

Supporting Information

Operando evidence on the chirality-enhanced oxygen evolution reaction in intrinsically chiral electrocatalysis

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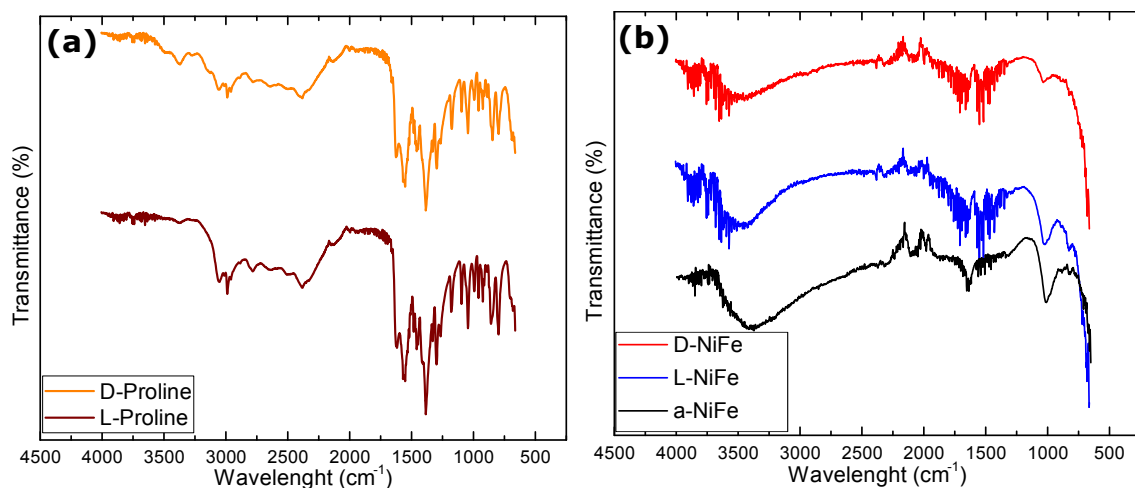


Fig. S1. Infrared spectrum. (a) from the selected amino acids, D- or L- Proline, (b) As synthesized chiral and achiral NiFe. The absence of all bands coming from organic moieties confirm the pure inorganic nature of the NiFe catalysts.

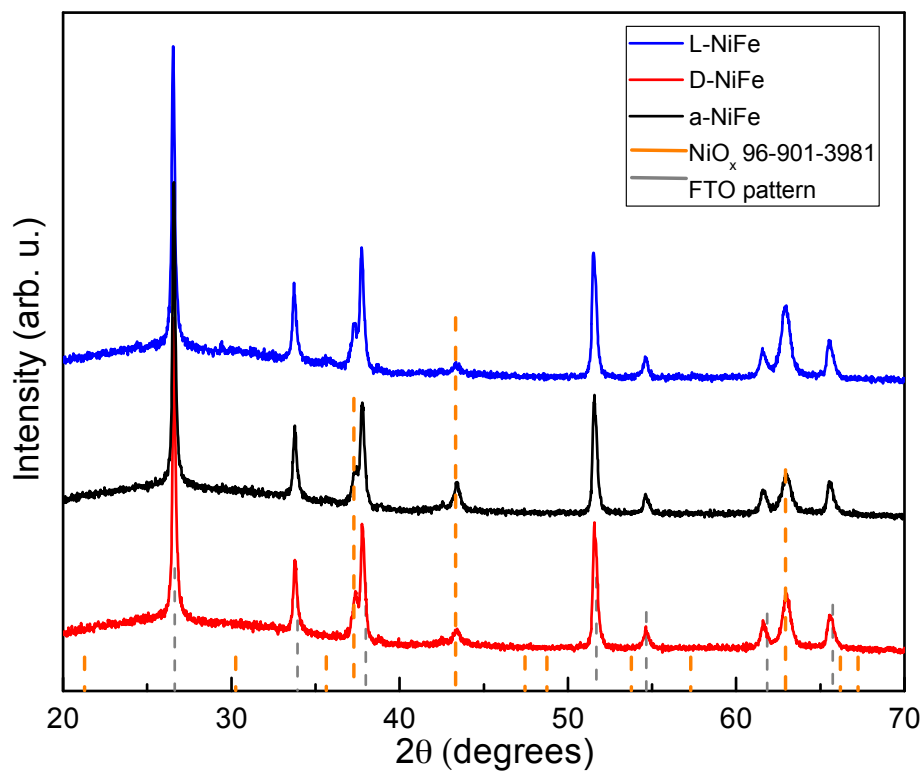


Fig. S2. X-ray Diffraction characterization from a-NiFe, L-NiFe and D-NiFe supported on FTO for in-situ measurements (Circular dichroism/Absorbance).

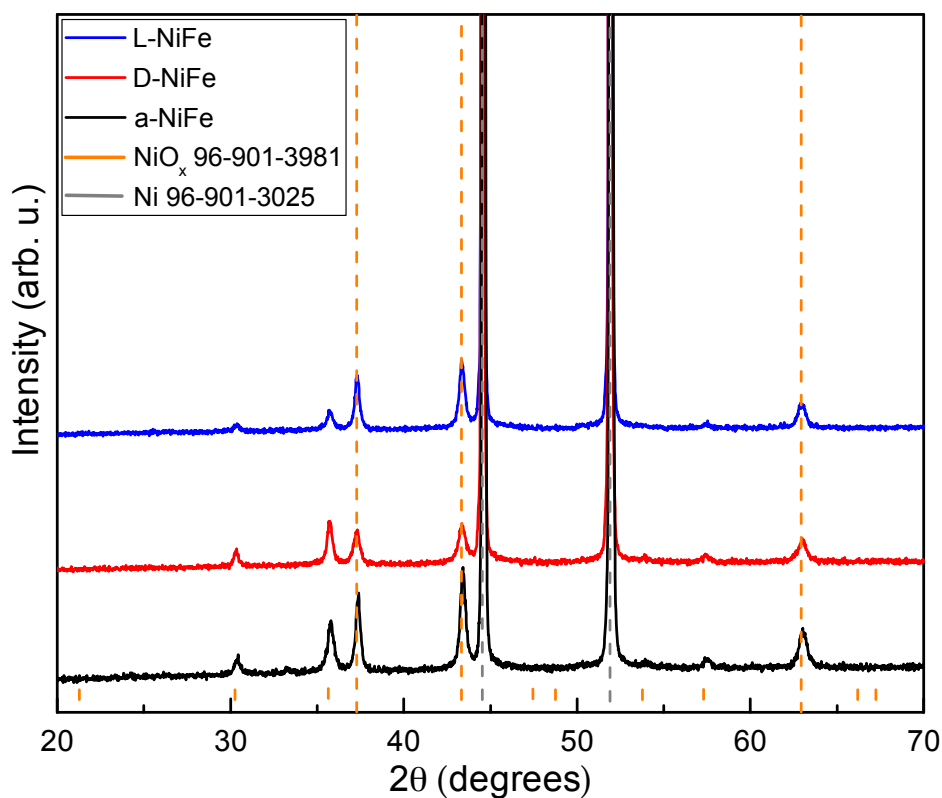


Fig. S3. X-ray Diffraction characterization from a-NiFe, L-NiFe and D-NiFe supported on Nickel foil for electrochemical characterization.

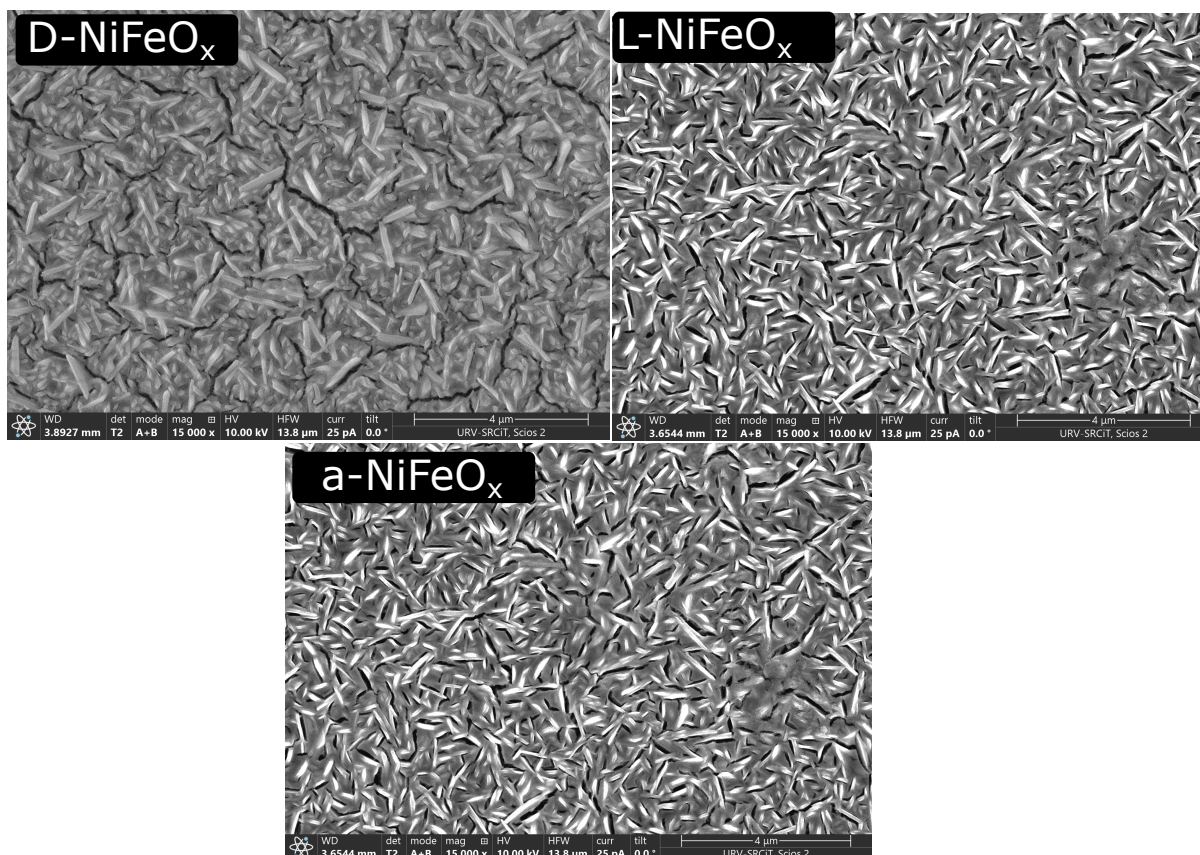


Fig.S4. Morphological and characterization of D-NiFe, L-NiFe and a-NiFe films on FTO substrates.

