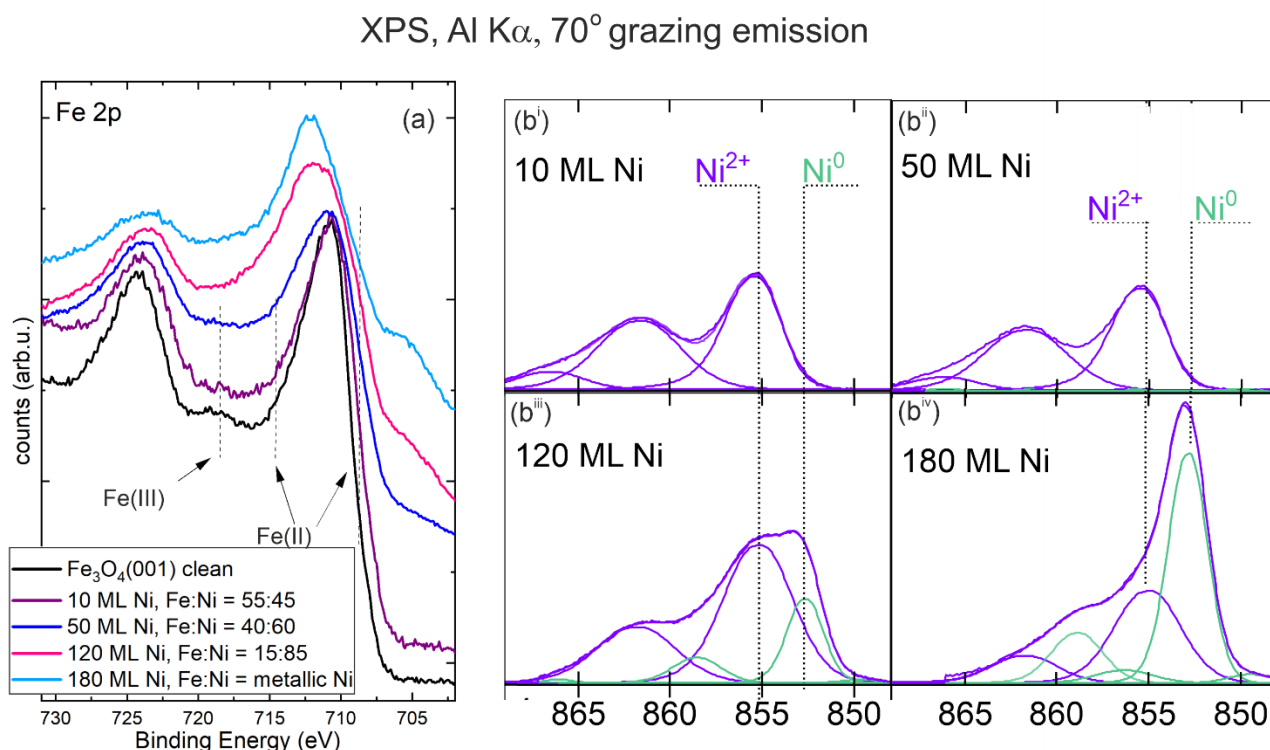


## Supporting Information

### Ni modified $\text{Fe}_3\text{O}_4(001)$ surface as a simple model system for understanding the Oxygen Evolution Reaction

