Supplementary Information

The Goldilocks Electrolyte: Examining the Performance of Iron/Nickel Oxide Thin Films as Catalysts for Electrochemical Water Splitting in Various Aqueous NaOH Solutions.

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Table S1: Nomenclature of OER materials

% of Fe compound in initial paste	% of Ni compound in initial paste	Nomenclature
100	0	Fe100
90	10	Fe 90
75	25	Fe 75
50	50	Fe 50
25	75	Fe 25
10	90	Fe 10
0	100	Fe 0/ Ni 100

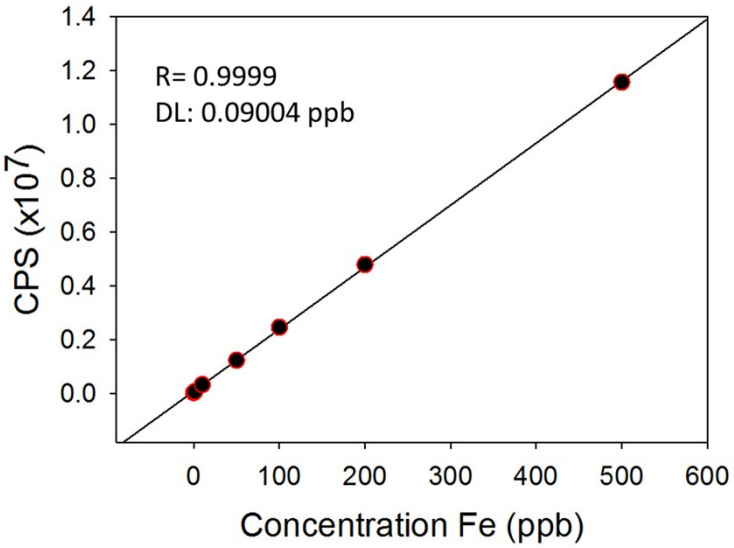


Figure S1. Inductive Coupled Plasma (ICP) calibration curve for the determination of the Fe concentration in the various electrolytes.

Table S2: Fe concentration in the NaOH electrolyte as determined by ICP.

Electrolyte	Fe concentration (ppb)
A	<1
B	5
C	102

Purification Procedure

1. The NaOH electrolyte(VWR, RECTAPUR grade ≥ 99%) containing a Fe content of 102 ppb was transferred into centrifuged tube containing precipitated nickel (II) sulfate heptahydrate (Sigma Aldrich, ≥99% metal basis, M. 280.86 g/mol). Prepared similarly to previously reported in the literature.[1]
2. The nickel hydroxide and NaOH solution was shaken until the nickel hydroxide was fully dispersed in the electrolyte.
3. The solution was left over night and centrifuged the following morning.
4. The electrolyte was only kept for a maximum of 2 days.

