

Supplementary materials

Effect of Fe on the Calcined Ni(OH)₂ Anode in Alkaline Water Electrolysis

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Abstract: Ni (hydr)oxide is a promising and inexpensive material for oxygen evolution reaction (OER) catalysts and is known to dramatically increase the activity when used with Fe. Herein, we basified a Ni(II) solution and coated layered Ni(OH)₂ on Ni coins to prepare a template with high stability and activity. To evaluate the stability and catalytic activity during high-current-density operation, we analyzed the electrochemical and physicochemical properties before and after constant current (CC) operation. The electrode with a Ni(OH)₂ surface exhibited higher initial activity than that with a NiO surface; however after the OER operation at a high-current density, degradation occurred owing to structural destruction. The activity of the electrodes with a NiO surface improved after the CC operation because of the changes on the electrode-surface caused by the CC operation and the subsequent Fe incorporation from the Fe impurity in the electrolyte. After confirming the improvement in activity due to Fe, we prepared NiFe-oxide electrodes with improved catalytic activity and optimized the Ni precursor and Fe loading solution concentrations. The Ni-Fe oxide electrode prepared under the optimal concentrations exhibited an overpotential of 287 mV at a current density of 10 mA/cm², and tafel slope of 37 mV dec⁻¹, indicating an improvement in the OER activity.

Keywords: Oxygen evolution reaction; Nickel hydroxide; Nickel oxide; Basification; Impregnation; High-current density

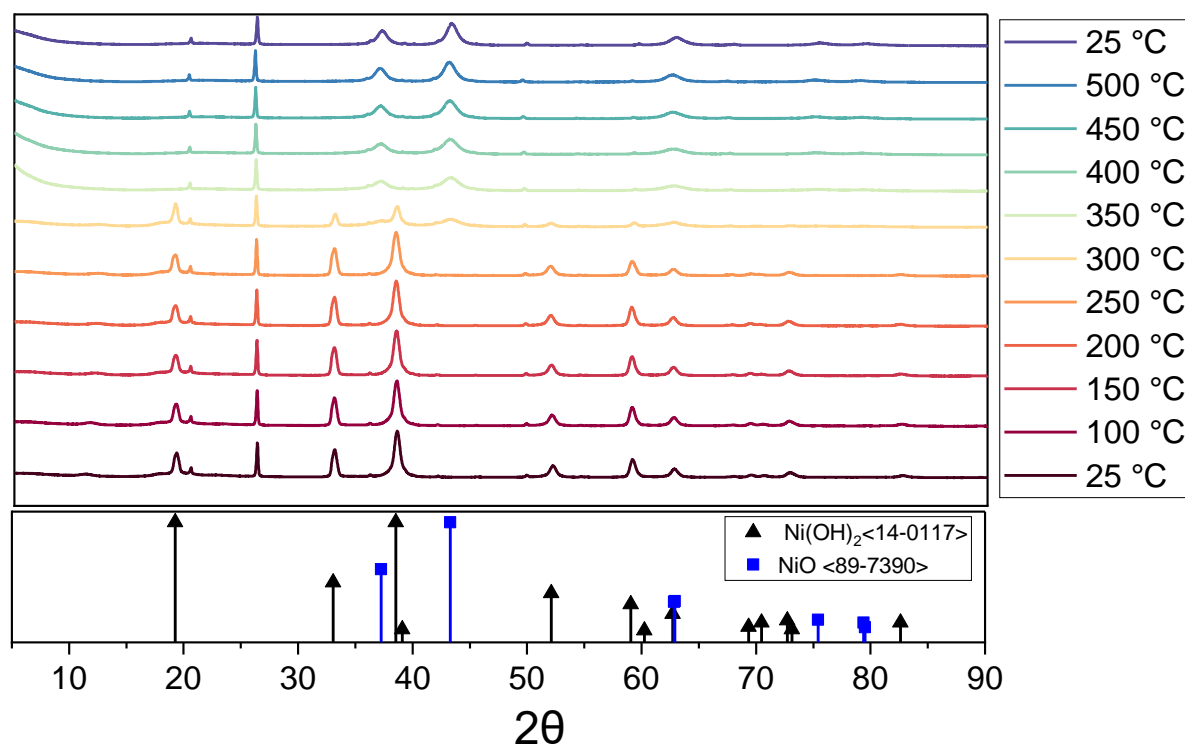


Figure S1: Stacked in-situ XRD patterns for coating material under air atmosphere with temperature ranges of 100 °C–500 °C. In the range of 25 °C–100 °C, the heating rate was 10 °C/min; it was 2 °C/min for a temperature range of 100 °C–500 °C. XRD was conducted at $2\theta = 5^\circ$ – 90° range, scan rate = 2°/min, and step size = 0.02. A peak corresponding to the (001), (100), (101) plane of β - Ni(OH)_2 at $2\theta = 19.26^\circ$, 33.06° , and 38.54° (JCPDS. 14-0117) appears between 25 °C and 350 °C. At 350 °C, peaks of the (111), (200), (220) plane of NiO appears at $2\theta = 37.16^\circ$, 43.18° , and 62.76° (JCPDS. 89-7390) while the peak of β - Ni(OH)_2 is reducing. XRD peaks of NiO remain almost same after additional heating and followed cooling.