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Figure S1



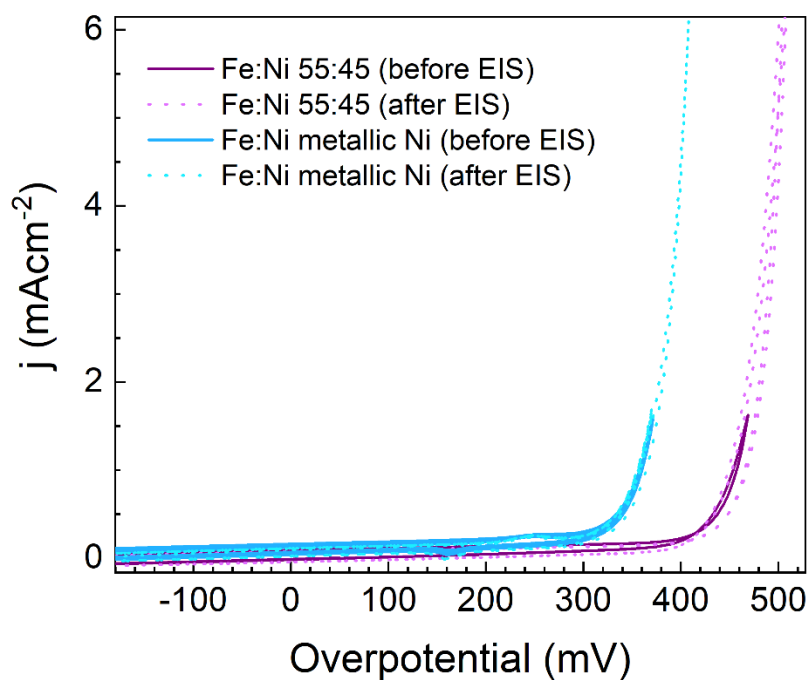
**Figure S1. XPS (Al  $K\alpha$ , 70° grazing emission) and corresponding fit.** (a) XPS spectra of the Fe 2p region after doping the  $\text{Fe}_3\text{O}_4(001)$ - $(\sqrt{2} \times \sqrt{2})R45^\circ$  surface with 10 ML Ni (purple), 50 ML Ni (blue), 120 ML Ni (pink), and 180 ML Ni (light blue). (b<sup>i</sup>)-(b<sup>iv</sup>) Fits of XPS spectra corresponding to the Ni 2p region shown in Figure 2a in the main text. The contribution from the Ni in the +2 state is shown in purple, whereas the contribution from the metallic Ni ( $\text{Ni}^0$ ) is displayed in green. The fits were obtained using the software CasaXPS.

The Fe 2p spectrum of the clean  $\text{Fe}_3\text{O}_4(001)$  surface is enriched in  $\text{Fe}^{3+}$  with respect to the bulk<sup>1</sup>, which is most evident in the appearance of a strong  $\text{Fe}^{3+}$  shake-up satellite at 718.5 eV<sup>2</sup>. Following 10 ML Ni doping, the overall intensity of the Fe 2p peak area is slightly attenuated and the  $\text{Fe}^{3+}$ -related satellite peak at 718.5 eV disappears, while the  $\text{Fe}^{2+}$ -related intensity at 715 eV increases. The enhancement of the  $\text{Fe}^{2+}$  in the surface region is also visible as an increased  $\text{Fe}^{2+}$  shoulder on the low-binding-energy side (at 708.1 eV) of the main  $2p_{3/2}$  peak<sup>2</sup>. The reduction of the surface Fe becomes more pronounced following progressively

higher Ni doping, with a systematic growth of the Fe<sup>2+</sup>-related<sup>2</sup> features. It must, however, be taken into account, that for high Ni-doping and especially when the metallic Ni starts forming onto the surface (120 ML and 180 ML Ni-doping), the interpretation of the Fe 2p spectra is not straightforward, due to the overlap with the Ni LMM Auger signals in the same region.

The Ni 2p XPS spectra is also rather complex, and has been often discussed in the literature<sup>3</sup>. We have attempted a fit (Figure S 1b<sup>i</sup>-b<sup>iv</sup>) using two contributions for the Ni in the 2+ state and two for the Ni in the metallic state (Ni<sup>0</sup>). The Ni 2p spectrum for the surfaces doped with 10 ML and 50 ML, shows only Ni<sup>2+</sup> contributions (purple fit in Figure S1 b<sup>i</sup>-b<sup>ii</sup>)<sup>4</sup>. For higher Ni-doping (120 ML), the fit in Figure S1 b<sup>iii</sup> shows an additional feature (green component), which is consistent with appearance on the surface of metallic feature<sup>3</sup>, coexisting with the Ni<sup>2+</sup>. Above 120 ML, the fit shows that the metallic Ni component dominates.

