Supporting Information

Unveiling the Anode Reaction Environment in a CO_2 Electrolyzer to Provide a Guideline for Anode Development

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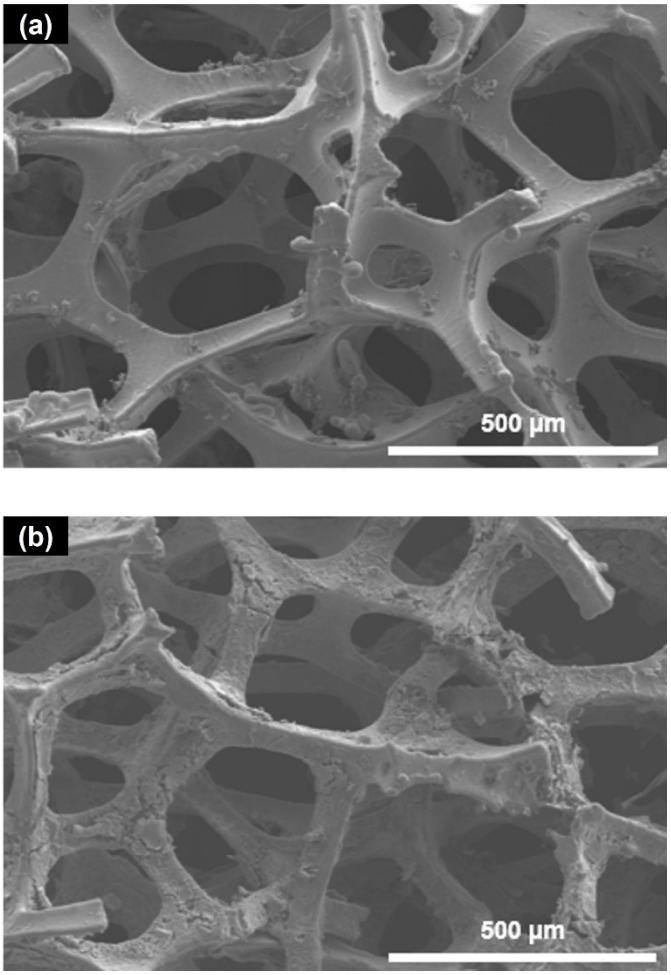


Figure S1. SEM images of (a) Ni-F and (b) NiFe-F at low magnification (x100).

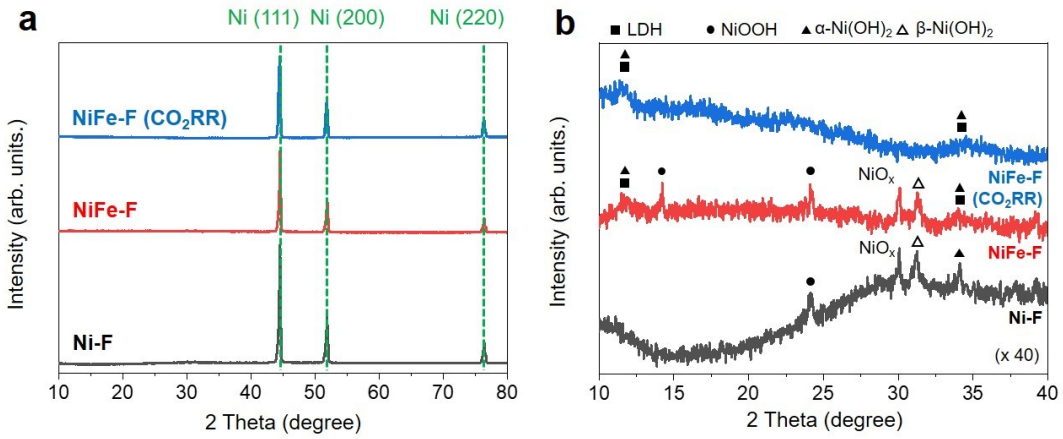


Figure S2. XRD patterns of Ni-F, NiFe-F and NiFe-F collected after CO_2RR in the range of (a) 10-80° (2 theta) and (b) 10-40° (2 theta).