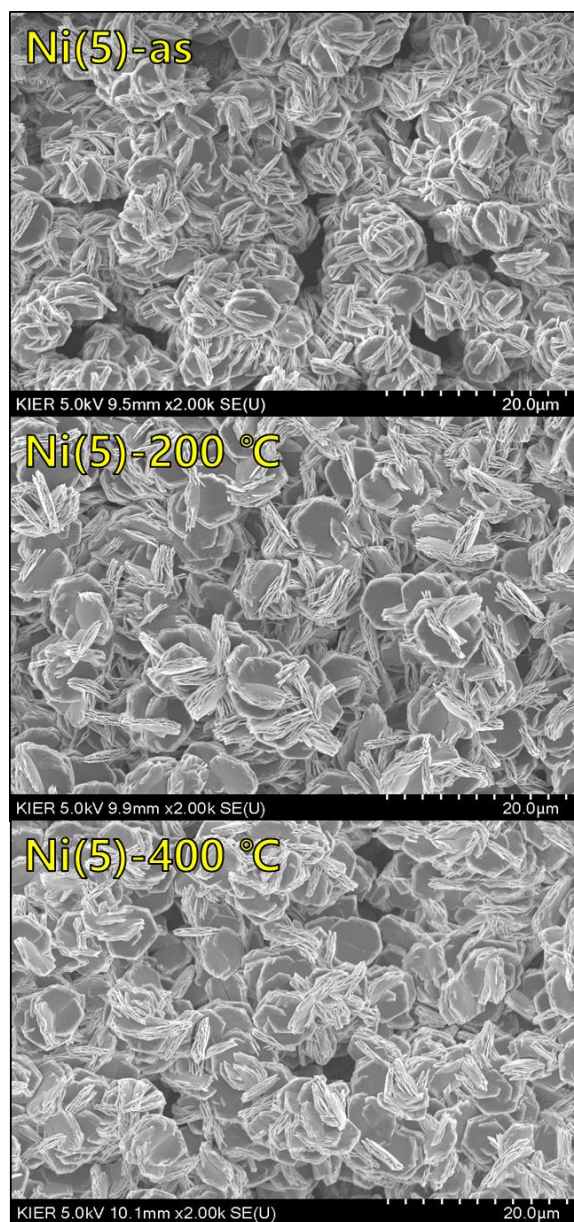


Figure S2: SEM images of Nickel-hydroxide electrodes under various calcination conditions.

