Supporting Information

Facile Route of Fluorine Incorporation into Nickel (Oxy) Hydroxide for Improving Oxygen Evolution Reaction

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Experimental methods

Electrode preparation

Prior to use, 0.1 mm thick nickel foil (99.5%, Thermo Fisher Scientific) underwent a pretreatment process involving immersion in 0.1 M hydrochloric acid (HCl, DUKSAN reagents) followed by sonication for one hour to eliminate any surface impurities. The resulting clean nickel foils were then utilized in the electrode preparation process. The fluorine-doped nickel electrodes were prepared using cyclic voltammetry (CV) in a mixture of 0.1 M potassium fluoride (KF, 99%, Thermoscientific) and 0.1 M potassium hydroxide (KOH, DUKSAN reagents). The potential cycling was performed over 60 cycles in a 1.2-1.7 V range vs RHE at a scan rate of 40 mV sec⁻¹.

Preparation of Fe-free KOH

The electrolyte (1 N KOH standard solution, DUKSAN reagents) underwent purification through a previously reported method using nickel nitrate hexahydrate $(Ni(NO_3)_2 \cdot 6H_2O, 98\%, MERCK)$.[8] To prepare the purified electrolyte, 0.5-1.0 g of Ni(NO₃)₂ $\cdot 6H_2O$ was dissolved in 5 mL of ultrapure water and added to 20 mL of 0.1 M KOH. The resultant Ni(OH)₂ precipitate was separated through centrifugation and subsequently washed three times with ultrapure water. Afterward, the Ni(OH)₂ precipitate was suspended in 50 mL of 1.0 M KOH and mechanically agitated overnight to absorb Fe impurities.

Electrochemical tests

All electrochemical tests were conducted using a multichannel potentiostat/galvanostat (VSP, Bio-Logic) electrochemical workstation with a three-electrode system. A clean platinum wire served as the counter electrode (CE), while a 1 M KOH solution (50 mL) was utilized as the electrolyte. The reference electrode (RE) was a Hg/HgO (1 M KOH solution). The pre-treated nickel foils were used directly as working electrodes, with the working areas defined using polyamide tape. The CV scans were recorded in the potential range of 1.2-1.7 V versus RHE at a scan rate of 40 mV sec⁻¹ and LSV curves were obtained in the same potential region at a scan rate of 1 mV sec⁻¹ to measure the Tafel slope. The current interrupt (CI) method available in the potentiostat software was used for Ohmic drop correction. All potentials were converted to the reversible hydrogen electrode (RHE) according to the Nernst equation: $E(RHE) = E(Hg/HgO) + 0.14 V + 0.0592 \times pH$.

Characterization

X-ray photoelectron spectroscopy (XPS) analyses were carried out using AXIS SUPRA+ (Kratos Analytical Ltd). A monochromated Al Kα excitation source (1,486 eV) was used to investigate electrode samples. The adventitious carbon 1s peak was employed for calibration and used as an internal standard. XPS data analysis was performed using the Versatile ESCApe software.

X-ray diffraction (XRD) (Rigaku, SmartLab SE) analysis was performed to characterize the structural properties of the samples. The spectra were collected in the 2θ range of 10-70°

with a step size of 0.01° at the scan rate of 0.5° min⁻¹.

The sample surfaces were observed using scanning electron microscopy (SEM) (JSM-7900F, JEOL Ltd.) and the corresponding elemental distribution was obtained by energy dispersive X-ray spectroscopy (EDX) mapping.

Operando Raman experiments were performed using a custom-made electrochemical Teflon cell at room temperature. The Raman microscope (XperRAM S, Nanobase) was coupled with a 60× water-immersed objective (Olympus), and the excitation light source had a wavenumber of 532 nm at a grating of 1800 l mm⁻¹. Each spectrum was produced with a resolution of 1 cm⁻¹ using 30 consecutive scans, with 1 s exposure time per scan. The peak shift was calibrated using the peaks of the acetaminophen standard to ensure high confidence and reproducibility in the quality of the obtained spectra. The counter electrode was a platinum wire, and the reference electrode was a double-junction Ag/AgCl electrode in a 3 M KCl solution (+ 0.22 V vs NHE at 25 °C). The Raman signals were recorded in situ at OCP and under different applied potentials spanning from 1.2 to 1.55 V vs RHE.



Fig. S1 The oxidative peaks for $F-NiO_xH_y$ and NiO_xH_y obtained from CV as a function of time at the scan rate of 40 mV sec⁻¹ in 1 M Fe-free KOH.



Fig. S2 (a, c) The deconvoluted XPS spectrum of Ni 2p for representative NiO_xH_y and F- NiO_xH_y samples. (b, d) The average compositions of Ni^0 , Ni^{2+} , and Ni^{3+} for three independent NiO_xH_y and F- NiO_xH_y samples determined by deconvolution of the spectrum.



Fig. S3 XRD patterns of NiO_xH_y and $F-NiO_xH_y$.



Fig. S4 Scheme of a custom-made electrochemical cell for operando Raman spectroscopic analysis.



Fig. S5 Operando Raman spectra of three independent F-NiO_xH_y samples obtained at 1.65 V.

Note: Operando Raman spectra were measured for three independent $\text{F-NiO}_x\text{H}_y$ samples under the same electrochemical condition. The peak positions of the two main bands were nearly identical among the samples. The I_B/I_S ratio for each sample was determined to be 1.97, 1.92, and 1.82 respectively, indicating a high reproducibility in F-doping and the resulting spectral changes compared to that of pristine NiO_xH_y (2.23).