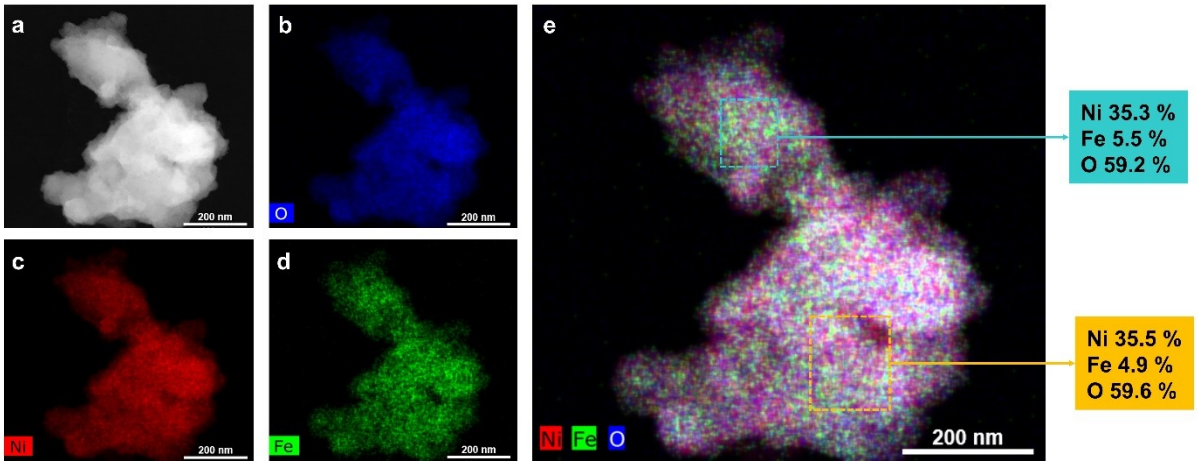
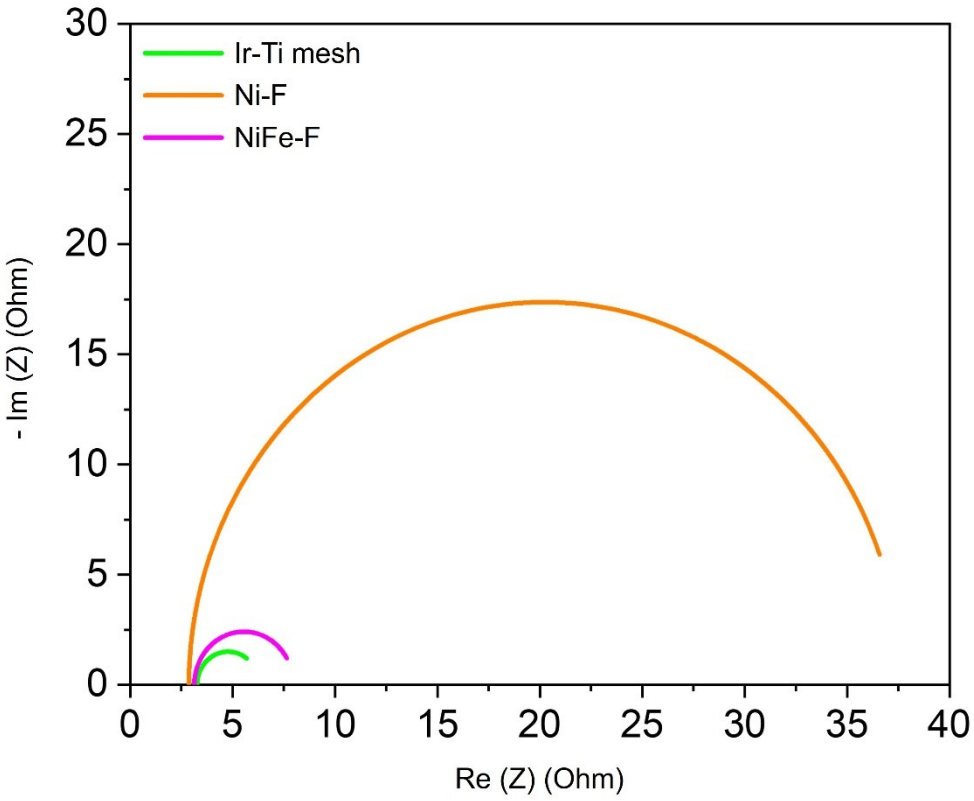


Figure S3. EDS elemental mapping images of NiFe-F using TEM. (a) HAADF image, (b) O element, (c) Ni element, (d) Fe element, (e) overlapped image and elemental composition comparison between different points. (x160k magnification)



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70 **Figure S4.** EIS Nyquist plots of Ir-Ti mesh, Ni-F, and NiFe-F in neutral (CO_2-purged 1 M

71 KHCO3) electrolyte, performed at 1.63 V (vs. RHE) under a frequency range from 100 kHz to

72 1 Hz.