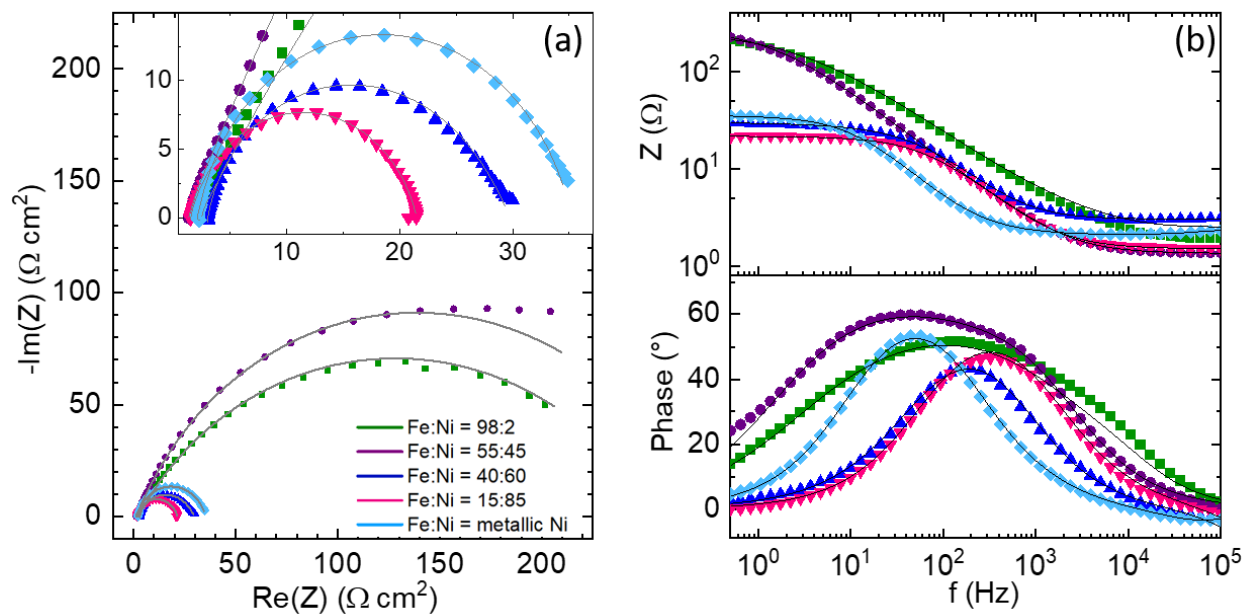
Figure S2



**Figure S2. CV curves of the Ni-modified magnetite surface before and after EIS measurements.** The figure shows the cyclic voltammetry of the Ni-doped Fe<sub>3</sub>O<sub>4</sub>(001) with a Fe:Ni ratio of 55:45 (purple) and the one covered in metallic Ni (light blue). The cyclic voltammograms were acquired in 1M NaOH, Ar atmosphere, and with a 10 mV/s scan speed before (solid line) and after (dotted line) EIS measurements.