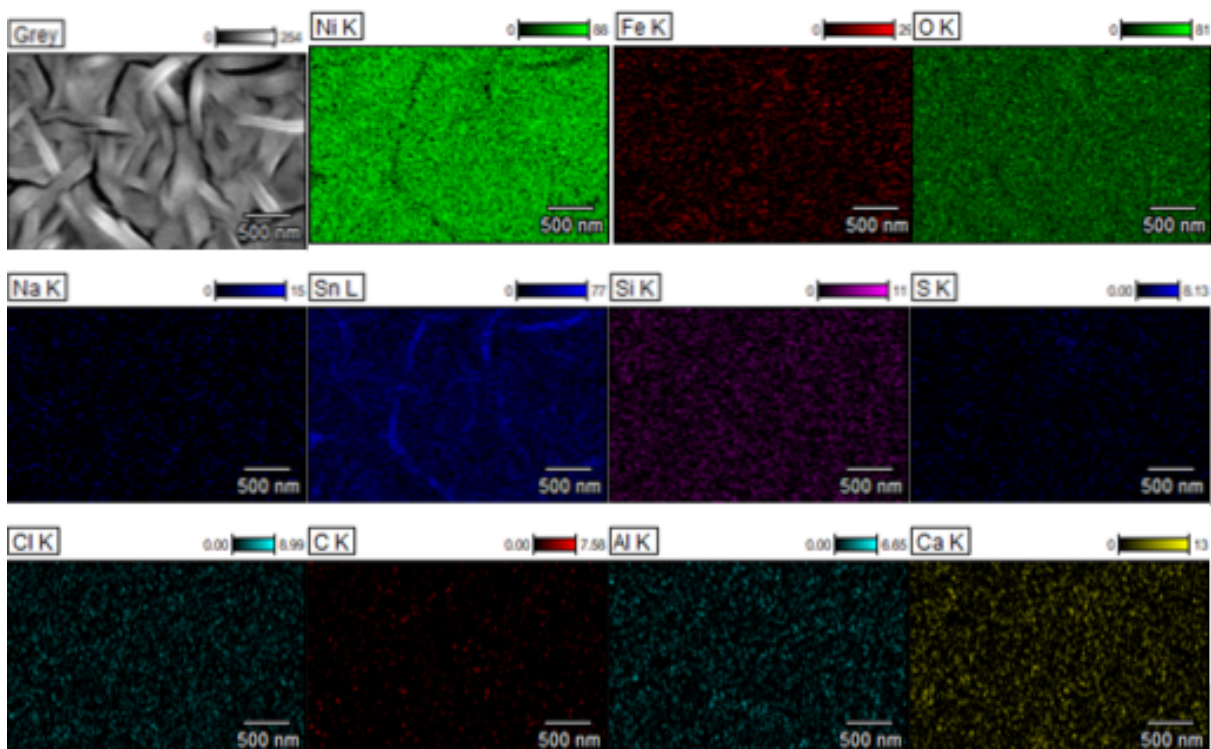


Fig. S5. EDS chemical characterization of **a-NiFe** film on FTO substrate.

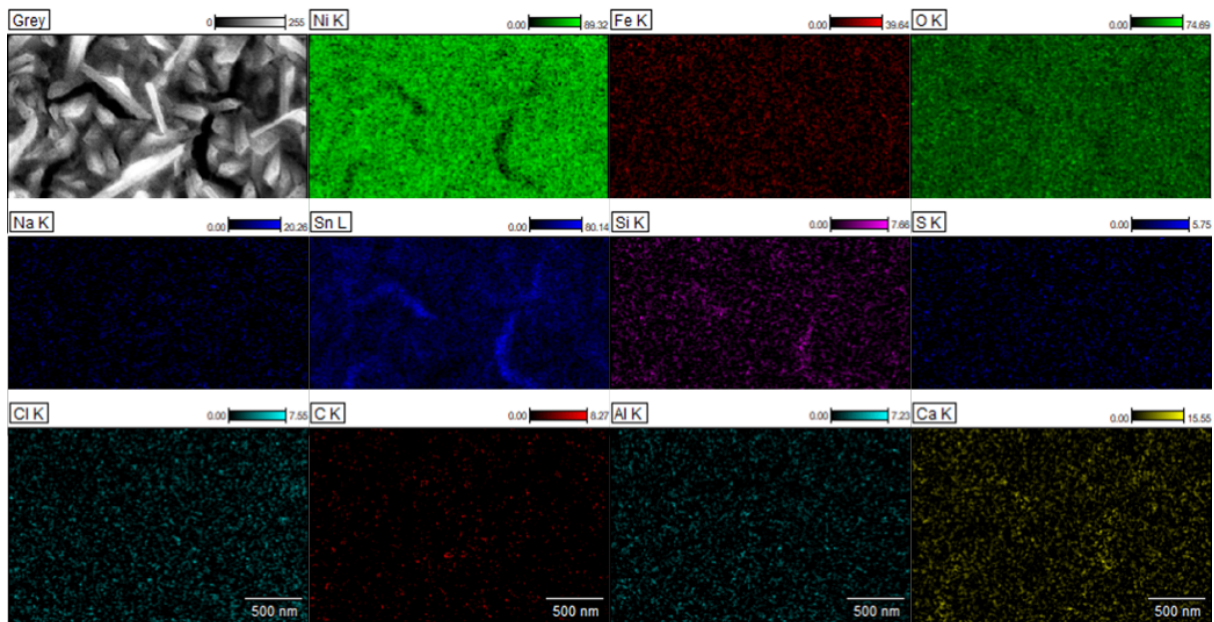


Fig. S6. EDS chemical characterization of **D-NiFe** film on FTO substrate.

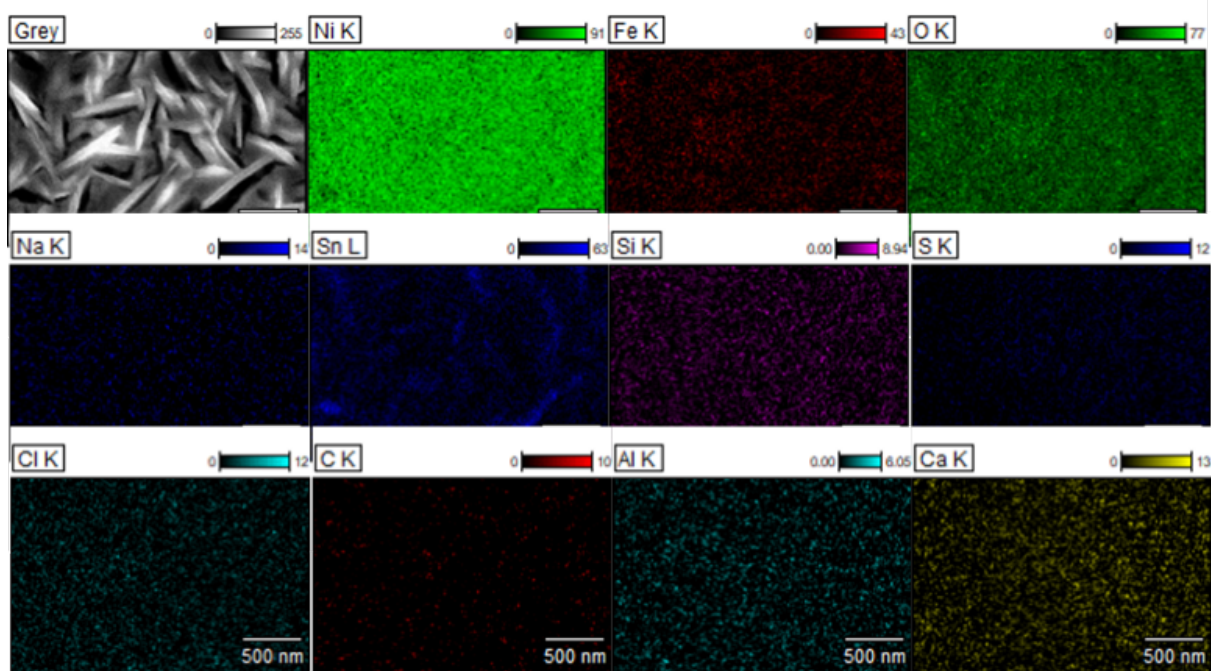


Fig. S7. EDS chemical characterization of L-NiFe film on FTO substrate.