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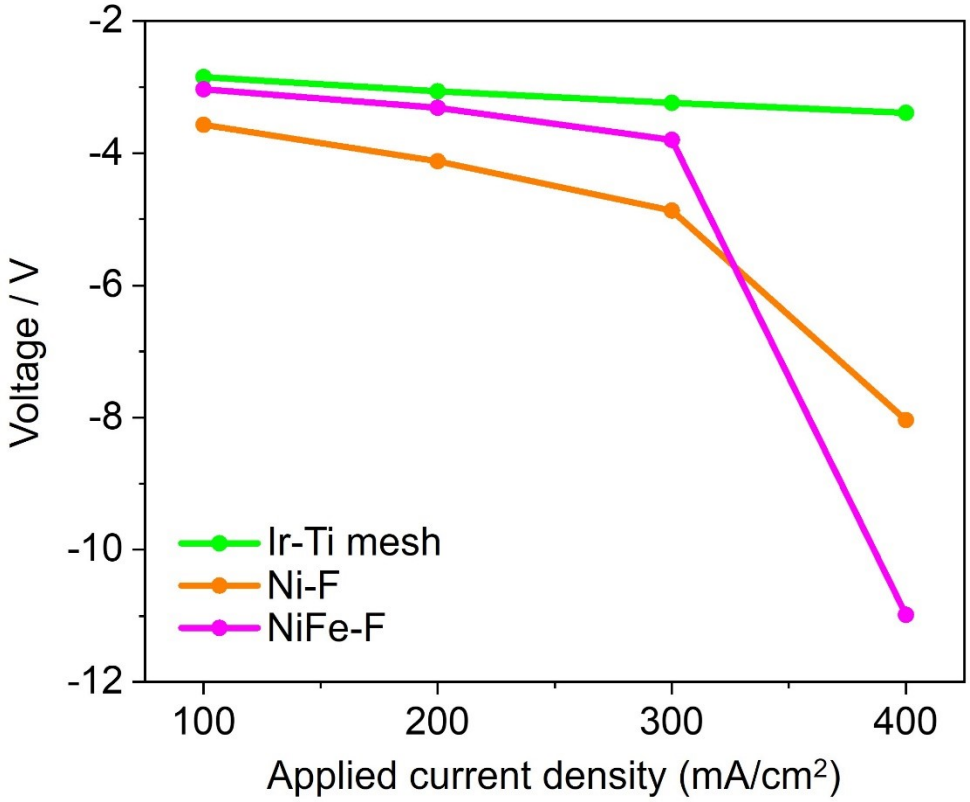
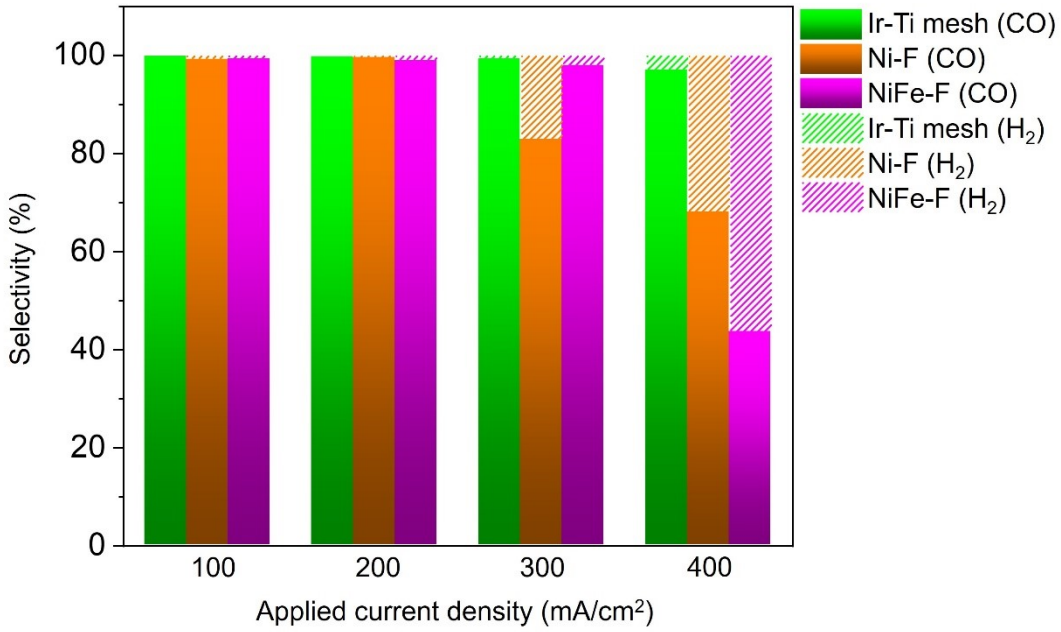


Figure S5. Cell voltages during zero-gap single cell neutral CO_2RR for each type of anode used, plotted as a function of applied current density (Figure 2b).