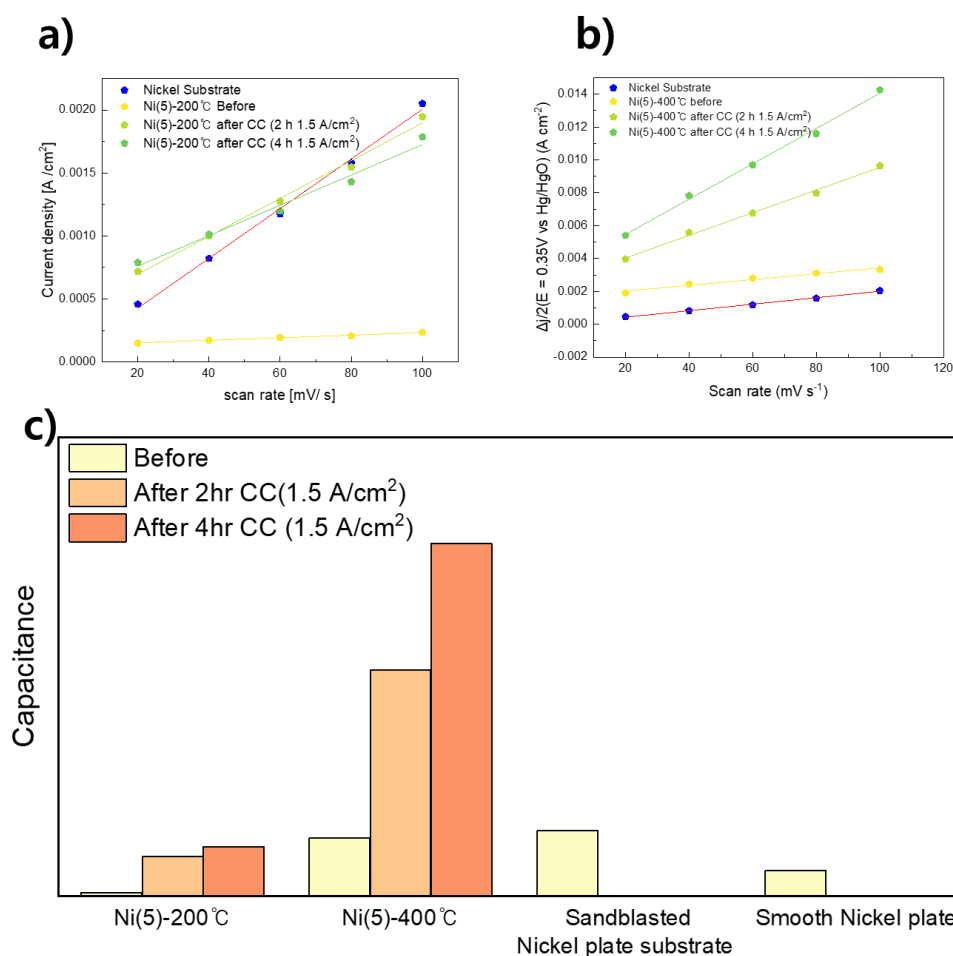


Figure S3: C_{dl} varying with operation time of a) Ni(5)-200 °C b) Ni(5)-400 °C, and c) comparison of the double-layer capacitance (C_{dl}) of the Ni(5)-400 °C Ni(5)-200 °C electrode.

In Fig. S3, the double-layer capacitance (C_{dl}), which is known to be proportional to the electrochemical active surface area (ECSA), is compared for the Ni-based electrodes. The discrepancy appears between the capacitance shown in Fig. S3 and the SEM image shown in Fig. 2 of the paper. This is assumed to be due to the electrical conductivity. According to the study by Jung et al., materials with low conductivity provide a small capacitance by exhibiting dielectric behavior. This additional capacitance can be described in series with the double-layer capacitance on the equivalent circuit and will dominate the total measured capacitance [1]. Jung's study only performed the analysis for low-conductivity oxides, such as NiO, but it is presumed to happen also in hydroxides. In the study by Zhang et al., Ni-Fe hydroxide synthesized on Ni foam was confirmed to have a large surface area via SEM analysis. However, C_{dl} showed values similar to those of Ni foam. It has been claimed that the double-layer capacitance can also be increased by the enhancement of electric conductivity when dealing with electrocatalysts having low conductivity [2].

Table S1. Changes in the CV peak area of Ni(5)-400°C and corresponding apparent coverage of the Ni site

Ni(5)-400°C	Q [mC]	apparent coverage [mol /cm ²]
before CC	0.08109	5.35×10^{-10}
after 2h	0.33913	2.24×10^{-9}
after 4 h	0.5394	3.56×10^{-9}