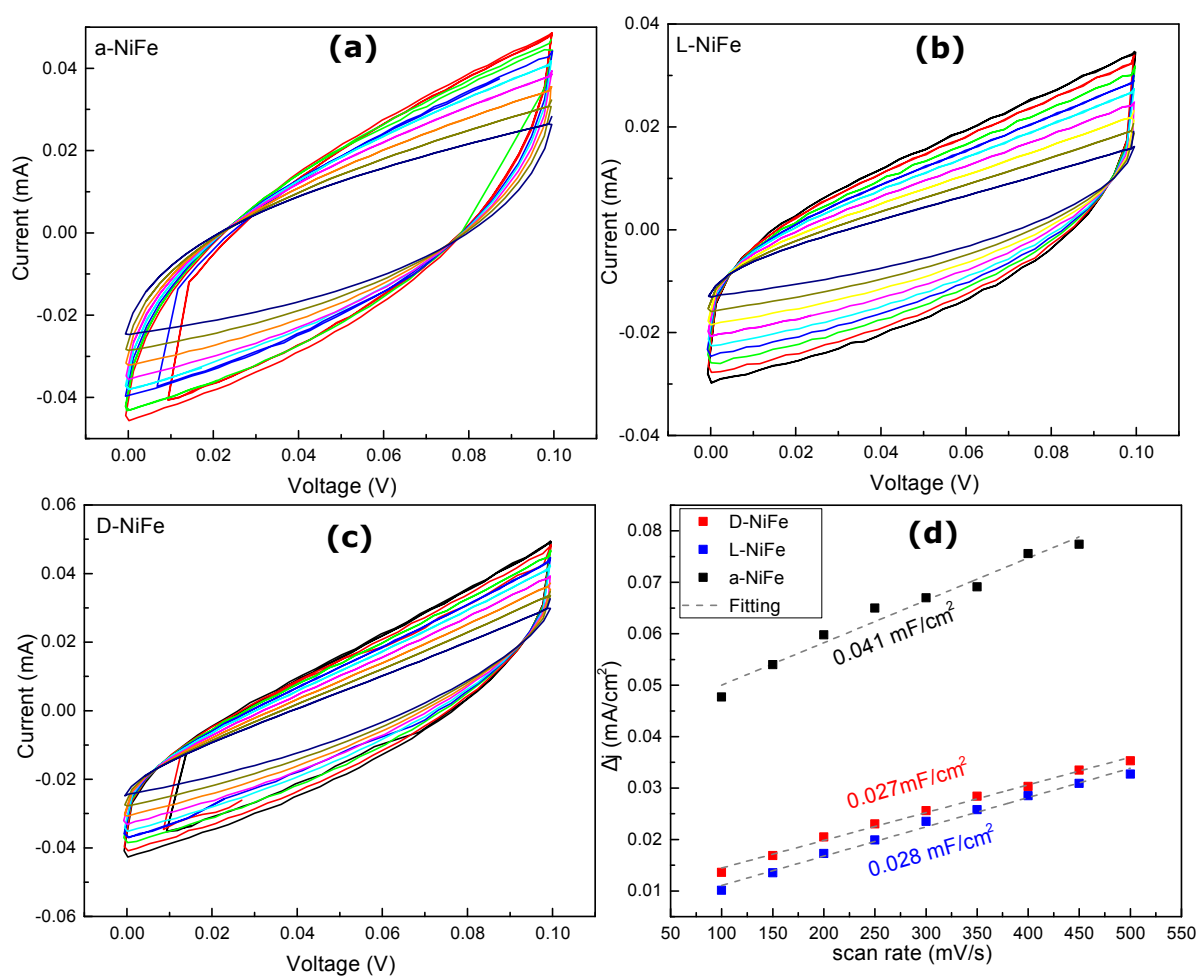


Fig. S8. Electrochemical double layer capacitance for a-NiFe, D-NiFe and L-NiFe. (a), (b) and (c) correspond to the Cyclovoltammetry protocols at different scan rates in the non-faradic region, between 100 and 500 mV/s. (d) Normalized capacitance of the different chiral and non-chiral oxides.

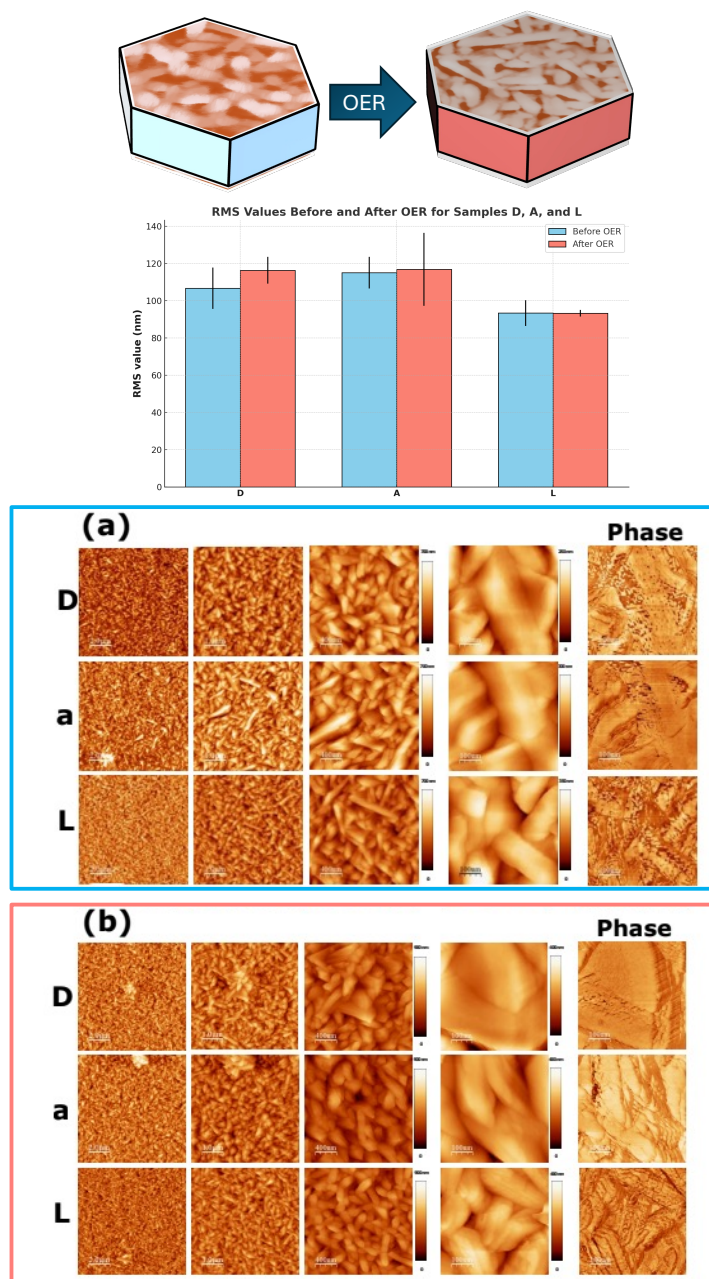
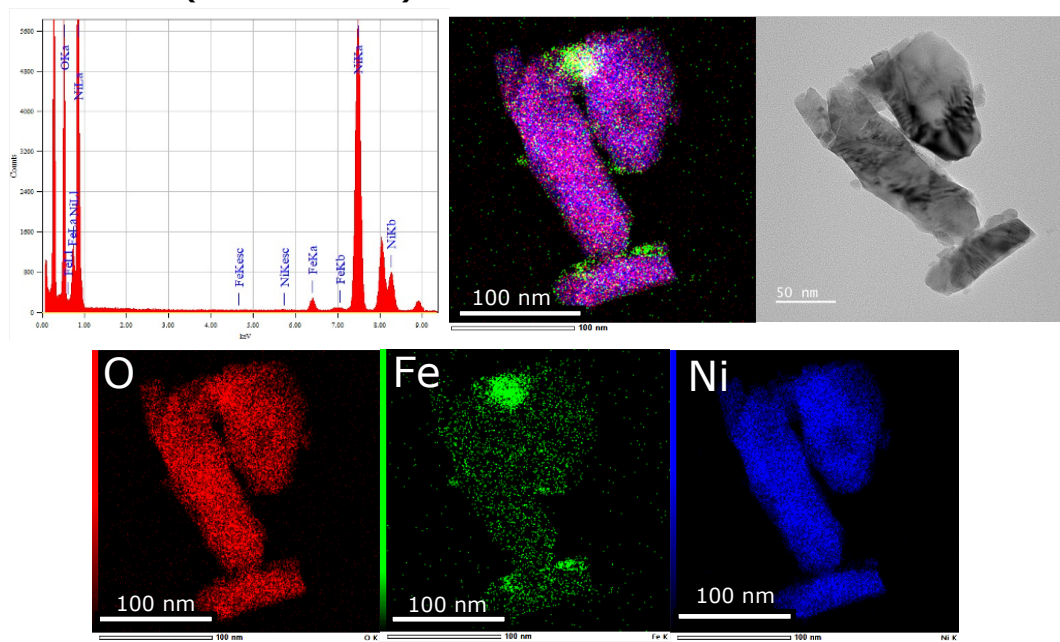


Fig. S9. Atomic force microscopy for the NiFe systems before (a) electrolysis and (b) after 2h at 10 mA/cm². A detail of the RMS before and after electrolysis is provided in the inset above

a-NiFe (before EC)



a-NiFe (after EC)

