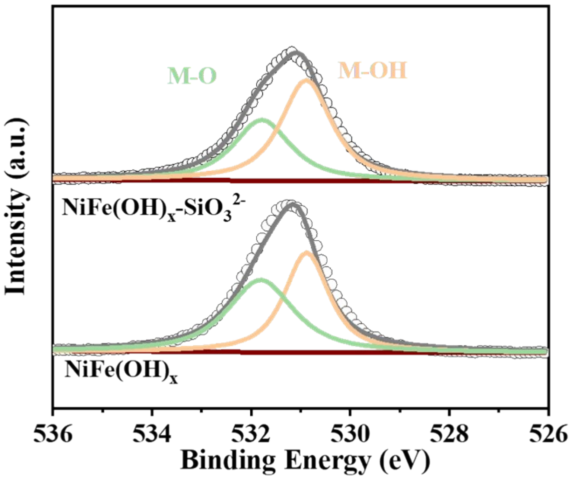

Fig. S10 The XPS spectra of O 2p for $NiFe(OH)_x$ and $NiFe(OH)_x$-SiO_3^{2-} after OER.

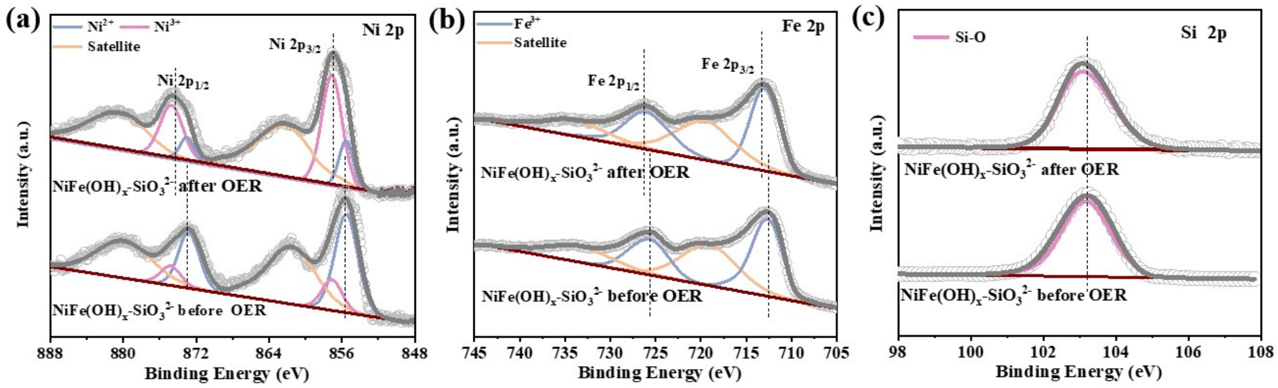

Fig. S11 The XPS spectra of Ni 2p, Fe 2p and Si 2p for $NiFe(OH)_x$-SiO_3^{2-} before and after OER.

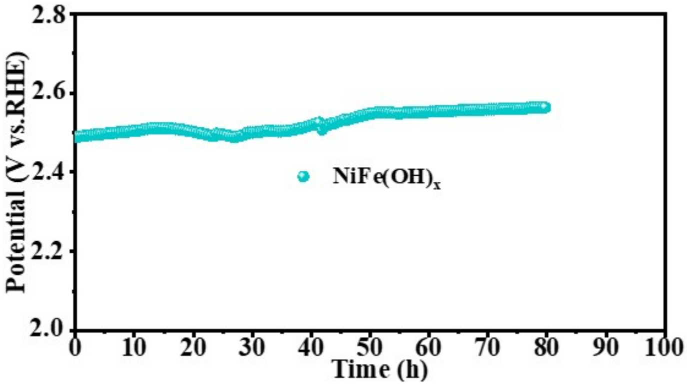

Fig. S12 Chronopotentiometry test of the $NiFe(OH)_x$ ||Pt/C electrocatalyst at 1.0 A cm^{-2} in the AEM electrolyzer.

3. Supplementary Notes

Note S1. Calculations of AEM electrolyzer efficiency

Electrolyzer efficiency:

1) H_2 production rate@1.0 A cm^{-2} = (j A cm^{-2}) (1 e^-/1.602×10^{-19} C) (1 H_2/2 e^-) = 5.18×10^{-6} mol H_2 cm^{-2} s^{-1}

2) LHV of H_2 = 2.42×10^5 J mol^{-1} H_2

3) H_2 power out = (5.18×10^{-6} mol cm^{-2} s^{-1})×(2.42×10^5 J mol^{-1}) = 1.254 W cm^{-2}

4) Electrolyzer Power $NiFe(OH)_x$-SiO_3^{2-}||Pt/C@1.0 A cm^{-2} (60℃) =1.0 A cm^{-2}×1.81 V =1.81 W cm^{-2}

5) Efficiency of $NiFe(OH)_x$-SiO_3^{2-}||Pt/C = (H_2 Power Out) / (Electrolyzer Power) = 1.254 W cm^{-2}/1.81W cm^{-2} =69.2%

6) Efficiency of RuO_2||Pt/C = (H_2 Power Out) / (Electrolyzer Power) = 1.254 W cm^{-2}/1.97 W cm^{-2} =63.6%

Note S2. Calculations of H_2 cost in AEMWEs.

Price per gasoline-gallon equivalent (GGE) H_2:

= 1GGE H_2 / H_2 production rate × Electrolyzer power × Electricity bill

The cost of $NiFe(OH)_x\text{-}SiO_3^{2-}$||Pt/C = 0.997 kg / ($5.18\times10^{-6}$ mol H_2.cm^{-2} s^{-1} × 2 kg/mol) × 1.81 W cm^{-2} × \$ 0.02/kW h = \$ 0.96/GGE H_2