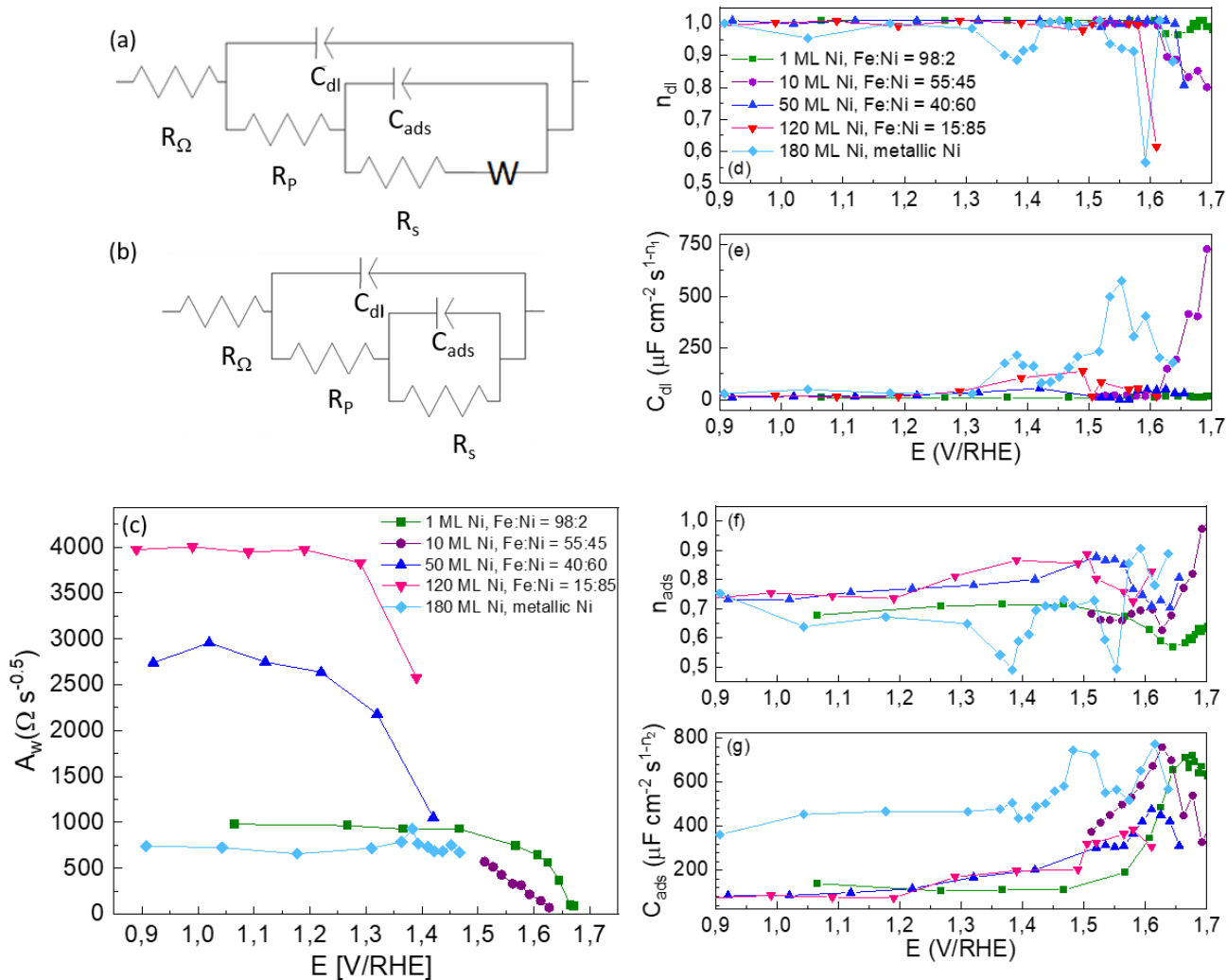
The stability of the Ni-doped magnetite was evaluated by recording CVs before measuring EIS up to more than 1 mA·cm<sup>-2</sup> (see Figure 6 in the main text) and afterwards. The same current densities were measured before (solid lines) and after (dotted lines) this measurement in the OER region on both the surface with Ni-doping (Fe:Ni 55:45, purple line) and the one covered in metallic Ni (180 ML Ni, light blue). The different surfaces are thus considered stable over the time of the measurements (typically 5-9 hours).