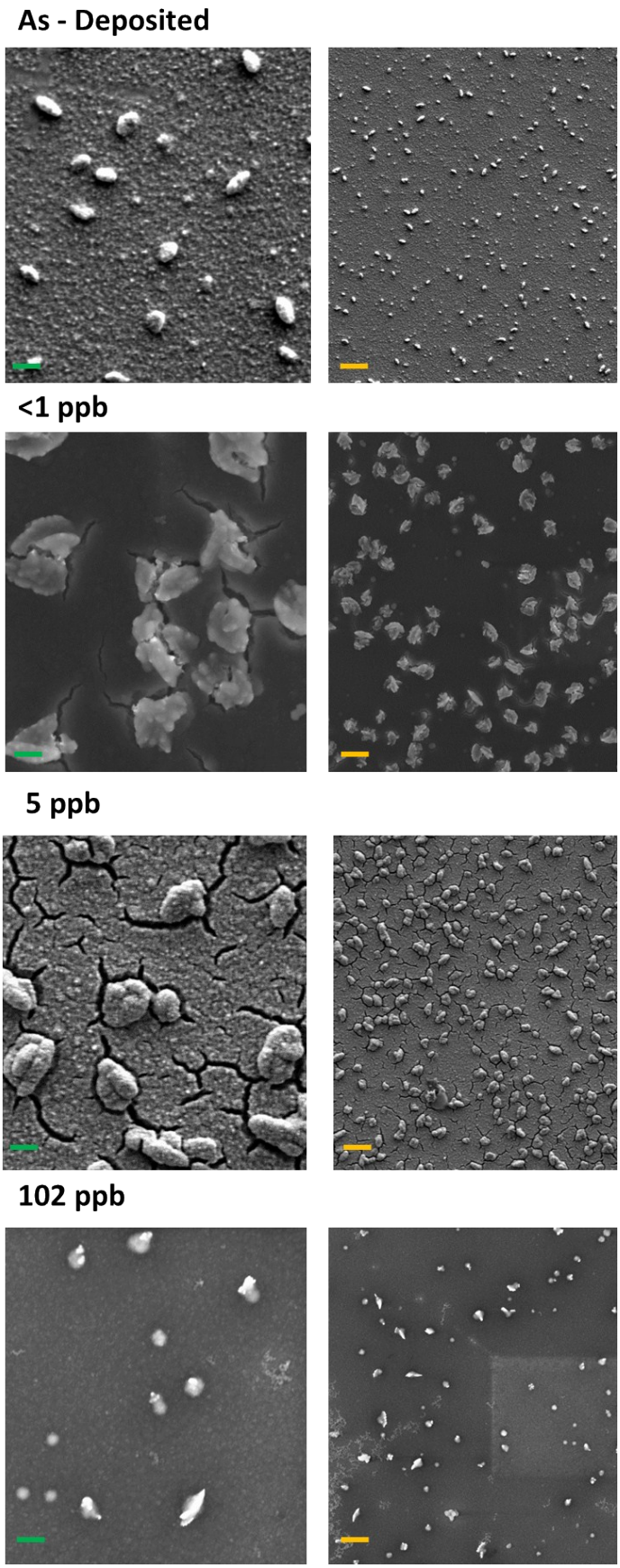


Figure S2: SEM images at a magnification of 200 nm (green scale bar) and 1 µm (orange scale bar) for the Fe 0/ Ni 100.

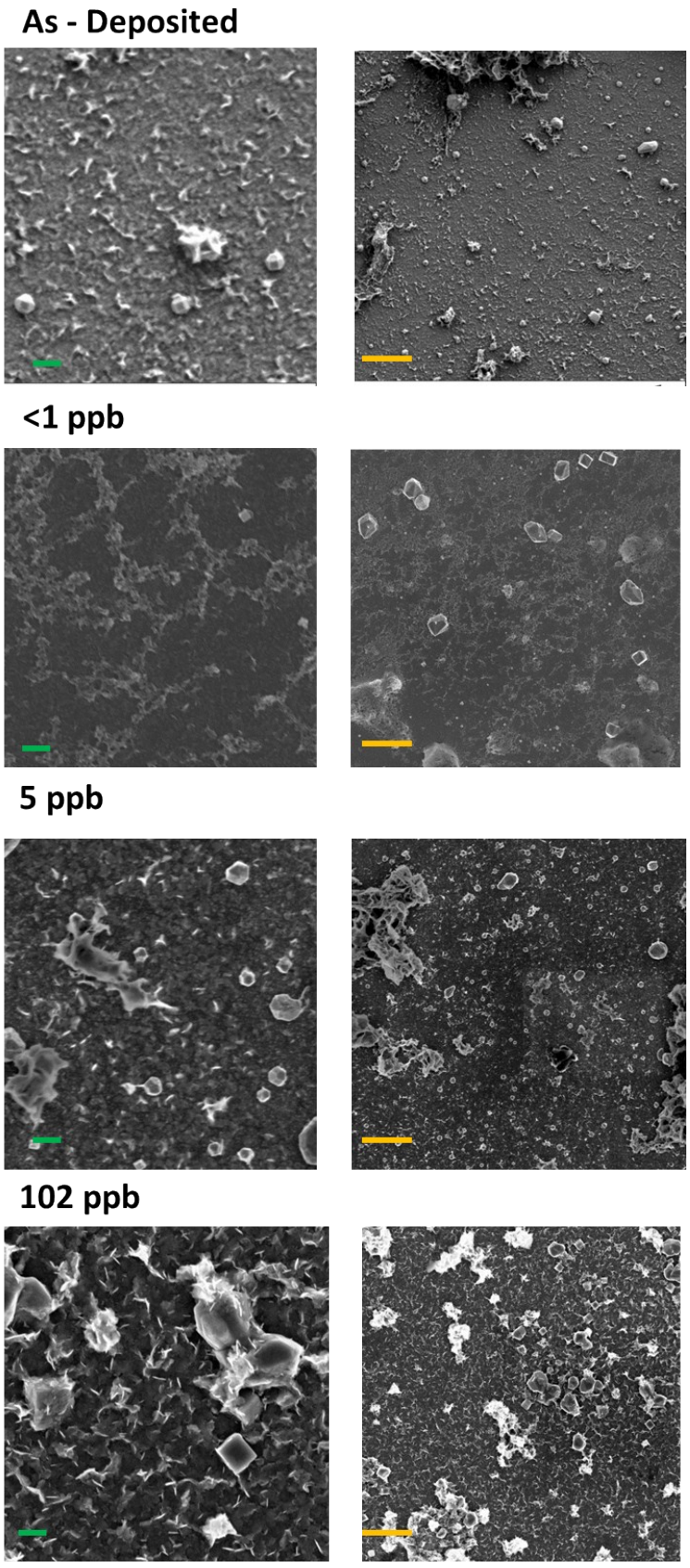


Figure S3: SEM images at a magnification of 200 nm (green scale bar) and 1 µm (orange scale bar) for the Fe 100.