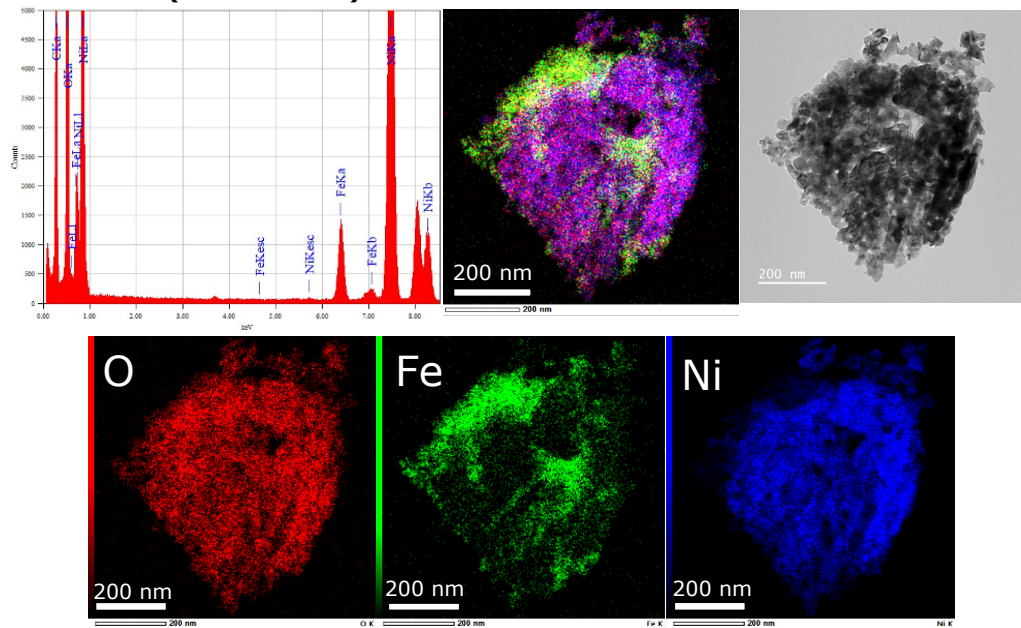
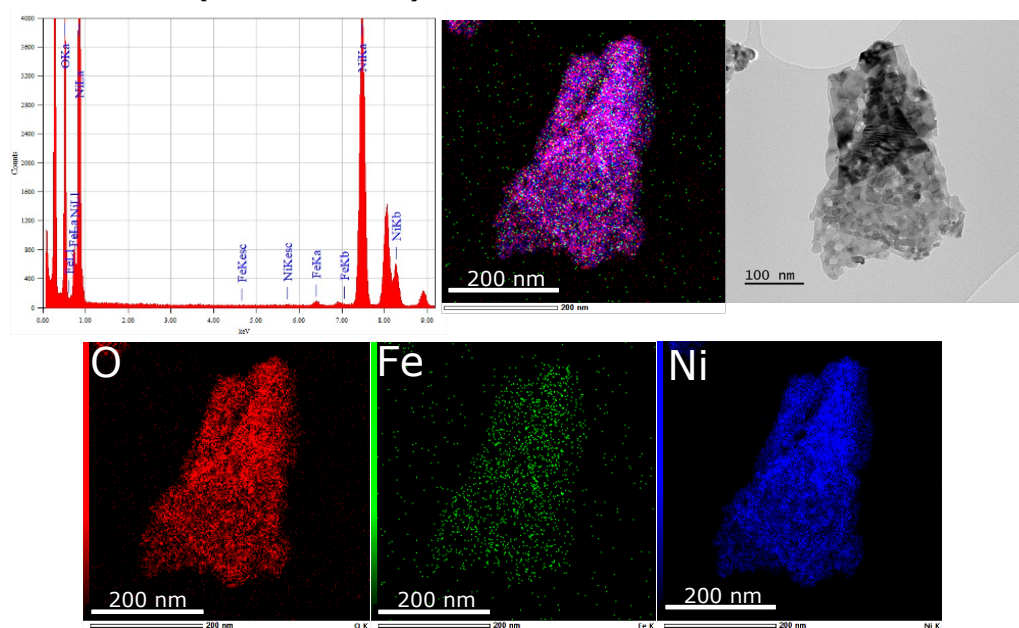


Fig. S10. HRTEM from a-NiFe, (a) before and (b) after electrochemical characterization during 2h at 10 mA/cm².

D-NiFe (before EC)



D-NiFe (after EC)

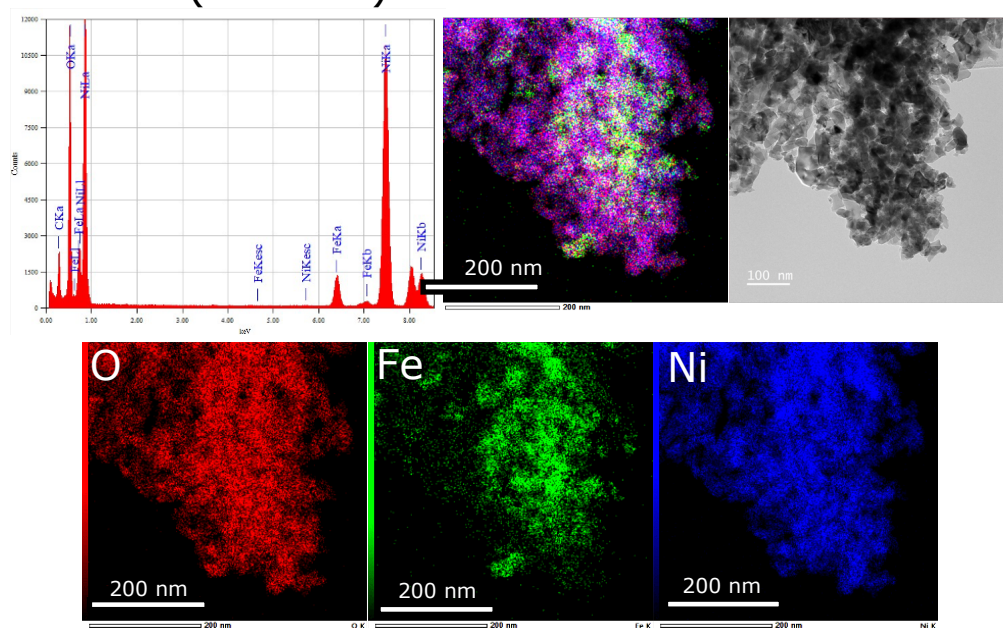
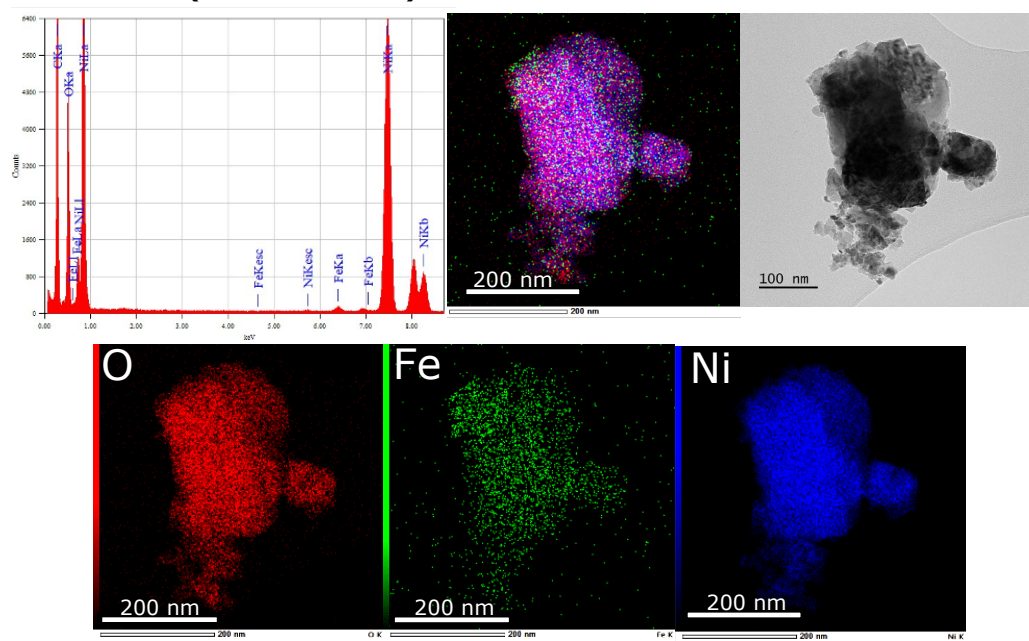


Fig. S11. HRTEM from D-NiFe, (a) before and (b) after electrochemical characterization during 2h at 10 mA/cm².

L-NiFe (before EC)



L-NiFe (after EC)

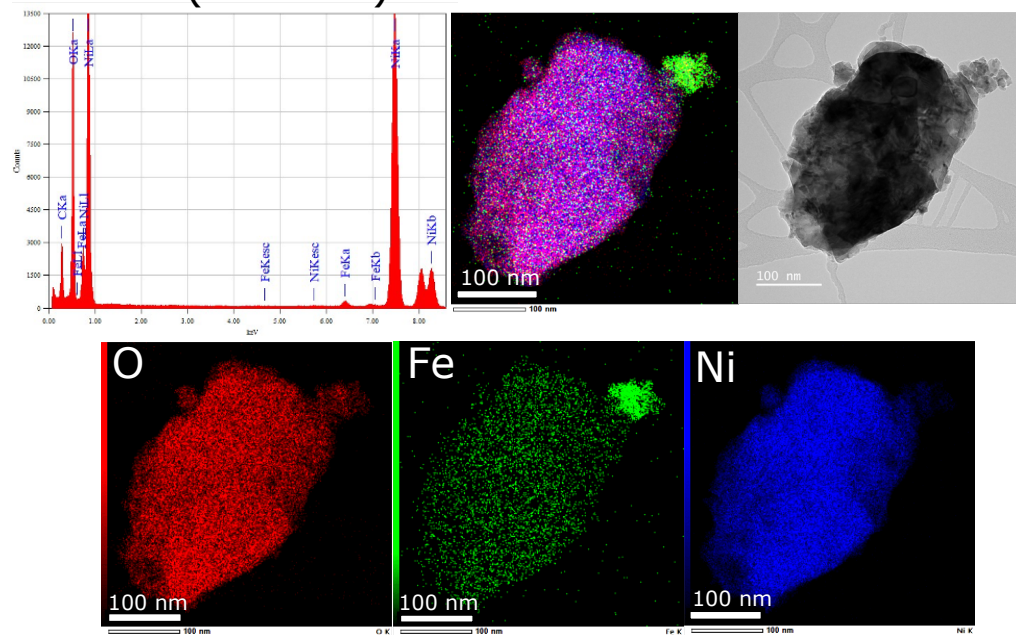


Fig. S12. HRTEM from L-NiFe, (a) before and (b) after electrochemical characterization during 2h at 10 mA/cm².

Fitting & Quantification

Data processing was performed using CasaXPS processing software version 2.3.23.PR1.0 (Casa Software Ltd., Teignmouth, UK). The atomic concentrations of the detected elements were calculated using integral peak intensities and the sensitivity supplied by the manufacturer. Binding energies were referenced to the C1s peak at 284.8 eV (adventitious carbon or aliphatic hydrocarbon).