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88 **Figure S6.** Selectivities for CO and H_2 at each applied current densities during zero-gap single

89 cell neutral CO_2RR.

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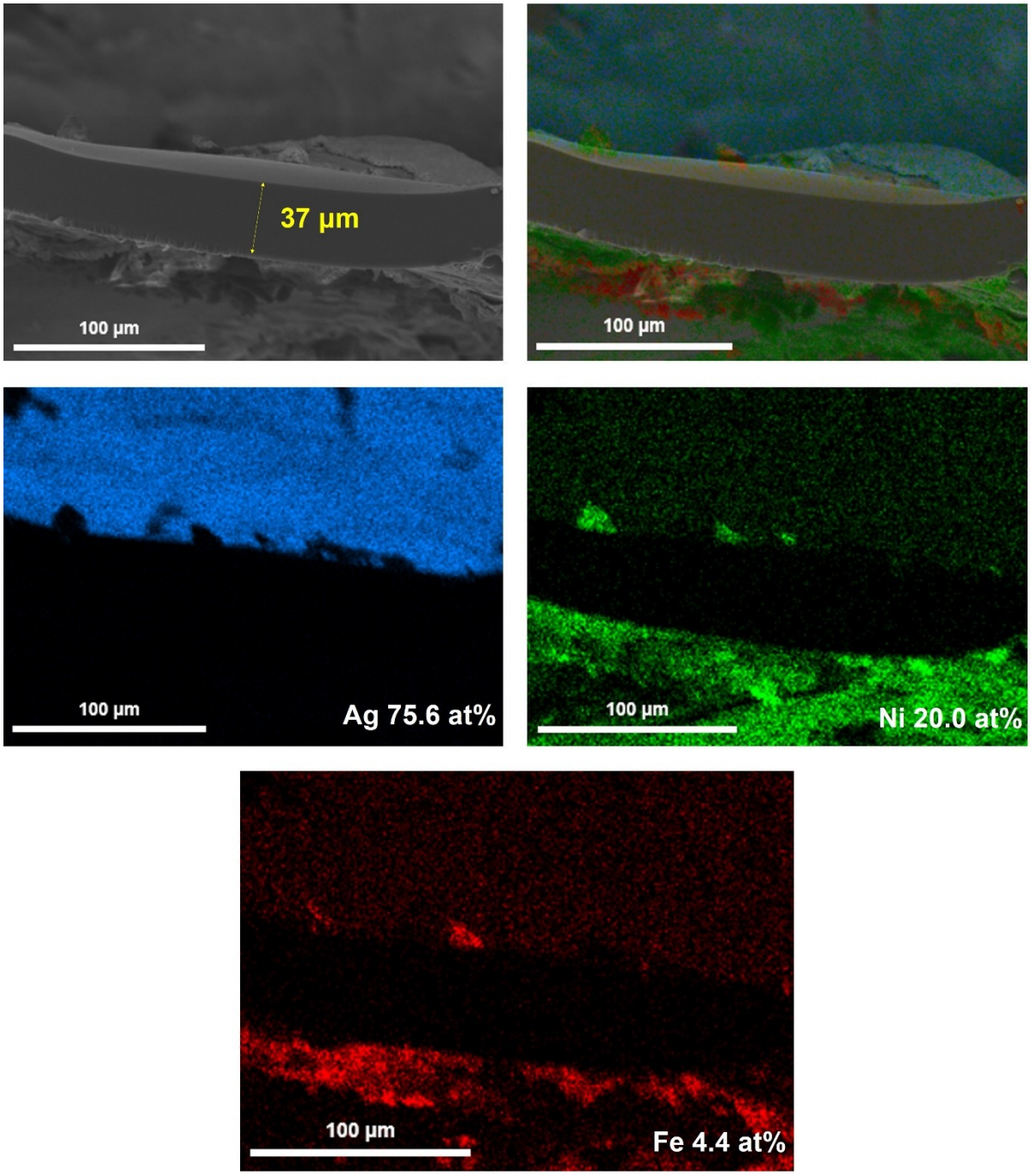
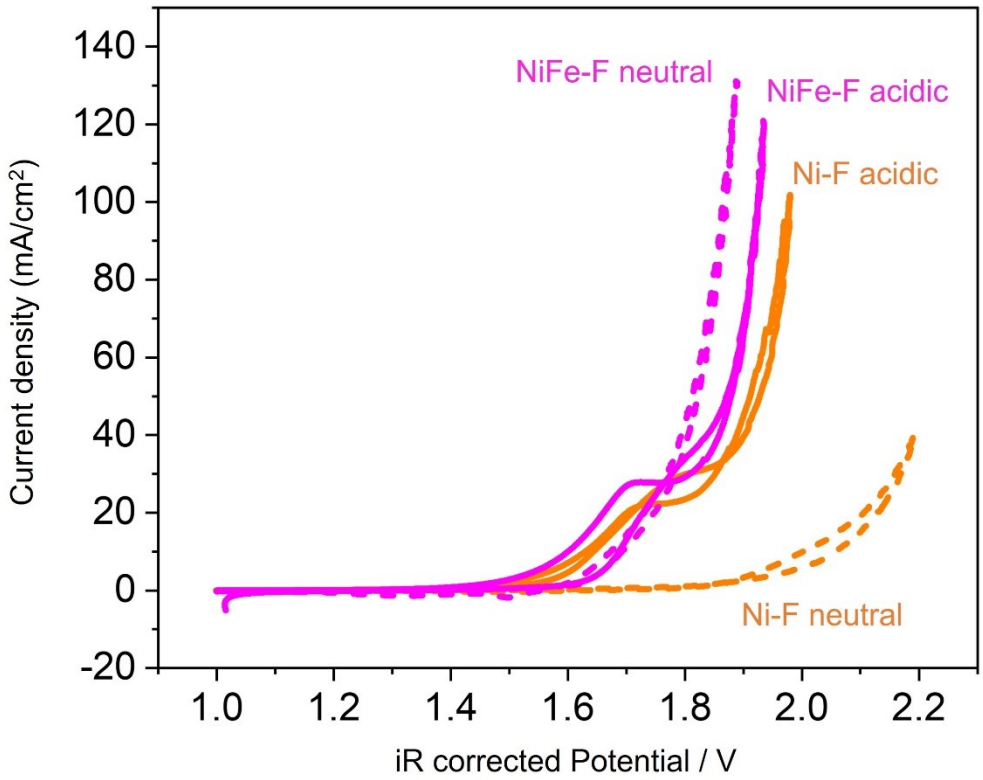