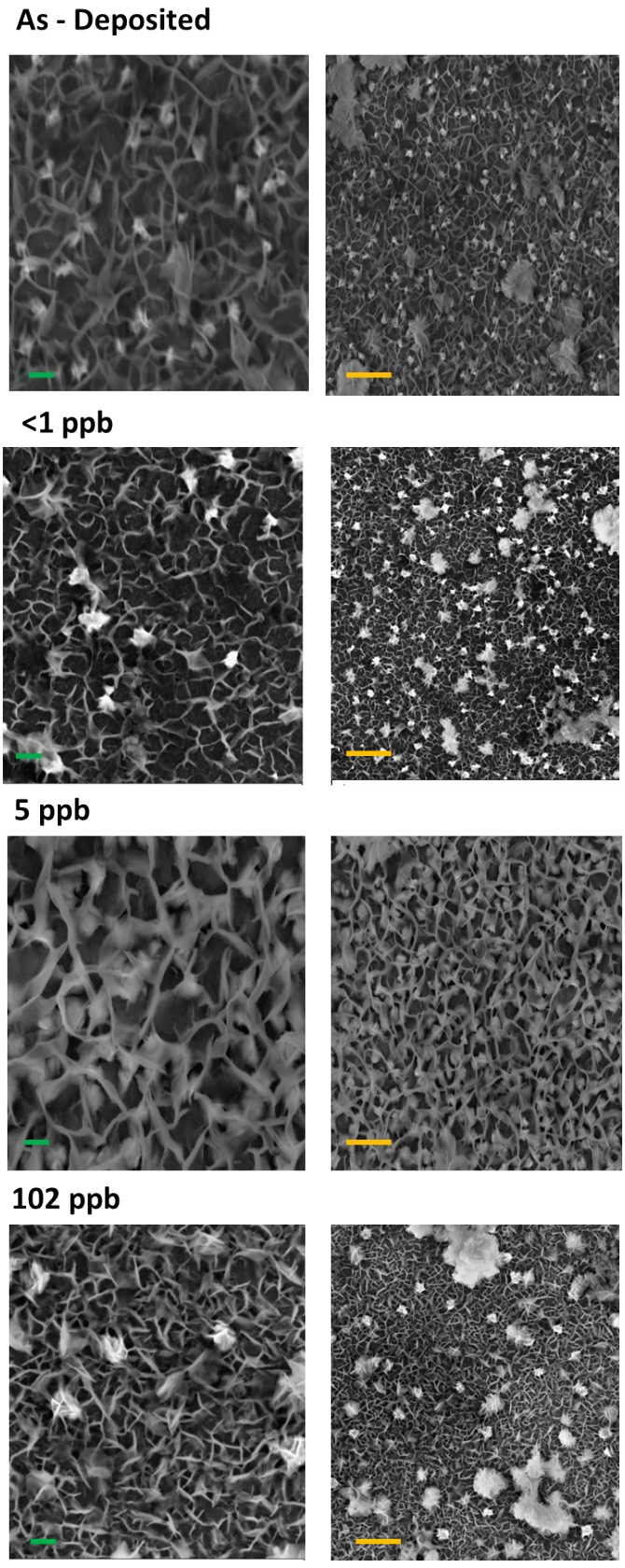


Figure S4: SEM images at a magnification of 200 nm (green scale bar) and 1 µm (orange scale bar) for the Fe 50.

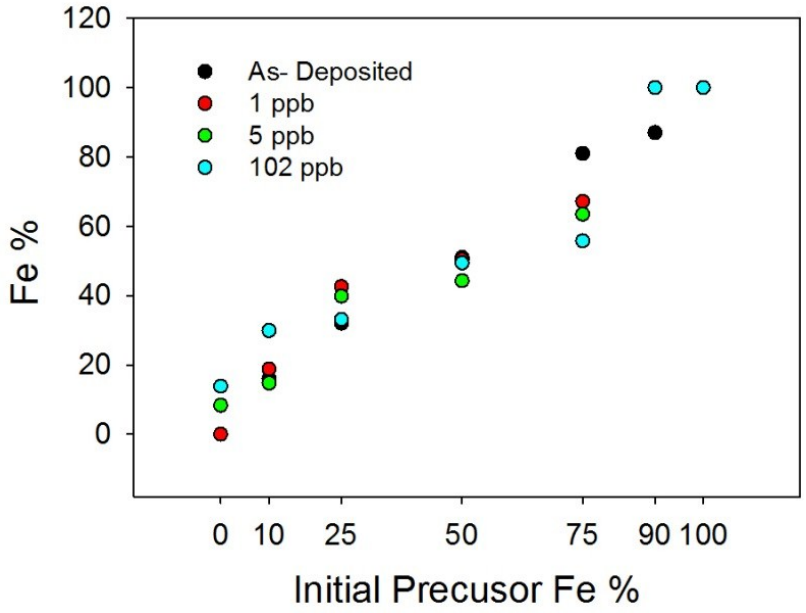


Figure S5: Electrode surface Fe concentration of all catalysts after OER in the 1 ppb, 5 ppb and 102 ppb NaOH electrolytes as determined by XPS.

Table S3: Electrode Surface Fe concentration values in Figure S5. Total Fe concentration vs. Total Ni concentration. The before and after OER Fe percentage determined on the basis of depositing solution proportions.

Initial Fe %	As-Dep (%)	1ppb (%)	5ppb (%)	100ppb (%)
100	100	100	100	100
90	87	100	100	100
75	81	67	63	55
50	51	50	44	49
25	32	42	39	33
10	16	18	14	29
0	0	1-2	13	13