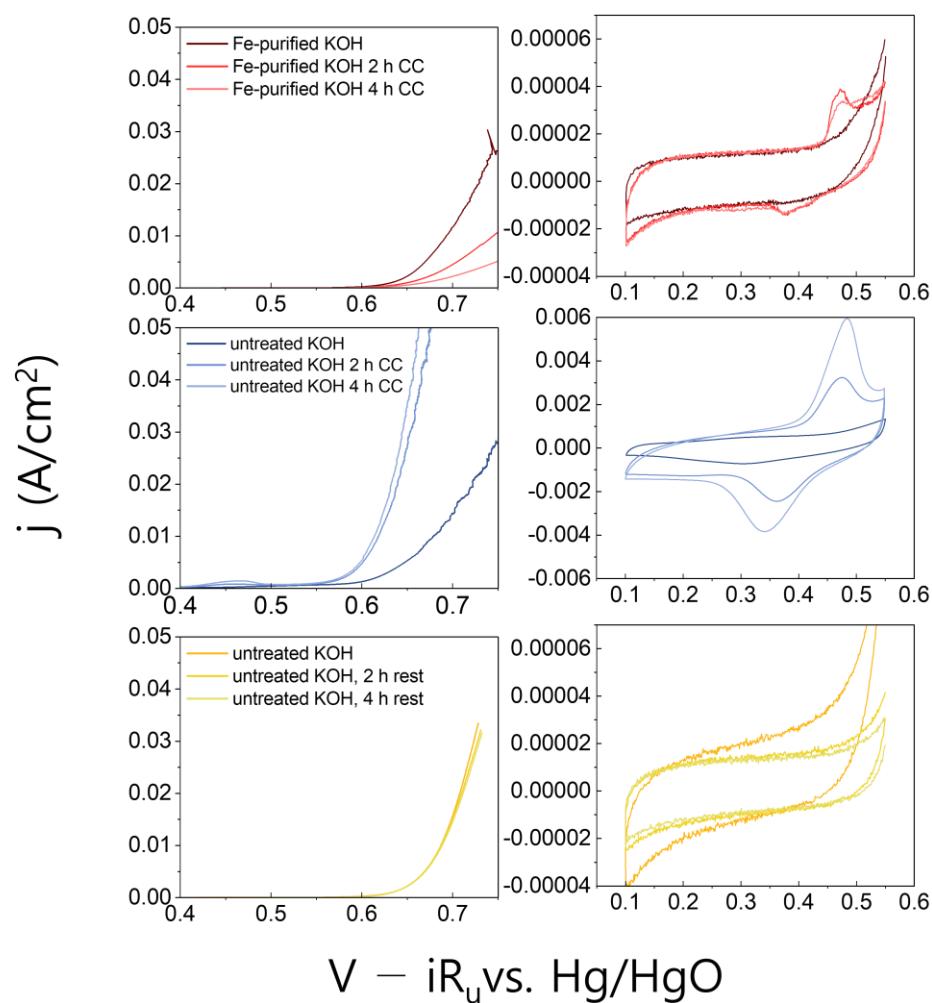


Figure S4: I–V and CV curves taken before CC and after 2h and 4 h CC in various conditions. Measured Ni(5)-400 °C electrodes were prepared with high-purity Ni precursor to avoid any Fe trace in the electrode. Different colors were assigned to each condition; CC operation in purified KOH solution (indicated in red color), CC operation in unpurified KOH solution (indicated in blue color), and CC operation in unpurified KOH solution, which did not undergo CC operation (indicated in yellow color).

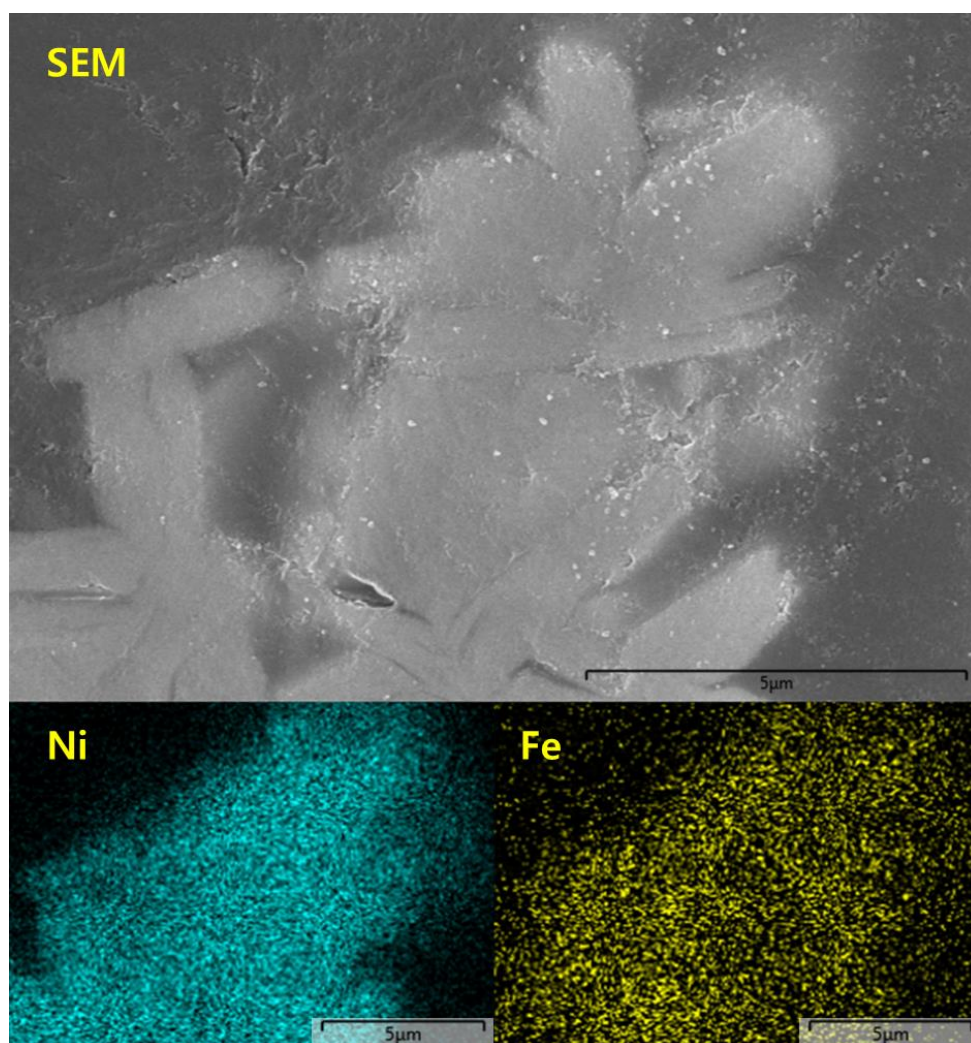


Figure S5: Cross-section SEM-EDS image of the Fe(50)/Ni(5)-400°C electrode prepared with epoxy molding followed by polishing. [Observed with magnification of $\times 10.0k$].