Figure S7. EDS mapping on Ag, Ni, and Fe over the cross-section of the AEM collected after CO_2RR reaction using SEM. NiFe-F was used as the anode (Blue: Ag, Green: Ni, Red: Fe).



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110 **Figure S8.** Half-cell OER activity of Ni-F and NiFe-F electrodes in acidic electrolyte (pH 2,

111 mixed solution of 0.5 M H_2SO_4 and 1 M $KHCO_3$). Scan range was 1.0 – 2.3 V (vs. RHE) and

112 scan rate was 2 mV/s. (Dotted lines: CV curves during neutral OER)

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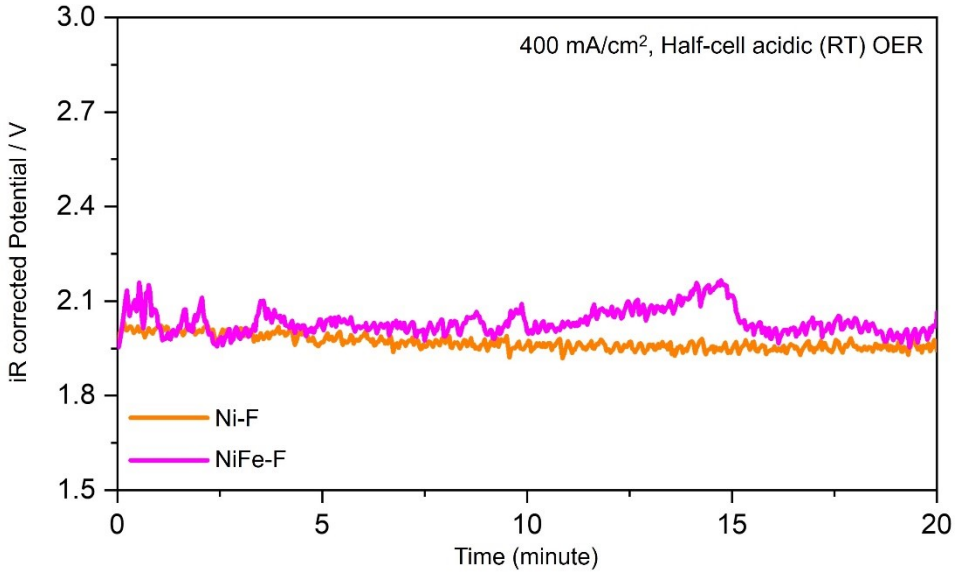