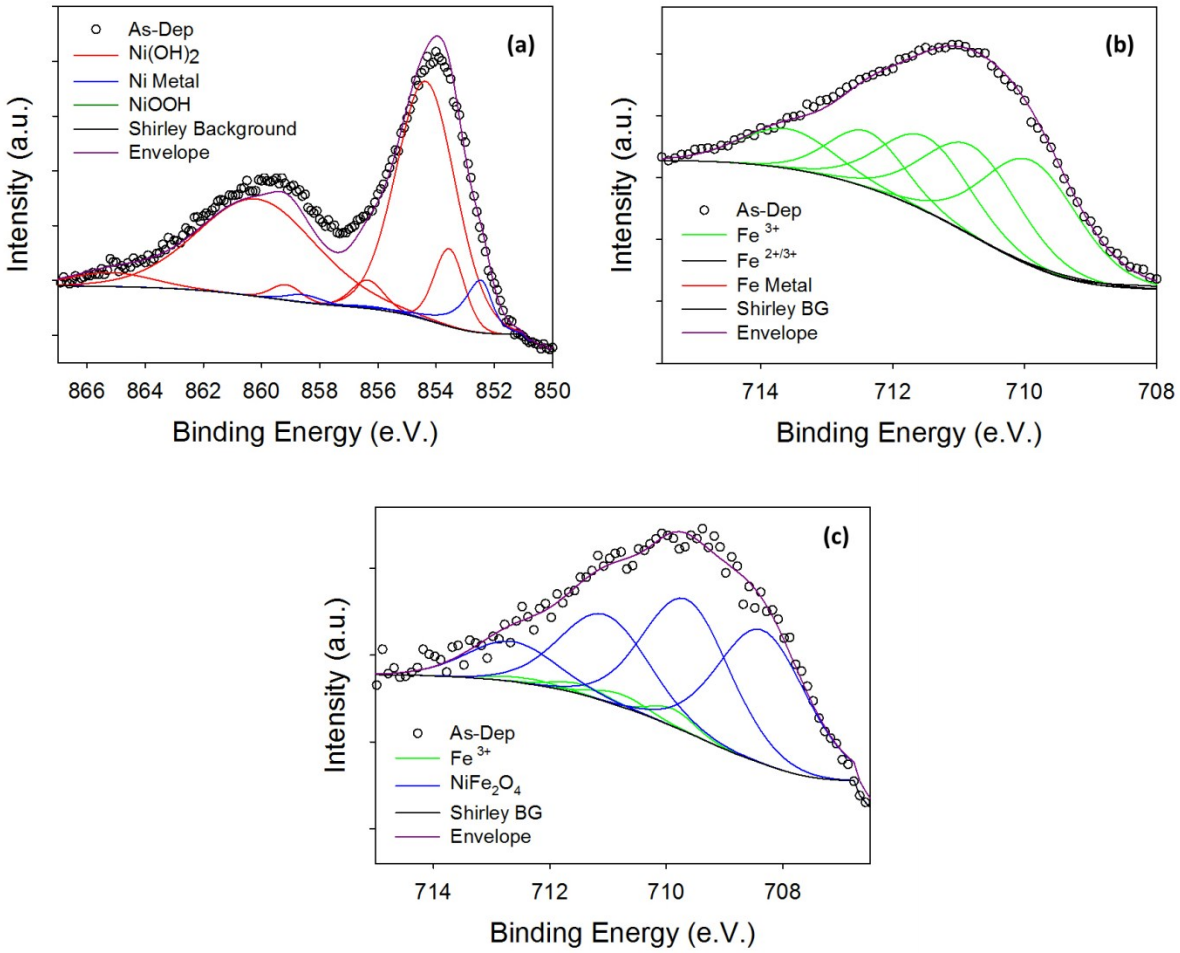


Figure S6. XPS Ni $_{2p}$ core level analysis of (a) Fe 0/ Ni 100 and the Fe $_{2p}$ core level analysis of (b) Fe 100 and (c) Fe 50.