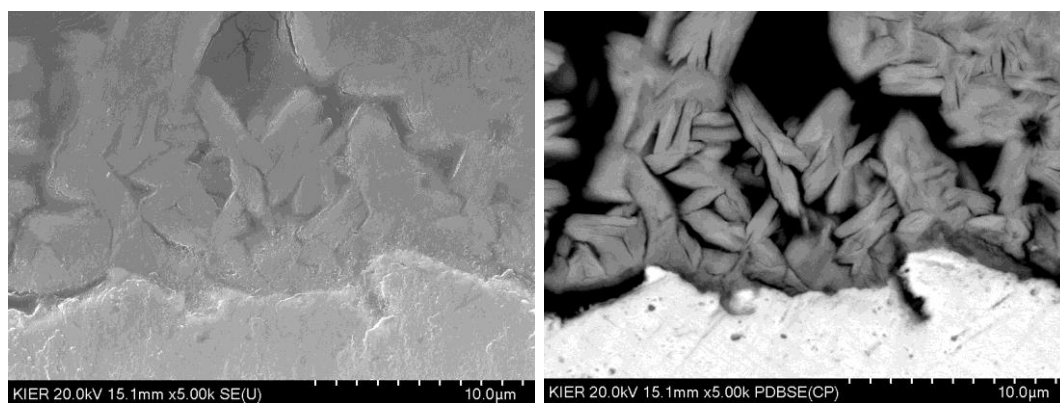


Figure S6: Cross-section SEM image (left) and BSE image (right) of the Fe(50)/Ni(5)-400°C electrode prepared with epoxy molding followed by polishing.

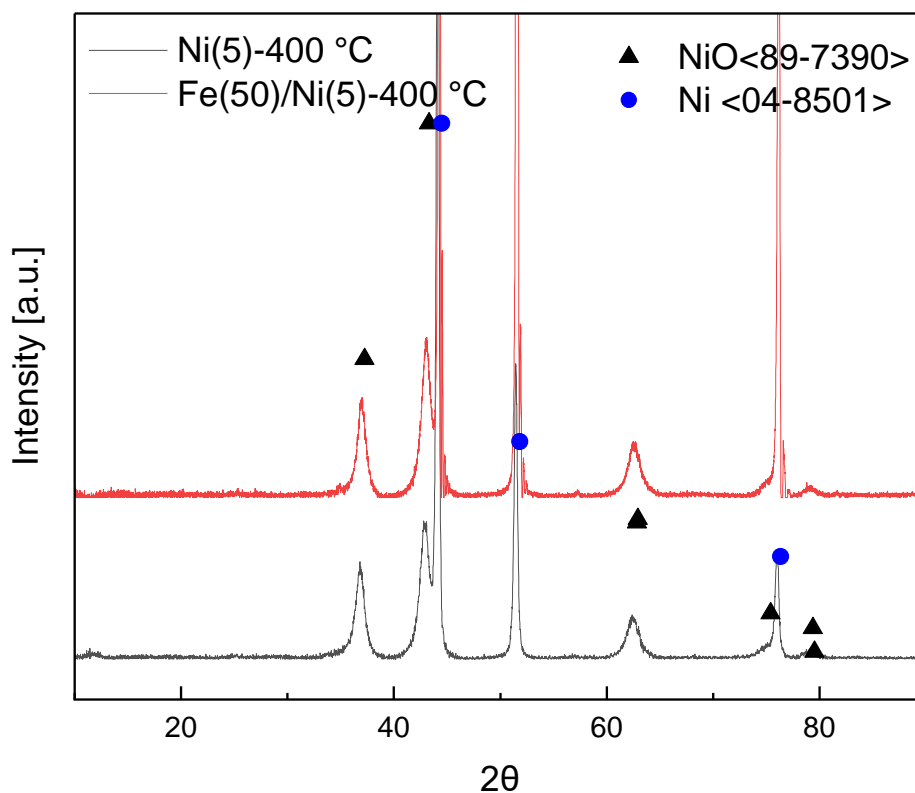


Figure S7: XRD diffraction pattern of Ni(5)-400 °C and Fe(50)/Ni(5)-400°C electrode with a scan rate of 2°/min. The Ni (JCPDS. 04-0850) and NiO(JCPDS. 89-7390) reference pattern was superimposed. XRD patterns of the Fe(50)/Ni(5)-400°C electrode have slightly lower NiO peak. Any other peak cannot be observed.