The spectra were fitted using the casaXPS software. A Shirley background was used, O1s, Fe2p and Ni2p3/2 region.¹

The spectra of O1s region were fitted using a symmetric Gaussian-Lorentzian GL(30) lineshape. Fe2p region was fitted using a symmetric Gaussian-Lorentzian GL(30) for the main peaks and for satellite peaks. This region has significantly split spin-orbit components, taken into account a shift of 13 eV between Fe2p3/2 and Fe2p1/2 components). Fe3p region was fitted using an asymmetric function LA (1.2,85,70) for Fe3+ and Fe2+ components due to the difficulty to fit this region, since the cross section of the photoelectron from Fe3p orbitals are ten times lower, for example, in comparison with Fe2p. Ni2p3/2 region, as has been observed in literature, cannot be satisfactorily fit with the unaltered Ni2+ multiplets or with FWHM variation alone. A satisfactory fit can only be achieved by allowing variation in the BE positions of the multiplet contributions to the main peak. For this reason, the fitting has been done similarly with this article.² Ni2p3/2 region was fitted using a symmetric Gaussian-Lorentzian GL(30) for the main peaks and for satellite peaks.

Relative atomic quantification has been calculated with casaXPS software taking into account the relative sensitivity factor. The photon incident energy used in the laboratory experiments was 1486.7 eV (AlK α) and the sensitivity factor (RSF) value was calculated using only the cross section, since the x-ray flux is constant and corrected to C1s (1): Ni2p = 22.18 (RSF), C1s = 1 (RSF), O1s (2.93 RSF), Fe2p (16.42) and K2p (3.97).³

Table S1. Relative atomic quantification (%) calculated with casaXPS software.

	before EC (D-NiFe)	After EC (D-NiFe)	Before EC (a-NiFe)	After EC (a-NiFe)	Before EC (L-NiFe)	After EC (L-NiFe)
Ni	24.19	22.93	18.47	19.76	22.01	23.27
Fe	10.37	8.39	12.83	10.75	10.30	9.58
Rest of elements (C,O,K)	65.44	68.68	68.70	69.49	67.69	67.15

Table S2. Relative atomic quantification (%) calculated with casaXPS software O1s region.

Sample/C species	% at. Lattice Oxygen (B.E)	% at. Organic O (C=O) and/or oxygen defects (B.E)	% at. -OH groups or organic contamination (B.E)
(Fresh D-NiFe)	83.34 (529.9 eV)	13.05 (531.6 eV)	3.61 (532.7 eV)
(Post D-NiFe)	70.74 (529.8 eV)	27.52 (531.5 eV)	1.74 (532.9 eV)
(Fresh a-NiFe)	85.77 (529.8 eV)	11.73 (531.5 eV)	2.49 (532.9 eV)
(Post a-NiFe)	79.19 (529.8 eV)	18.37 (531.4 eV)	2.44 (532.9 eV)
(Fresh L-NiFe)	81.17 (529.8 eV)	15.50 (531.4 eV)	3.33 (532.7 eV)
(Post L-NiFe)	63.77 (529.8 eV)	32.40 (531.3 eV)	3.83 (532.9 eV)

In fresh samples, three different peaks have been observed at 529.8 eV, 531.5 eV and 532.7 eV, associated in literature with oxygen metal oxides lattice (i.e. NiO)³⁻⁵, organic C=O^{6,7} and/or oxygen defects in the matrix of metal oxides⁸⁻¹⁰ which are related to oxygen vacancies, and the hydroxyl oxygen atoms and/or organic contamination,^{8,11-12} respectively. As you can see in Table S2, no significant changes in the relative quantification of oxygen species have been observed in these fresh samples, showing that ~83 % are lattice oxygen species, ~13% organic O (C=O) and/or oxygen defects species and ~3% -OH groups and/or organic contamination.

Nevertheless, significant changes between fresh and post-reaction samples (D- & L-) have been observed in this region. A relevant increase in the amount of organic O and/or oxygen defects has been noticed, increasing in more than 100 % the relative percent of these species (111% in D- and 109 % in L-). On the other hand, the less active catalyst (M-) presents lower concentration of these species, which would be in line with the catalytic activity. Moreover, species Ni³⁺ have been observed after reaction, due to the oxidation process which would be consistent with the formation of oxygen vacancies.

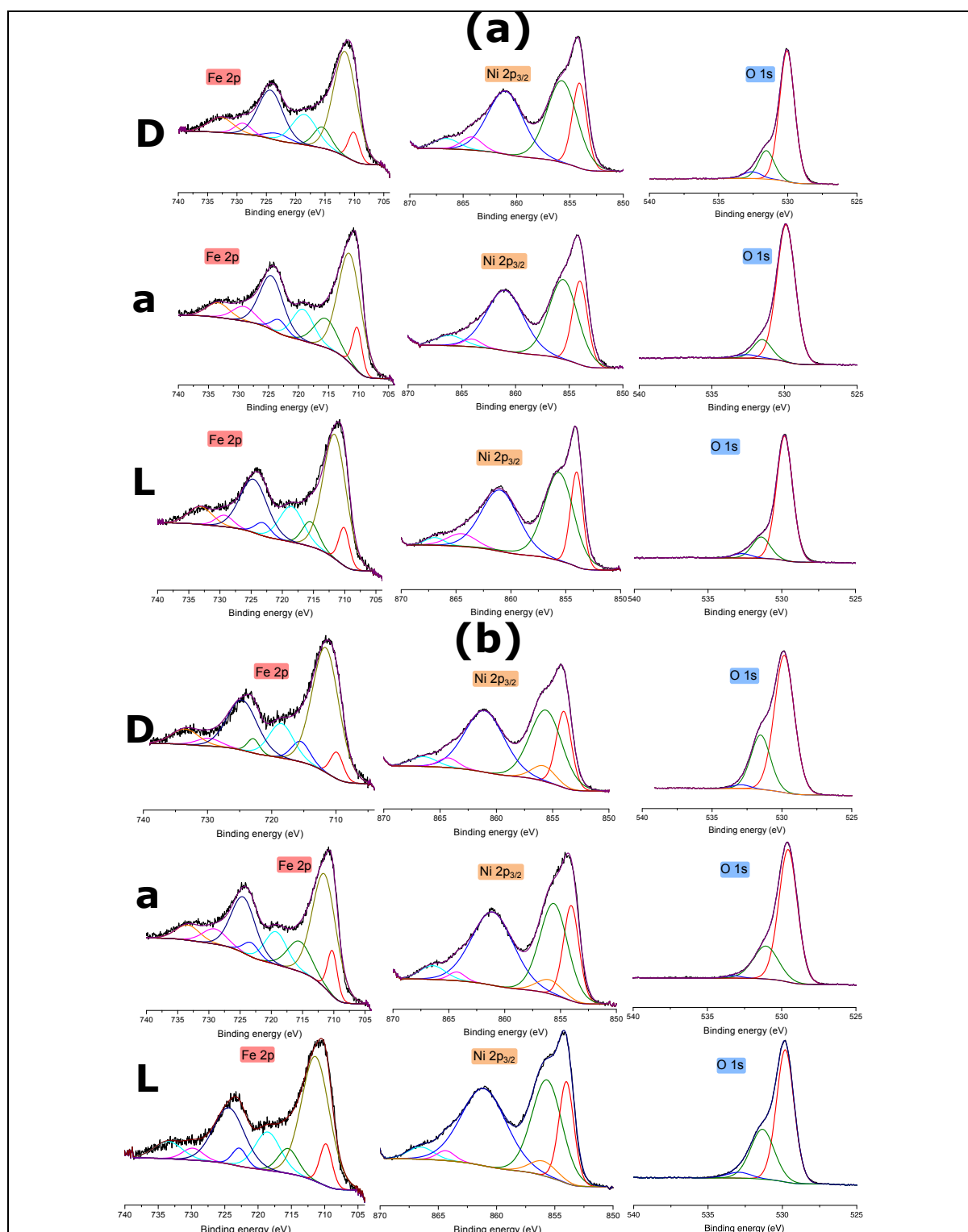


Fig. S13. XPS characterization (Fe2p, Ni2p_{3/2} and O1s core lines acquired with $h\nu = 1486.7$ eV): **a)** before, and **b)** after electrochemical tests.

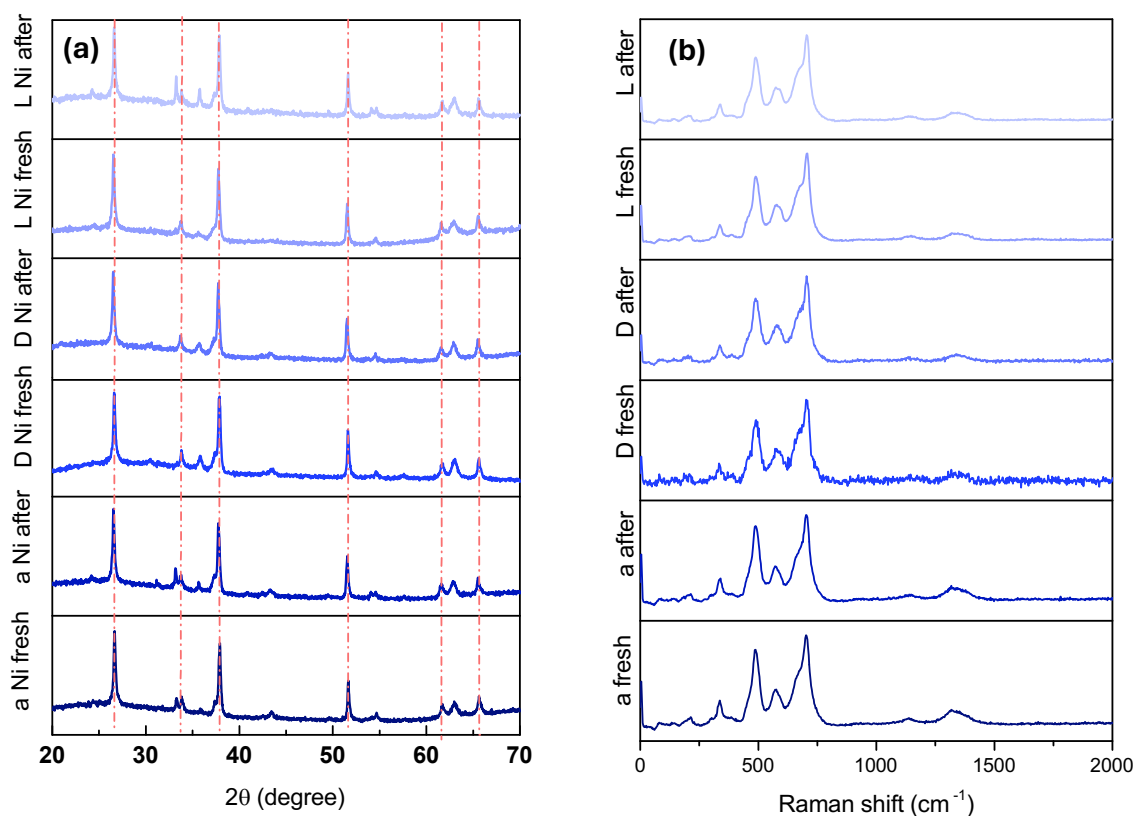


Fig. S14. Additional structural data: (a) XRD and (b) RAMAN spectroscopy from the different oxides, before and after electrochemistry during 2h at 10 mA/cm^2 in KOH 1M.