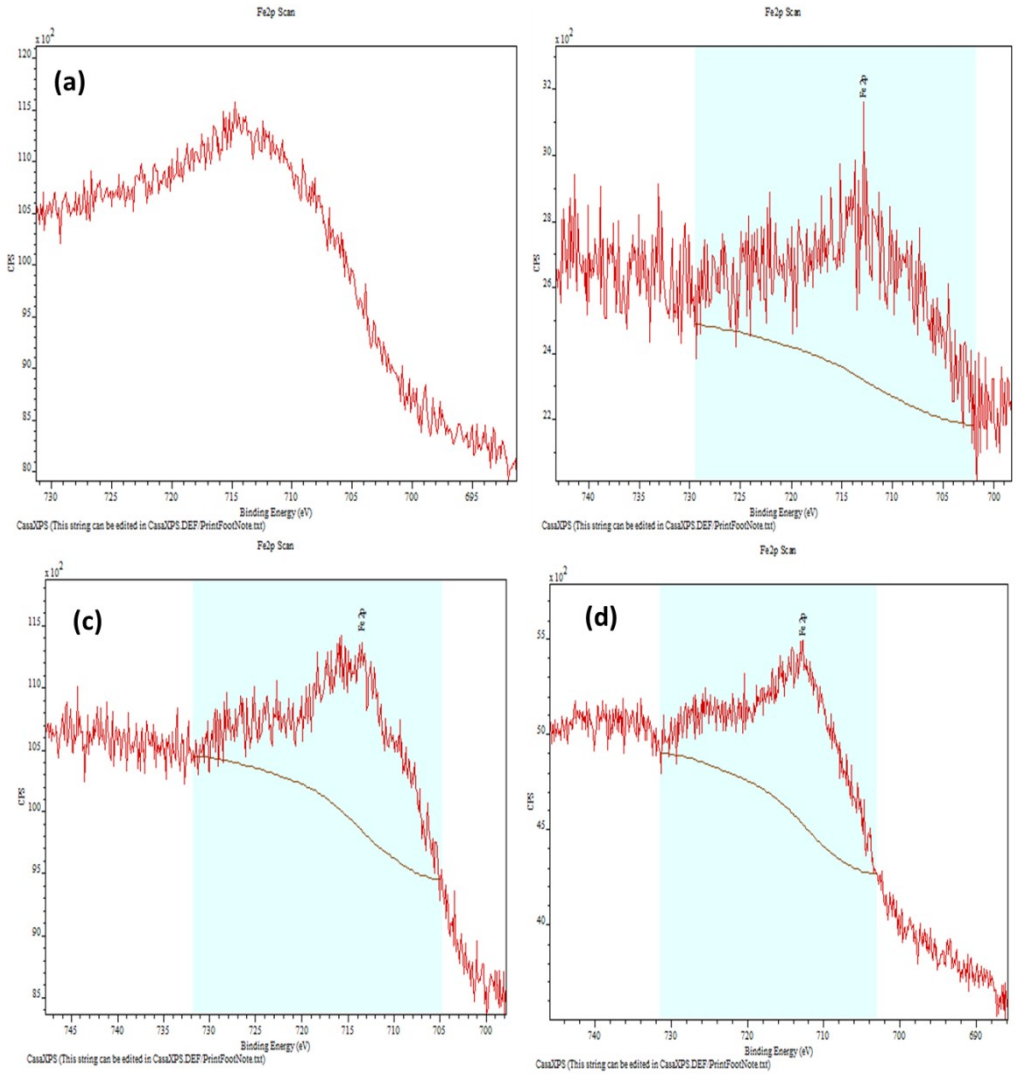


Figure S7. XPS of the Fe $2p_{3/2}$ core level for the Fe 0/ Ni 100 catalysts in the NaOH electrolyte with an Fe concentration of (a) as-deposited (b) 1 ppb (c) 5 ppb and (d) 102 ppb. These graphs are extracted for the Casa XPS software to illustrate the difference between the as-deposited film and the films after OER, which shows that after OER Fe can be detected by the presence of two peaks instead of one across the binding energy range of 700-730 eV. Raw data from Casa is shown here as it is easier to observe the new iron peaks than in the otherwise used deconvoluted data format.

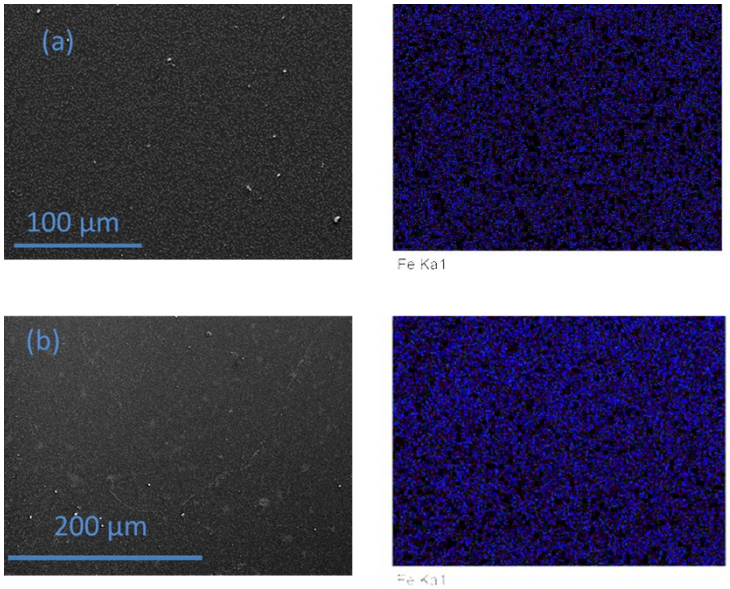
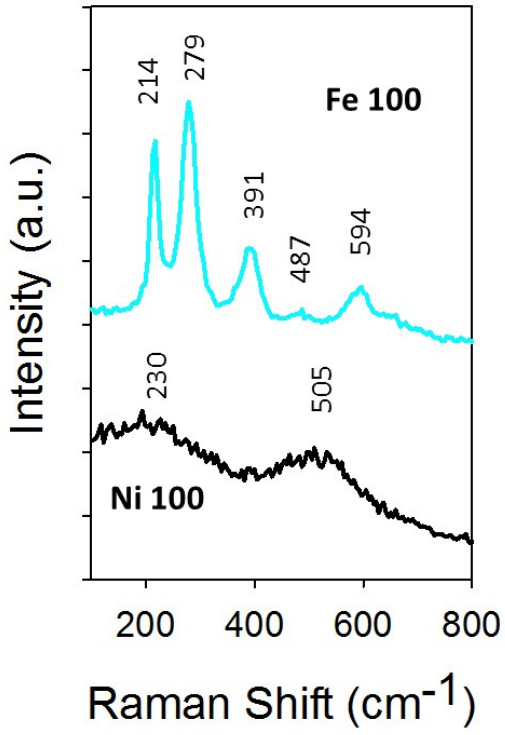


Figure S8. EDX- mapping of the Fe K alpha line for the Fe 0 / Ni 100 electrode after OER in NaOH with a Fe concentration of (a) 1 ppb and (b) 102 ppb