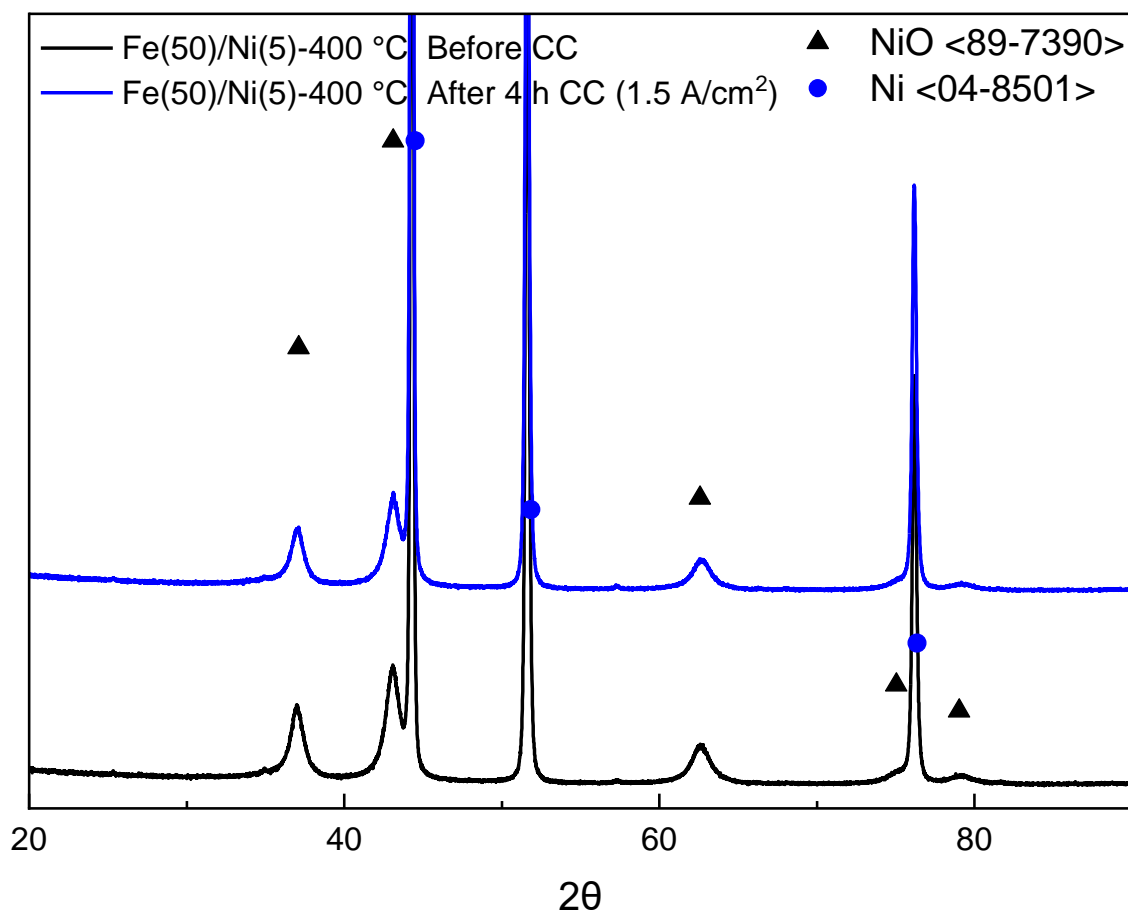


Figure S8: XRD diffraction pattern of the Fe(50)/Ni(5)-400 °C electrode, before reaction and after CC(1.5 A/cm² in 25 °C 1 M KOH) reaction with a scan rate of 2°/min.

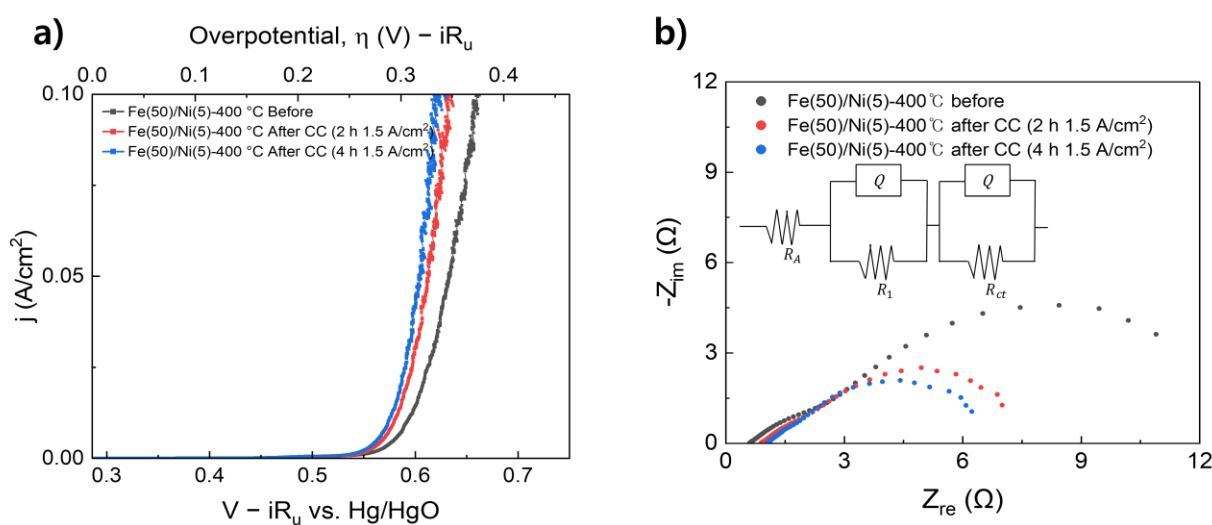


Figure S9: a) I-V curves of Fe(50)/Ni(5)-400 °C with a scan rate of 0.2 mV/s. b) EIS spectra of Fe(50)/Ni(5)-400 °C at bias potential of 580 mV, measured before and after CC (1.5 A/cm²) operation.

Fig. S9 shows the I-V curve and EIS spectra of the Fe(50)/Ni(5)-400 °C electrode. The Nyquist plot is interpreted as the existence of two small semicircles, which means that the electrode surface is porous. Reflecting this, the equivalent circuit includes two pairs of CPE-resistor sets. In Table. S2, the electric property of elements are calculated and summarized. In Fig.S9 a), the phenomenon that the activity improves as the constant current operation is performed is consistent with the decrease in the diameter of the semicircle and the decrease in the size of R_{ct} .