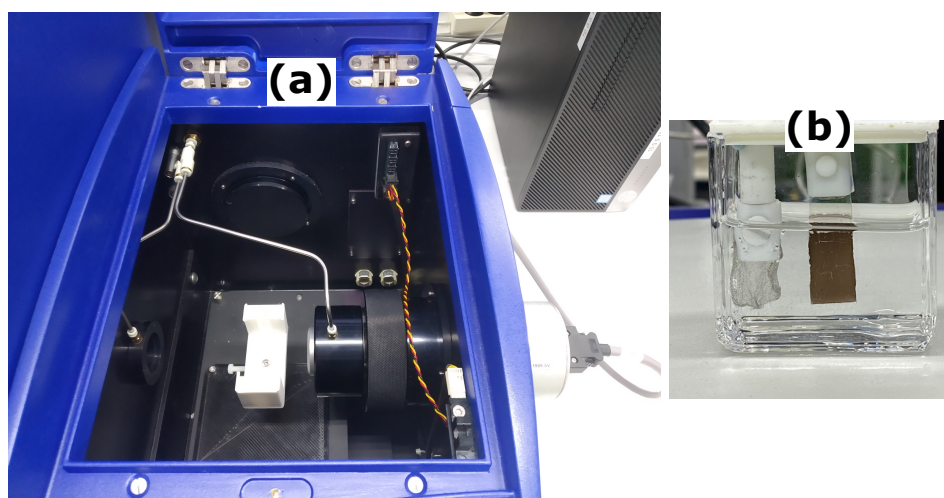


Fig. S15. Spectro-Electrochemical setup. (a) Circular Dichroism (CD) device and (b) 3 electrodes electrochemical cell.

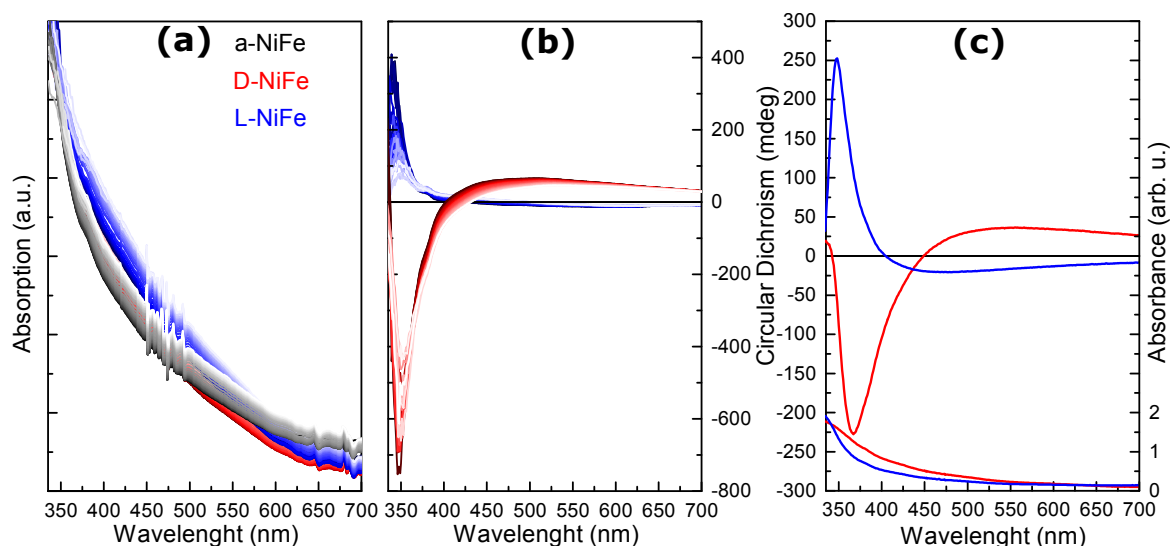


Fig. S16. Spectro-electrochemical analysis from the non- and chiral oxides(a-NiFe, L-NiFe and D-NiFe) in KOH 1M. (a) Operando absorbance (b) Operando CD and (c) CD after 2-hour stability and recovery.

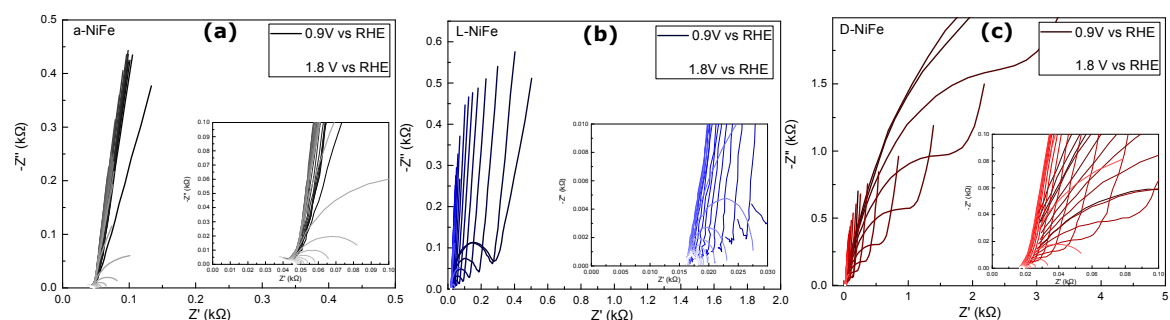


Fig. S17. Nyquist plots extracted from EIS analysis at 0.9-1.8 V vs RHE for (a) a-NiFe, (b) L-NiFe and (c) D-NiFe in KOH.

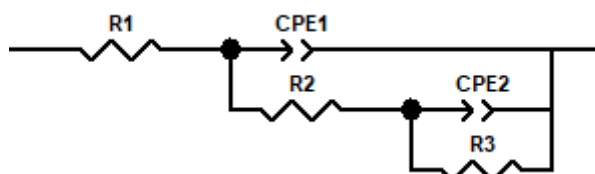


Fig.18. Equivalent circuit used for fitting the EIS data obtained in Figure S18.

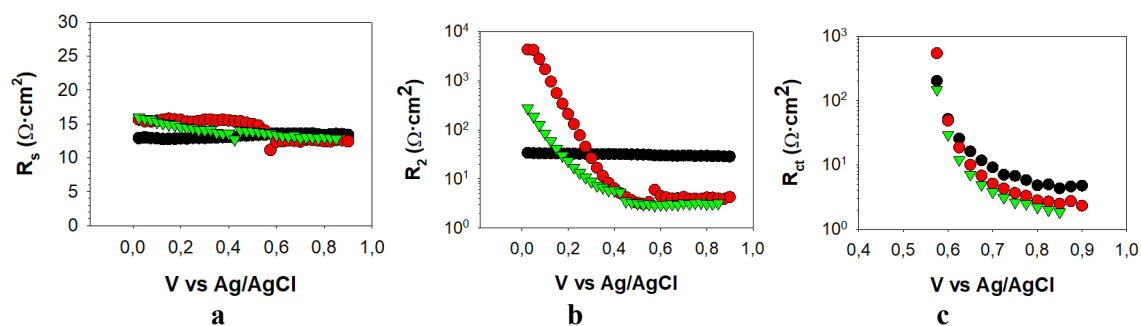


Fig. S19. Impedance analysis: (a) Resistance in series ($R_s = R_1$), (b) Resistance in parallel, (c) Charge transfer resistance for a-NiFe (black), L-NiFe (green) and D-NiFe (red) as a function of applied potential extracted from the data in Figure S18.

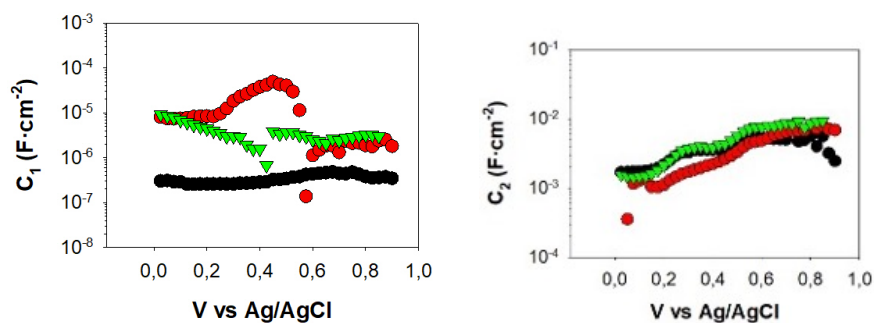


Fig. S20. Impedance analysis: (a) Capacitance C_1 and (b) Capacitance C_2 as a function of applied potential, extracted from the data in Figure S18.