Wavenumber Fe 100	Mode	Ref
214	A_{1g}	2,3
279	E_g	2,3
391	E_g	2,3
487	A_{1g}	2,3
594	E_g	2,3
Wavenumber Ni 100	**Mode**	**Ref**
230	E_g	4
505	E_g	5

Figure S9. Raman spectra of the pure Fe 100 (cyan) and pure Ni 100/ Fe 0 (black) as-deposited catalysts

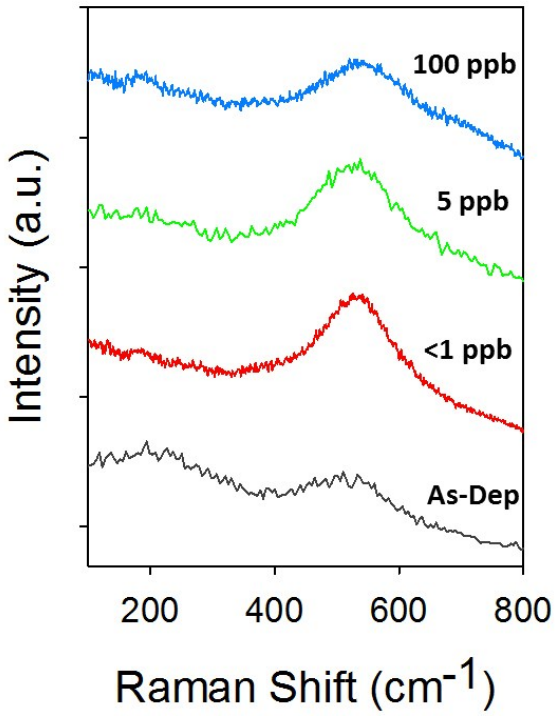


Figure S10. Raman spectra of the Fe 0/Ni 100 film in in the NaOH electrolyte with an Fe concentration of as-deposited (black), 1 ppb (red), 5 ppb (green) and 102 ppb (blue). No NiOOH is observed on any film after OER for any of the NaOH electrolytes.[6]

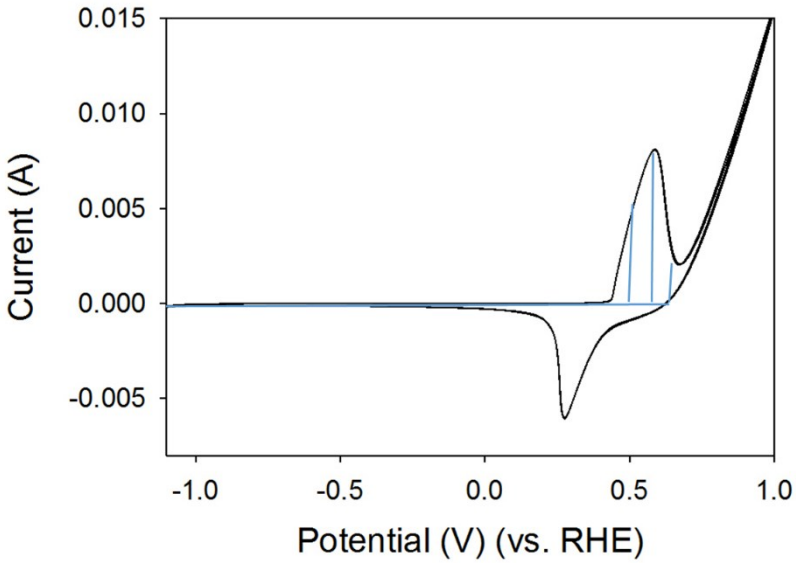


Figure S11. CV of Fe 0/ Ni 100 with the shaded region showing the potential limits from where the charge is calculated.

To investigate if certain parameters have an effect on the varying OER performances of the pure and mixed Ni/Fe oxide catalysts, the solution resistance and charge density of all the catalysts in each of the NaOH solutions were determined and compared against the overpotential at 10 mA cm^{-2} and TOF values, Figure S12-13.