Figure S9. CP measurements during half-cell OER activity of Ni-F and NiFe-F electrodes in acidic electrolyte (pH 2, mixed solution of 0.5 M H_2SO_4 and 1 M $KHCO_3$) at 400 mA/cm^2 for 20 minutes.

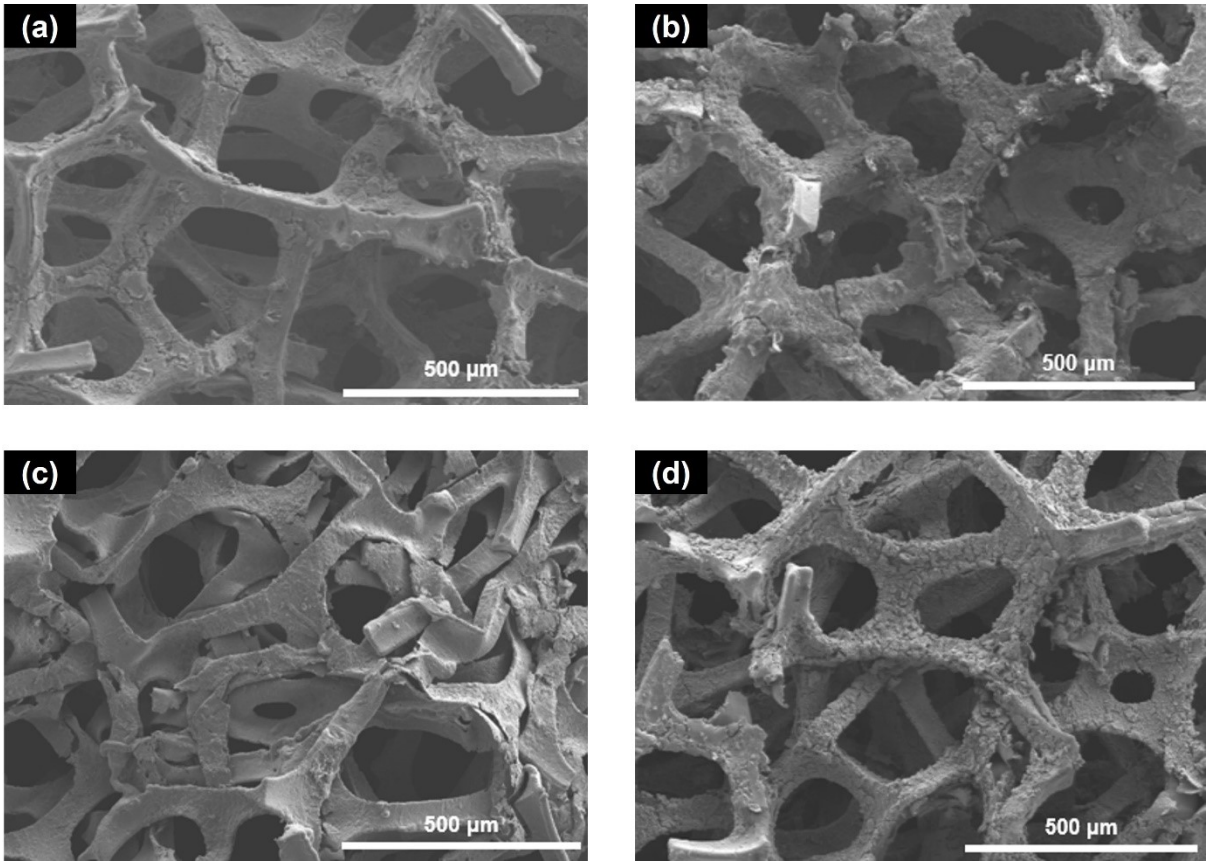

Figure S10. SEM images of NiFe-F electrodes (a) after electrochemical oxidation at 1 M KOH (alkaline activation), (b) after half-cell neutral OER, (c) after half-cell acidic OER, and (d) after CO_2RR single-cell activity test (x100 magnification).