Figure S3



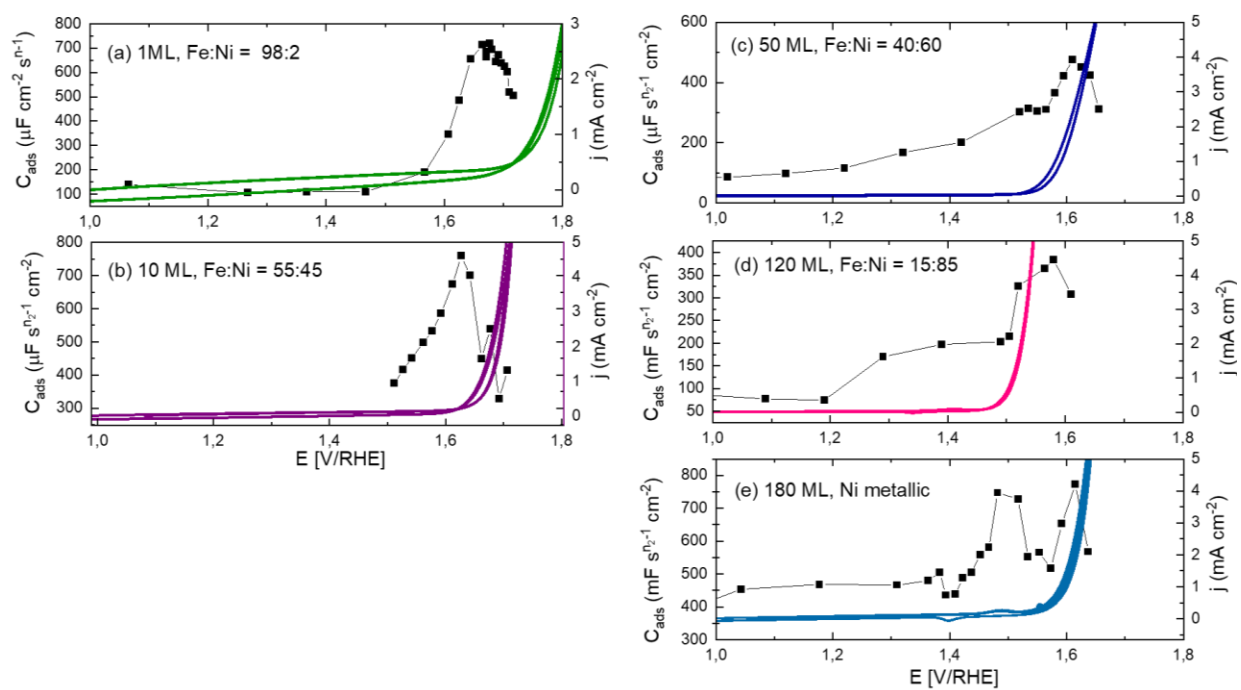
**Figure S3. Nyquist and Bode plots of electrochemical impedance spectroscopy in the OER region on Ni-doped magnetite electrodes in 1 M NaOH in the 0.5 Hz–100 kHz frequency range. The (a) Nyquist and (b) Bode plots are given at the potential at which the maximum of the adsorption capacitance is observed (Figure S4g). The dots represent the experimental results and the black lines are the simulated plots obtained with results of fitting the data with the equivalent circuit (b) given in Figure S4. The inset in Figure S5 a is a zoom of the Nyquist plots for the samples with the highest activity.**