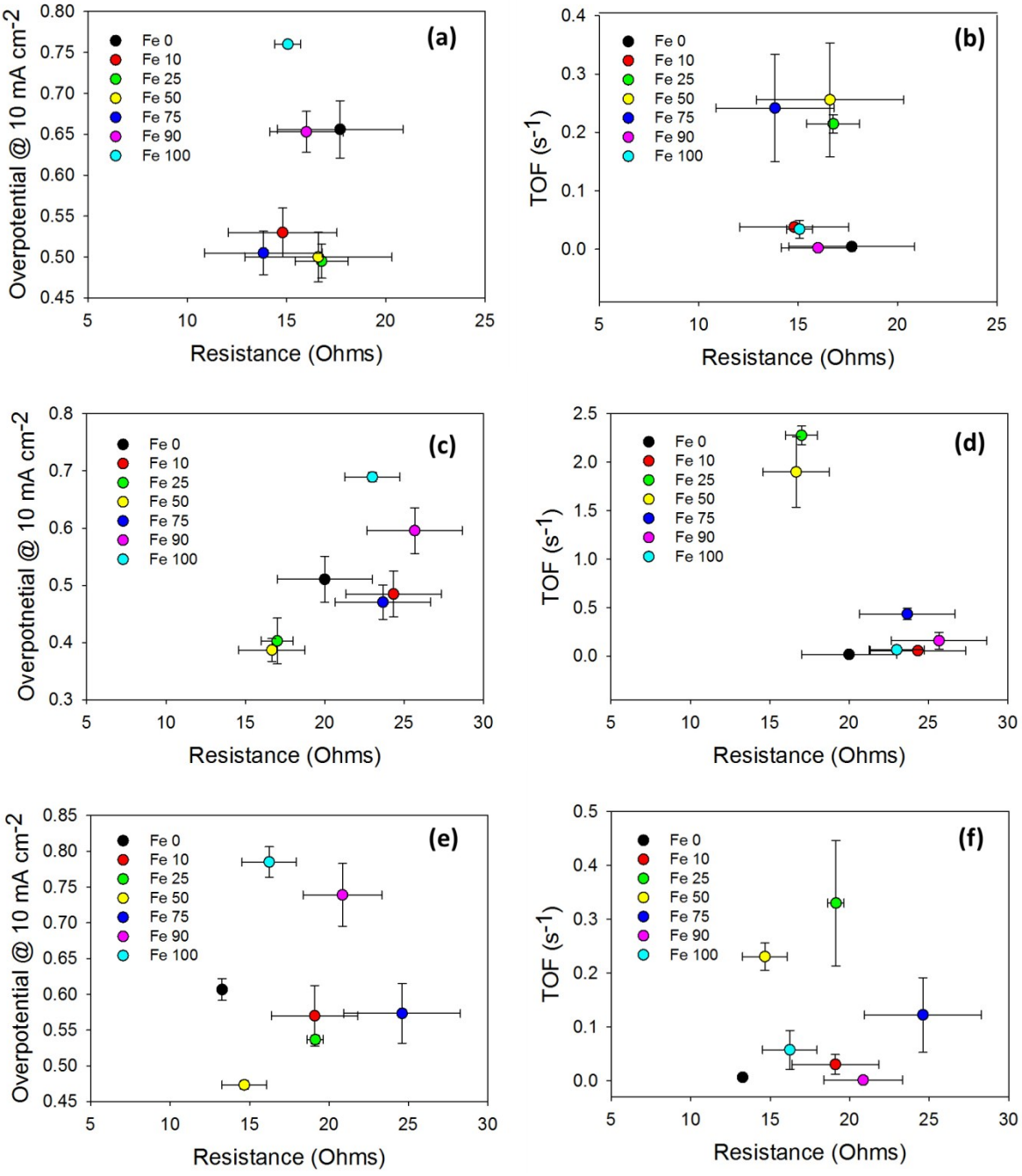


Figure S12. Solution resistance values for all catalysts compared to OER activity for NaOH 1 ppb compared to (a) overpotential at 10 mA cm^{-2} (b) TOF, for NaOH 5 ppb compared to (c) overpotential at 10 mA cm^{-2} (d) TOF and For NaOH 102 ppb compared to (e) overpotential at 10 mA cm^{-2} and (f) TOF.