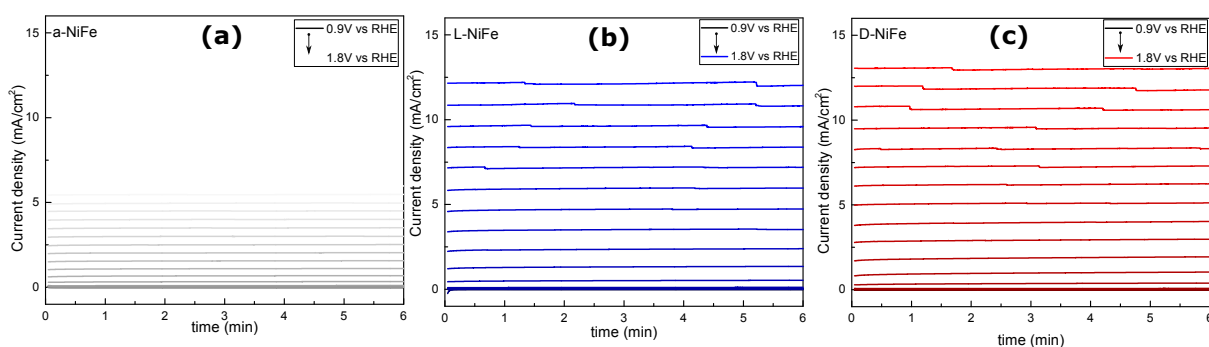


Fig. S21. Chronoamperometric measurements for (a) a-NiFe, (b) L-NiFe and (c) D-NiFe, changing the potential between 0.9 V and 1.8 V vs RHE (steps of 25 mV).

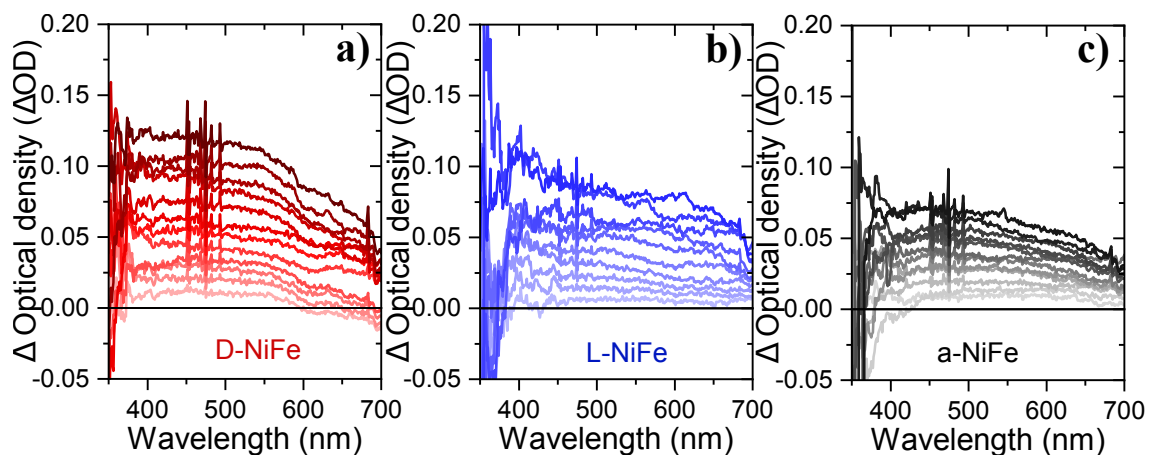


Fig. S22. Spectro-electrochemical analysis from the non- and chiral oxides. Optical density versus wavelength. (a) D-NiFe, (b) L-NiFe and (c) D-NiFe in KOH 1M.

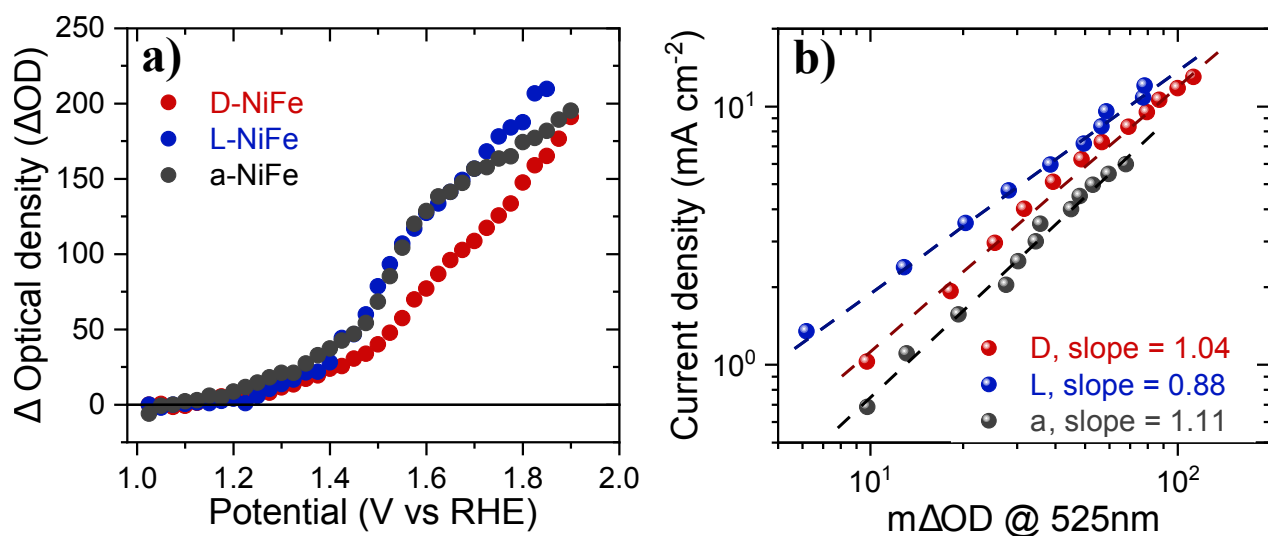


Fig. S23. Spectroelectrochemical analysis from the non- and chiral oxides. a) Optical density extracted from the absorption data of the L-NiFe, D-NiFe and a-NiFe, at different applied voltages during OER in a KOH (1M) electrolyte. b) Rate law analysis, log-log plot of the current density as a function of optical density.

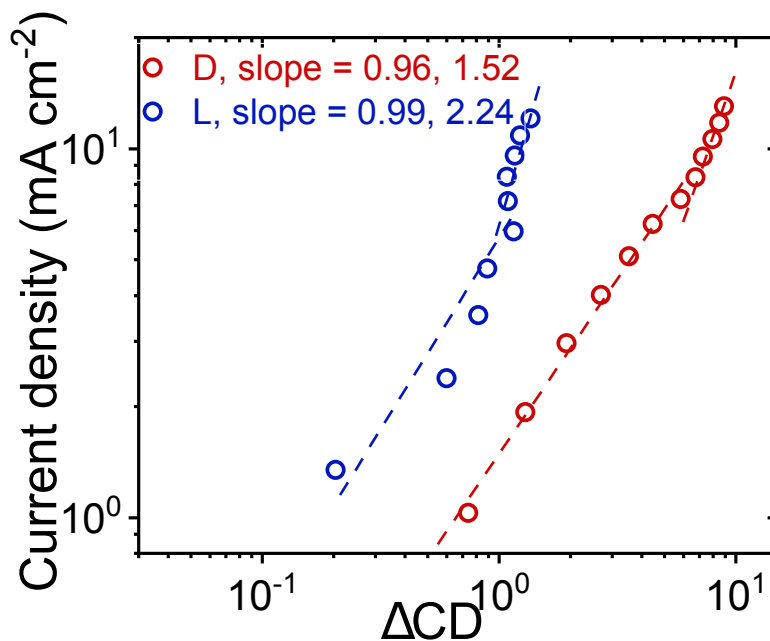


Fig. S24. Rate law analysis, log-log plot of the current density as a function of the optical density from the dichroism signal of the a-NiFe, L-NiFe and D-NiFe in KOH 1M.

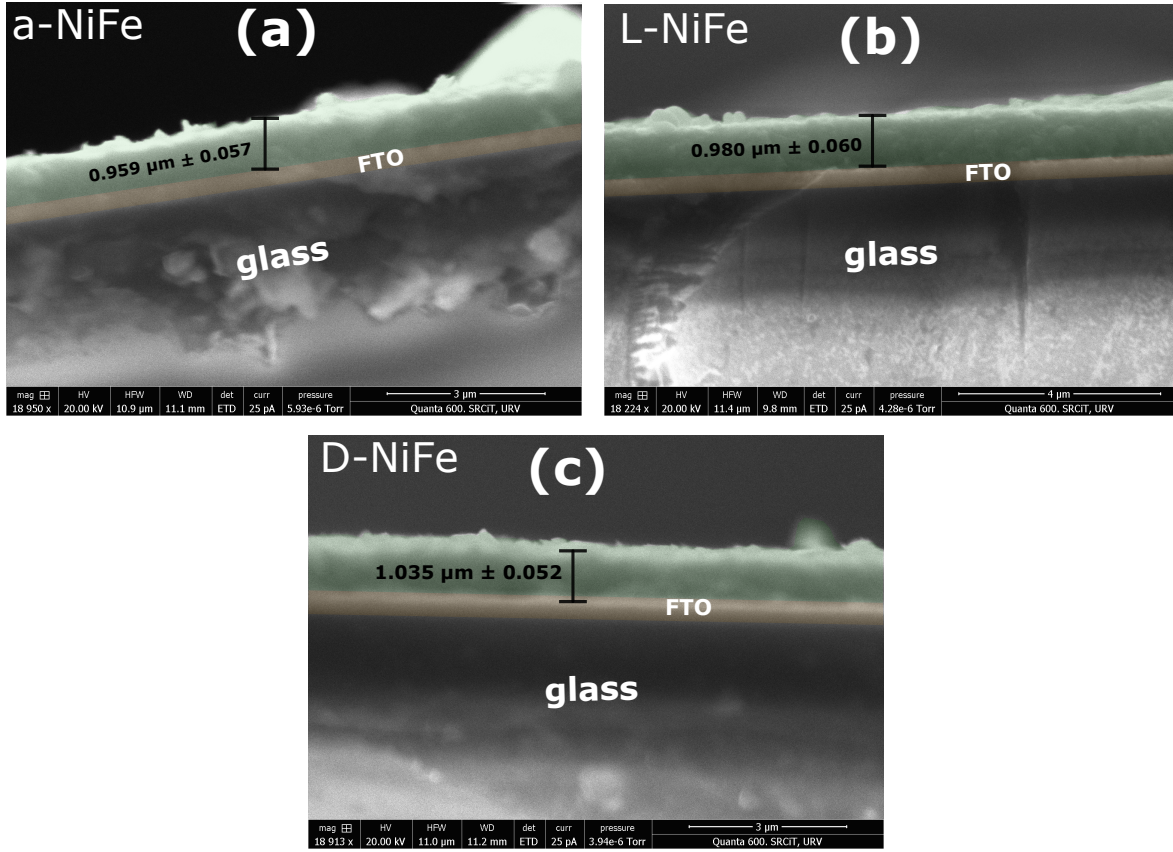


Fig. S25. Scanning electron Microscopy (ESEM) images from profiles of (a) a-NiFe, (b) L-NiFe and (c) D-NiFe, showing the film thickness of Nickel oxide layer in green and the Fluorine Tin Oxide in orange.