Table S2. Simulated parameters of the elements in equivalent circuits for OER of Fe(50)/Ni(5)-400°C

Fe(50)/Ni(5) -400°C	R_u (Ω)	R_{ct} (Ω)	Q_1		R_2 (Ω)	Q_2	
			Q_1	n_1		Q_e	n_2
before CC	0.599	2.90	0.830	0.556	10.8	0.232	0.864
after 2 h	0.900	1.69	0.133	0.567	5.30	0.261	0.866
after 4 h	1.06	0.967	0.154	0.610	5.10	0.248	0.843

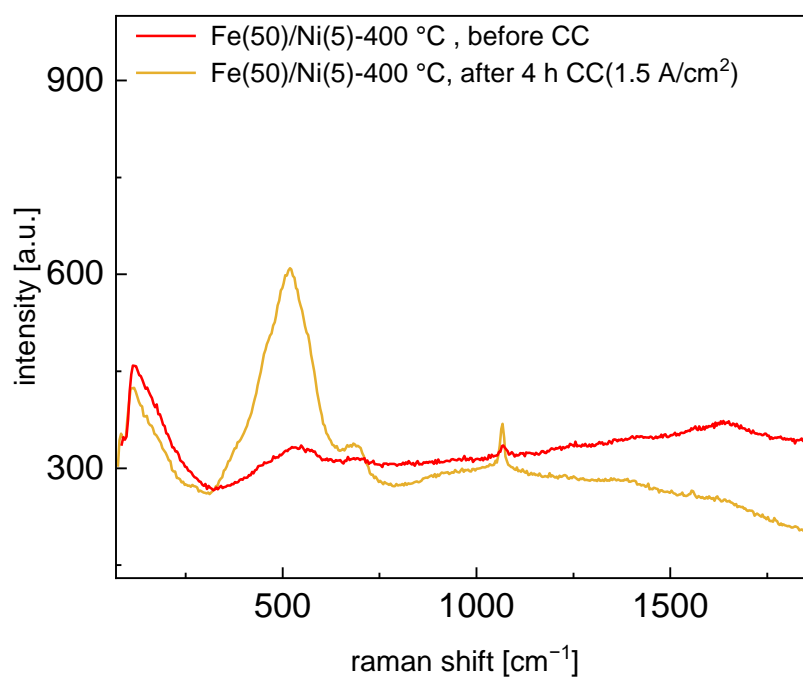


Figure S10: Raman spectroscopy of the Fe(50)/Ni(5)-400 °C electrode, before reaction and after CC(1.5 A/cm² in 25 °C 1 M KOH) reaction with 532 nm excitation.