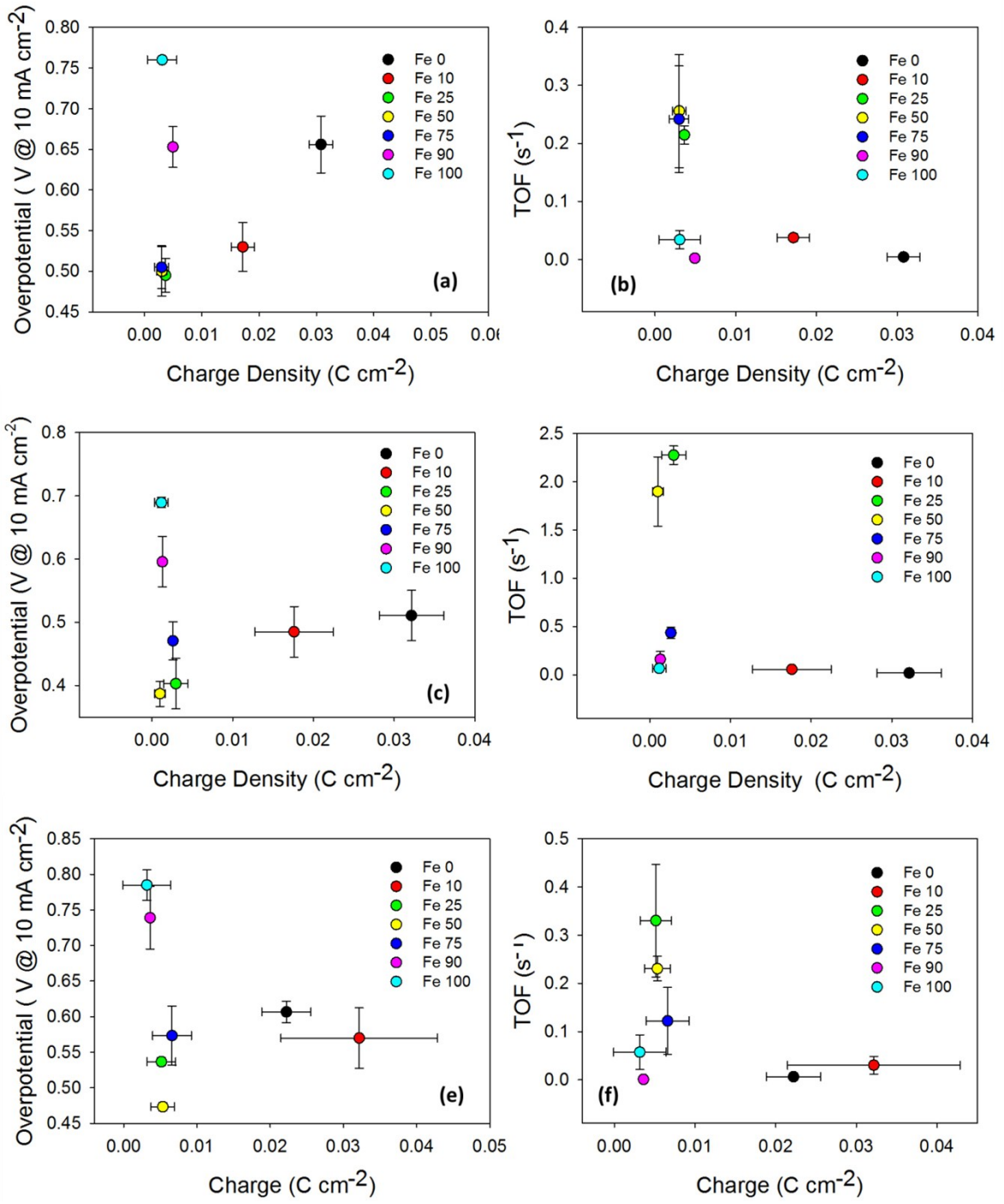


Figure S13. Charge density values for all catalysts compared to OER activity for NaOH 1 ppb compared to (a) overpotential at 10 mA cm^{-2} (b) TOF, for NaOH 5 ppb compared to (c) overpotential at 10 mA cm^{-2} (d) TOF and For NaOH 102 ppb compared to (e) overpotential at 10 mA cm^{-2} and (f) TOF.

Table S4: Ni species and oxidation state concentrations in the Fe 0/ Ni 100 sample in all electrolytes as determined by XPS.

Fe 0 sample	**Ni Metal (%)**	**$Ni(OH)_2$(%)**	**NiOOH (%)**
As-Deposited	Minor	Major	0
< 1 ppb	9	91	0
5 ppb	15	85	0
102 ppb	5	95	0

Table S5: Fe species and oxidation state concentrations in the Fe 100 samples in all electrolytes as determined by XPS.

Fe 100 sample	**Fe Metal (%)**	**Fe_3O_4 (%)**	**Fe_2O_3 (%)**
As-Deposited	0	12.74	87.27
< 1 ppb	0	11.26	88.74
5 ppb	26.51	59.61	13.87
102 ppb	9.62	67.87	22.52

Table S6: Fe/ Ni species and oxidation state concentrations in the Fe 50 sample in all electrolytes as determined by XPS.

Fe 50 sample	**Fe Metal (%)**	**$NiFe_2O_4$**	**Fe_2O_3 (%)**	**FeOOH (%)**
As-Deposited	0	Major	Minor	0
< 1 ppb	3.19	64.93	0	31.67
5 ppb	3.45	90.61	0	5.95
102 ppb	0	42.48	0	57.51

Table S7: Cost of Electrolyte

Electrolyte (99.99% purity)	**Euro per 500g (Sigma Aldrich – April 2016)**
NaOH	390
KOH	406

Table S8: Potential at 10 mA cm^{-2} vs. RHE for all the materials in this study.

Initial Fe %	**1 ppb (V)**	**5ppb (V)**	**102ppb (V)**
100	1.9900	1.9193	2.0150
90	1.8833	1.8257	1.9690
75	1.7300	1.7007	1.8033
50	1.7333	1.6170	1.7033
25	1.7267	1.6329	1.7667
10	1.7600	1.7150	1.8000
0	1.8860	1.7407	1.8367

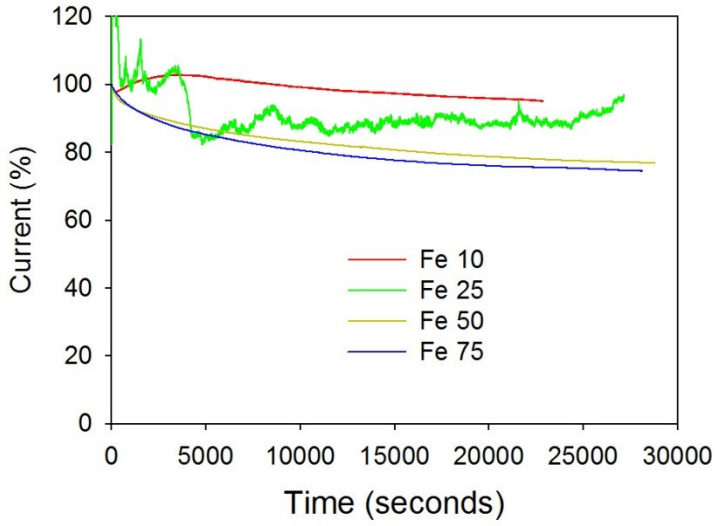


Figure S14. Stability tests for the optimum OER catalysts

References

(1) Trotochaud, L.; Young, S. L.; Ranney, J. K.; Boettcher, S. W. *J. Am. Chem. Soc.* **2014**, *136*, 6744-6753.

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