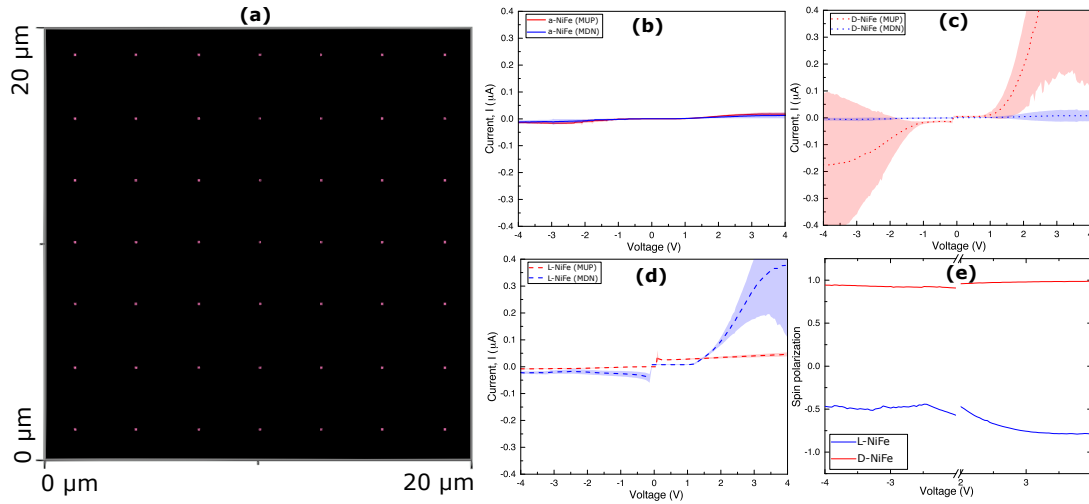


Fig. S26. Atomic Force Mycroscopy (magnetic-conductive tip): (a) $20 \mu\text{m} \times \mu\text{m}$ scan for the mc-AFM measurements, in total 49 assays were carry out per sample: (b) a-NiFe in both configurations magnet UP (MUP) and magnet down (MDN), (c) D-NiFe oxide, (d) L-NiFe oxide and (e) correspond to the relative spin polarization for L and D NiFe. The shadow in (b), (c) and (d), correspond to the experimental error during the mc-AFM tests.

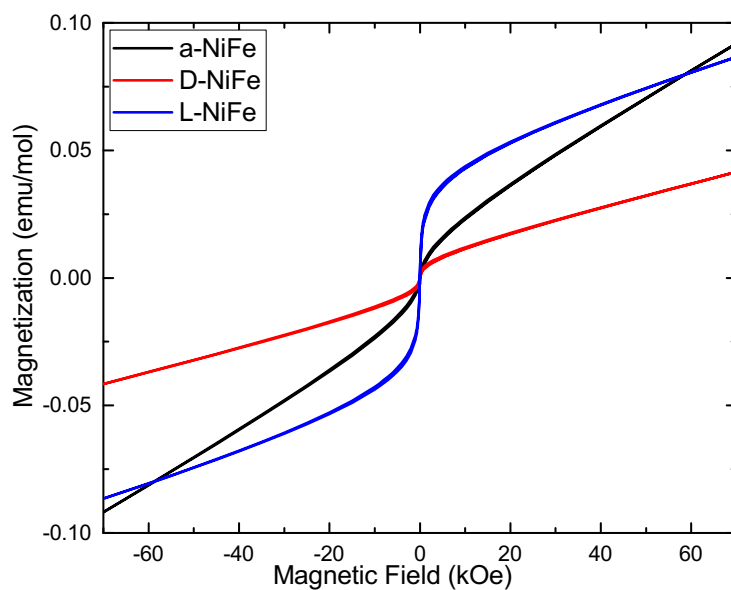


Fig. S27. Magnetization curves for achiral and chiral Nickel oxides.

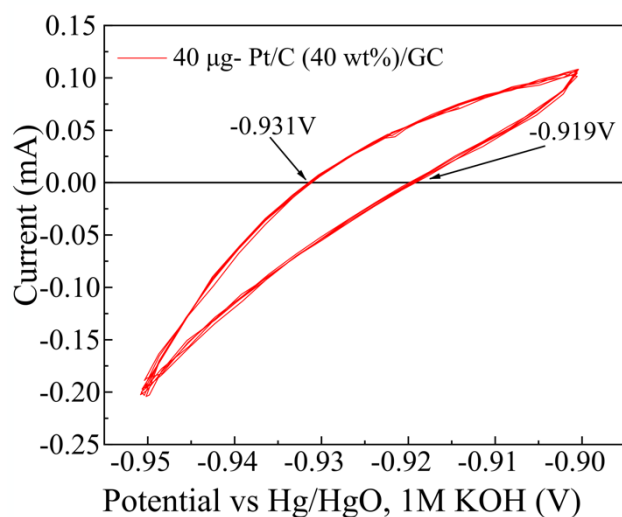


Fig. S28. Additional electrochemical data: Calibration of the actual value of the potential of the Hg/HgO (1 M KOH) vs. the reversible hydrogen electrode (RHE) by using a hydrogen electrode reaction with 40 μg Pt/C (40 wt%)/GC, the Hg/HgO electrode as the reference electrode, and carbon rod as the counter electrode in a hydrogen-saturated 1 M KOH electrolyte.

Table S3. Comparative data on OER performance, using chiral catalyst

Catalyst	Type of chirality	Electrolyte	$\eta(\text{OER}) @ 10 \text{ mA cm}^{-2} / \text{mV}$	Tafel slope / mV dec^{-1}	AEMEL Current density @ $2 \text{ V} / \text{mA cm}^{-2}$	Ref
D-NiO _x :Fe	Intrinsic	KOH 1M	340	50	230	This work
L-NiO _x :Fe	Intrinsic	KOH 1M	355	52	275	This work
L-Co ₃ O ₄	Surface functionalization	NaOH 1M	386	59	--	13
L-D Co _{3-x} Fe _x O ₄	Surface functionalization	NaOH 1M	320	34	--	13
Ni/Cys	Surface functionalization	KOH 0.1M	500	206	--	14
Ni/Au/Cys	Surface functionalization	KOH 0.1M	210	114	--	14
L-CuO	Intrinsic	KOH 1M	308	94	--	15
R-h-Au-NAs	Surface functionalization	KOH 1M	355	88	--	16
L-D CuO	Surface functionalization	KOH 0.1M	621	117	--	17
L-D Fe ₃ O ₄	Surface functionalization	KOH 0.1M	780	120	--	18
L-D Fe ₃ O ₄ nps	Surface functionalization	KOH 1M	--	92	--	19
L-D CoO _x	Surface functionalization	KOH 0.1M	500	--	--	20
2D-L-D NiO _x NiFeOOH	Sandwiched configuration: Au-chiral molecule-catalyst	KOH 0.1M	416	--	--	21

References

- [1] T. Yamashita et al., *Appl. Surf. Sci.* **2008**, 254, 2441.
- [2] M.C. Biesinger, *Surf. Interfaces Anal.* **2009** 41, 324.
- [3] J.H. Scofield, *J. Electron Spectros. Relat. Phenomena* **1976**, 8,129.
- [4] Oxygen | XPS Periodic Table | Thermo Fisher Scientific - ES
- [5] Sci-Hub | The Electrochemical Behavior of Electroless Plated Ni-P Alloys in Concentrated NaOH Solution | 10.1149/1.2043954 (53yu.com)
- [6] Structural and Chemical Properties of NiO_x Thin Films: Oxygen Vacancy Formation in O₂ Atmosphere (wiley.com)
- [7] Oxygen | XPS Periodic Table | Thermo Fisher Scientific - ES
- [8] Facile radiolytic synthesis of ruthenium nanoparticles on graphene oxide and carbon nanotubes - ScienceDirect
- [9] S. Jain et al. *Int. J. Energy Res.* **2019**, 43, 4743.
- [10] The role of oxygen States in NiO for Oxygen Evolution Reactions https://www.fhi.mpg.de/981311/The-role-of-Oxygen-States_in_NiO_for_Oxygen_Evolution_Reactions
- [11] B. O. Payne, M. C. Biesinger, N. S. McIntyre, *J. Electron Spectros. Relat. Phenomena* **2012**, 185, 159.
- [12] D. Koushik, W. J. H. Verhees, D. Zhang, Y. Kuang, S. Veenstra, M. Creatore, R. E. I. Schropp, *Adv. Mater. Interfaces* **2017**, 4, 1700043.
- [13] A. Vadakkayil, et al. *Nat. Comm.* **2023**, 14,1067.
- [14] P.K. Bhartiya, et al. *Int. J. Hydrogen Energy* **2022**, 47, 42160.
- [15] Y. Li, et al. *Small* **2024**, 20, 2408248.
- [16] L. Huang, et al., *Sci. Chin. Chem.* **2024**, 67, 3767.
- [17] Y. Yin, et al. *J. Am. Chem. Soc.* **2024** 146, 2798.
- [18] W. Zhang, et al., *Mat. Adv.* **2024**, 5, 1340.
- [19] A.N. Nair, et al., *Nano Lett.* **2023**, 23, 9042.
- [20] S. Ghosh, et al., *J. Phys. Chem. C* **2020**, 124, 22610
- [21] Y.C. Liang, et al., *Nat. Comm.* **2022**, 13, 3356