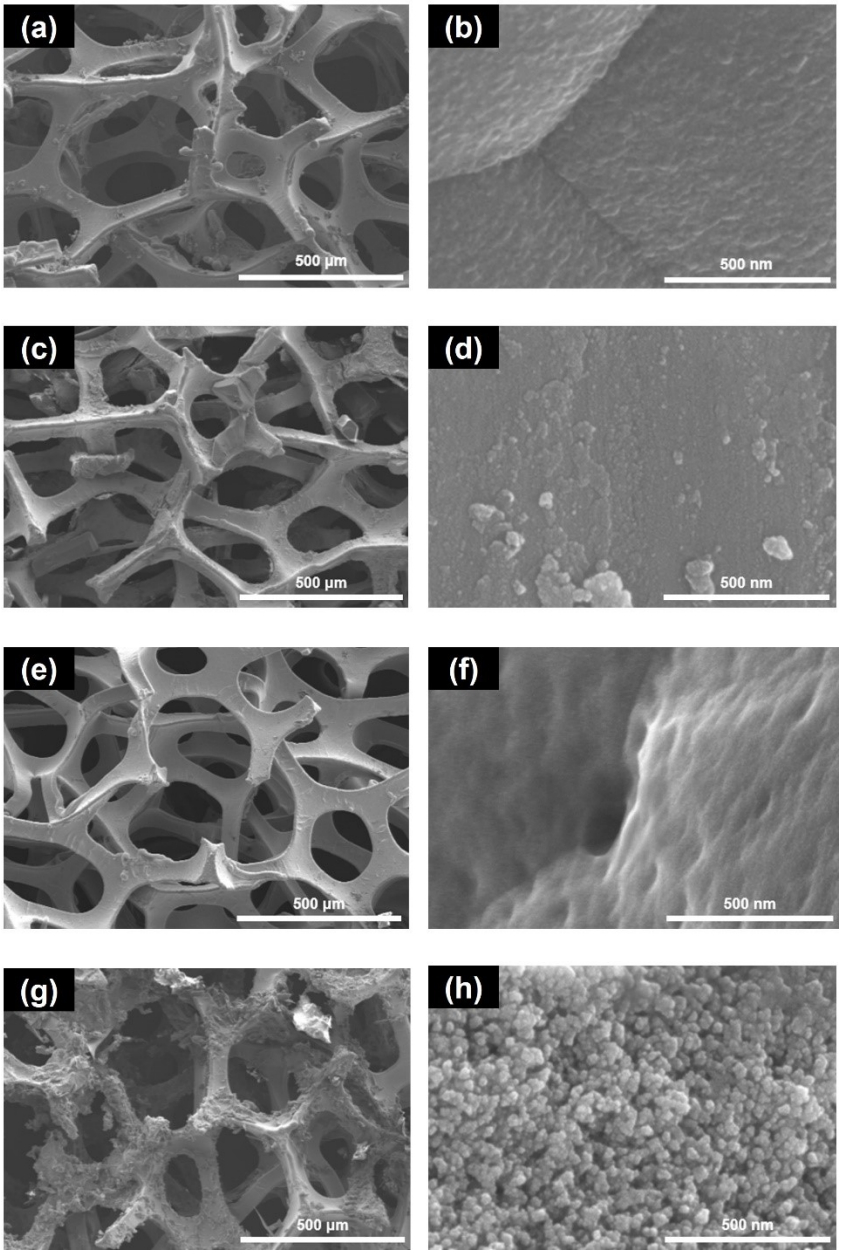

Figure S11. SEM images of Ni-F electrodes (a), (b) after electrochemical oxidation at 1 M KOH (alkaline activation), (c), (d) after half-cell neutral OER, (e), (f) after half-cell acidic OER, and (g), (h) after CO_2RR single-cell activity test. ((a), (c), (e), (g): x100 magnification) ((b), (d), (f), (h): 100k magnification)