Figure S4



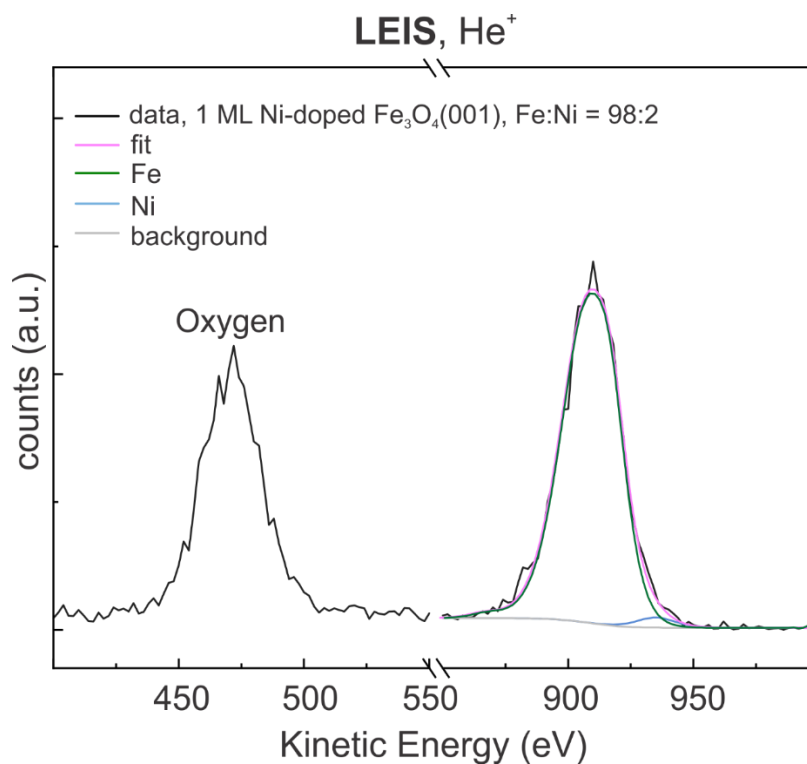
**Figure S4. Electrochemical Impedance Spectroscopy on Ni-doped magnetite electrodes in 1 M NaOH.** (a) Equivalent circuit used in the double-layer region (before the onset of the OER). The W element stands for the semi-infinite diffusion element (Warburg). It is defined by an impedance  $Z_W = A_w (\omega^{-0.5} - j\omega^{-0.5})$  where  $A_w$  is the Warburg coefficient ( $\Omega s^{-0.5}$ ),  $j$  is the imaginary number and  $\omega$  the angular frequency; (b) equivalent circuit used to fit EIS in the OER region as described in the main text; (c) values of the Warburg coefficient as a function of potential: its value is steady before the onset of the OER and drops to 0 making the equivalent circuit (a) equivalent to (b). The diffusion process occurring in this potential region is not clear yet but obviously depends on the Ni-doping as well as on the nature of the exposed material as it increases from 1 to 120 ML but drops again to lower values when the surface is covered with Ni (oxy)hydroxide. Thus, we assume this diffusion has to be related with species diffusing in the bulk of the material and not in the electrolyte. Further studies will be needed to identify its nature; (d)-(e) CPE exponent and  $C_{dl}$  for the double-layer capacitance; (f)-(g) CPE exponent and  $C_{ads}$  for the adsorption capacitance.

Figure S5



**Figure S5. Overlaid adsorption capacitance and cyclic voltammograms on Ni-doped magnetite electrodes in 1 M NaOH.** The CVs are taken from Figure 4a (main text) and the  $C_{ads}$  plots (black squares) from Figure 6c (main text).

Figure S6



**Figure S6.** LEIS (1.225 keV He<sup>+</sup>, 137°) of the 1ML Ni-doped Fe<sub>3</sub>O<sub>4</sub>(001)-(√2 × √2)R45° surface and corresponding fit. The fitted spectrum shows the almost no Ni is detected on the outermost surface layer following 1 ML Ni-doping, with a surface Fe:Ni ratio of 98:2.

## References

1. Bliem, R., McDermott, E., Ferstl, P., Setvin, M., Gamba, O., Pavelec, J., Schneider, M.A., Schmid, M., Diebold, U., Blaha, P., Hammer, L., Parkinson, G.S. Subsurface Cation Vacancy Stabilization of the Magnetite (001) Surface. *Science* **346**, 1215–1218 (2014).
2. Grosvenor, A. P., Kobe, B. A., Biesinger, M. C. & McIntyre, N. S. Investigation of multiplet splitting of Fe 2p XPS spectra and bonding in iron compounds. *Surf. Interface Anal.* **36**, 1564–1574 (2004).
3. Grosvenor, A. P., Biesinger, M. C., Smart, R. S. C. & McIntyre, N. S. New interpretations of XPS spectra of nickel metal and oxides. *Surf. Sci.* **600**, 1771–1779 (2006).
4. Bliem, R., Pavelec, J., Gamba, O., McDermott, E., Wang, Z., Gerhold, S., Wagner, M., Osiecki, J., Schulte, K., Schmid, M., Blaha, P., Diebold, U., Parkinson, G. S. Adsorption and incorporation of transition metals at the magnetite Fe<sub>3</sub>O<sub>4</sub>(001) surface. *Phys. Rev. B* **92**, 075440 (2015).