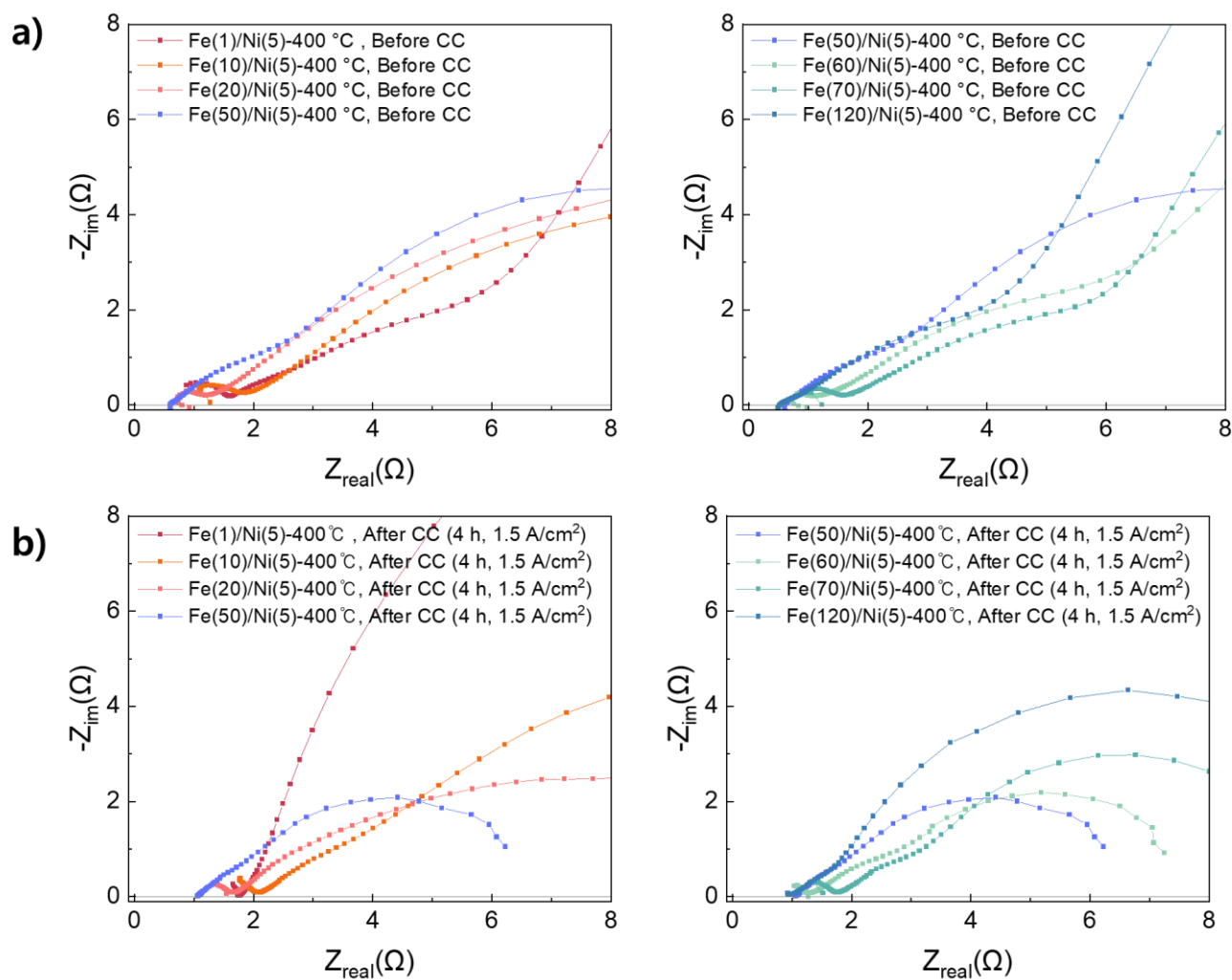


Figure S11: EIS spectra of Fe(y)/Ni(5)-400 °C ($y = 1, 10, 20, 50, 60, 70, 120$) at a bias potential of 580 mV, measured a) before and b) after CC (4 h, 1.5 A/cm²) operation.

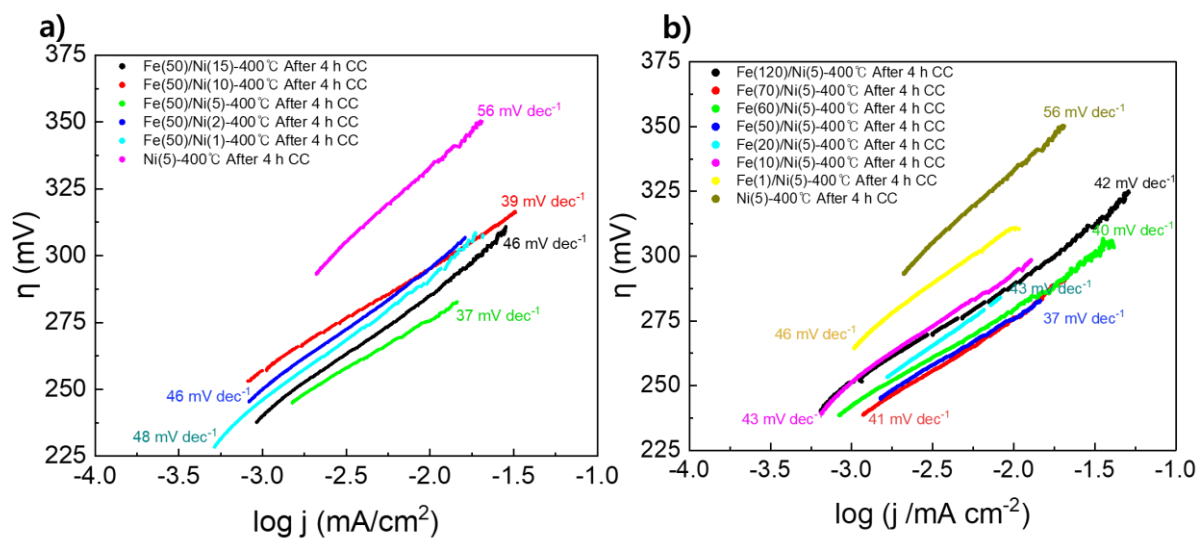


Figure S12: Tafel slope of 400°C-calcined electrodes obtained after 4 h of OER CC(1.5 A/cm²) operation.

References

1. Jung, S.; McCrory, C.C.L.; Ferrer, I.M.; Peters, J.C.; Jaramillo, T.F. Benchmarking Nanoparticulate Metal Oxide Electrocatalysts for the Alkaline Water Oxidation Reaction. *J Mater Chem A Mater* **2016**, *4*, 3068–3076, doi:10.1039/c5ta07586f.
2. Zhang, B.; Lui, Y.H.; Zhou, L.; Tang, X.; Hu, S. An Alkaline Electro-Activated Fe-Ni Phosphide Nanoparticle-Stack Array for High-Performance Oxygen Evolution under Alkaline and Neutral Conditions. *J Mater Chem A Mater* **2017**, *5*, 13329–13335, doi:10.1039/c7ta03163g.