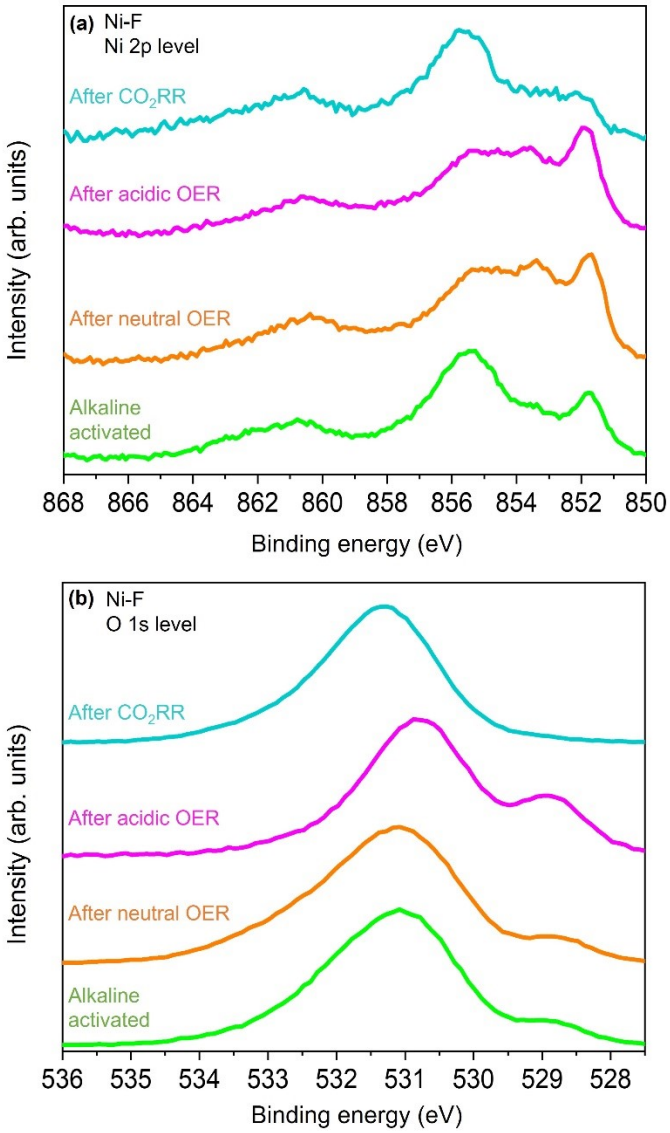

Figure S12. XPS spectra of Ni-F electrodes after alkaline activation, neutral OER, acidic OER, CO_2RR, (a) Ni 2p level and (b) O 1s level.

Table S1. Half-cell neutral OER overpotentials for each electrodes (Figure 1g)

Working electrode	**Overpotential (mV) at 100 mA/cm^2**
Ir-Ti mesh	637.6
Ni foam	827.0*
NiFe foam	640.6

* At 10 mA/cm^2

Table S2. ICP-OES analyses of the electrolytes after half-cell, half-cell acidic OER and CO_2RR MEA

Reactions	Anode	Ni (ppm)	Fe (ppm)	Ir (ppm)	Ag (ppm)
Half-cell OER*	Ni-F	1.2	-	-	-
Half-cell OER*	NiFe-F	4.6	< 1	-	-
Half-cell acidic OER*	Ni-F	56.4	-		
Half-cell acidic OER*	NiFe-F	70.5	3.3		
CO_2RR (MEA)**	Ni-F	20.4	-	-	n.d.
CO_2RR (MEA)**	NiFe-F	87.4	< 1	-	n.d.
CO_2RR (MEA)**	Ir-Ti mesh	-	-	< 1	n.d.

* Electrolytes collected after 20 minutes of OER operation at 400 mA/cm^2

** Electrolytes collected after CO_2RR operation at 400 mA/cm^2 (Figure 2b)

Table S3. ICP-OES analyses comparison between pristine Ni-F and alkaline activated Ni-F (dissolution rate comparison in acidic media)

Element	Pristine Ni-F (Ni^0)	Alkaline activated* Ni-F (Ni^{2+})
Ni (ppm)**	2.7	5.7

* Activated in 1 M KOH solution, at 2 V (vs. RHE) for 5 minutes (Reference electrode: Hg/HgO, Counter electrode: graphite)

** Analyzed after treating in $H_2SO_4/KHCO_3$ (~pH 2) solution, at 2 V (vs. RHE) for 2 minutes (Reference electrode: $Hg/HgSO_4$, Counter electrode: graphite)