Supplementary Information (SI) for Journal of Materials Chemistry A.

Supporting information

Fe, Co, and ZIF-8 co-doped catalysts with carbon nanotube and SiOC composite backbone for high-temperature PEM fuel cell cathode

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S1. Preparation of PDC precursor powder

The PDC was prepared according to the route from the previous investigation [1]. The precursor solution for PDC was prepared via constant stirring at room temperature of the solution in xylene (Sigma-Aldrich) containing 12.8 wt% poly(methyl phenyl silsesquioxane) (SILRES® H44, Wacker Chemie AG), 12.8 wt% silicon resin poly(methylsilsesquioxane) (BELSIL® PMS MK, Wacker Chemie AG), 33.7 wt% graphite (IMERYL Graphite & Carbon), 19.6 wt% azodicarboxamide (Sigma-Aldrich), and 20.0 wt% (3-Aminopropyl)triethoxysilane (Sigma-Aldrich). The cross-linking was initiated via the addition of 1.1 wt% imidazole (Alfa Aesar) followed by further stirring for 20 min. The dried mixture was pyrolysed under a N_2 atmosphere using 2 °C min^{-1} up to 900 °C, 0.5 °C min^{-1} from 900 to 1000 °C, followed by dwelling time at 1000 °C for 4 h. After cooling down to room temperature at a rate of 2 °C min^{-1}, the materials were firstly crushed manually and secondly ball-milled (PM 400, Retsch) at 350 rpm min^{-1} for 4 h. The obtained fine powder was sieved to particle sizes <100 μm, and this sieved fraction is used as the PDC precursor powder.

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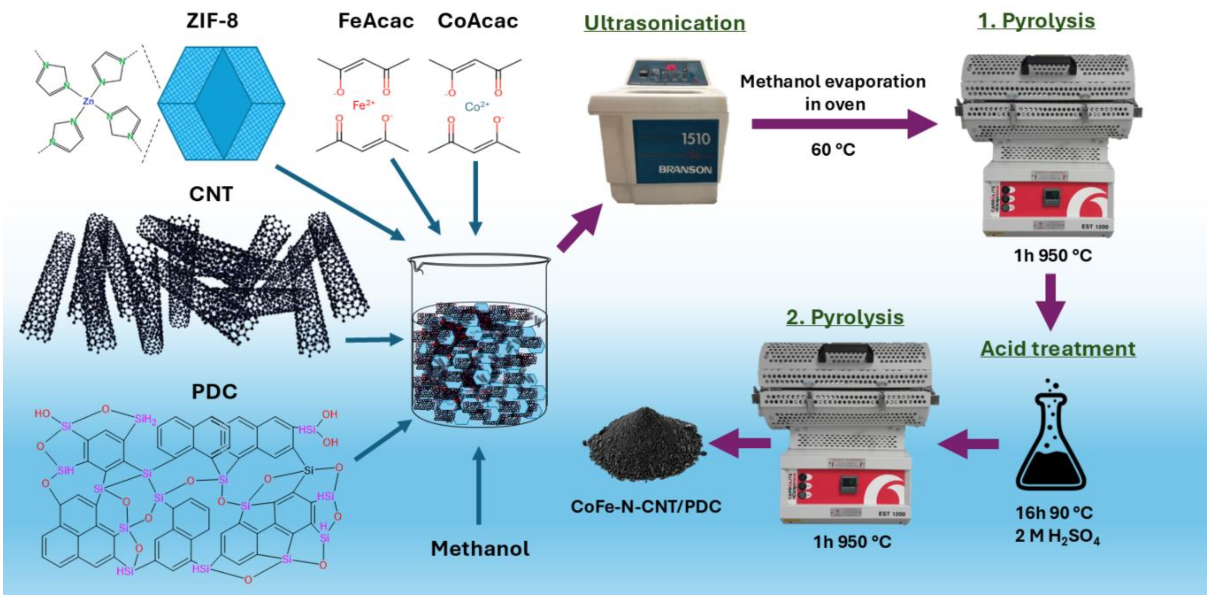
Table S1. Precursors and their amounts (wt%) used in the methanol solution for bi- or trimetallic M-N-C preparation.

Catalyst designation	CNT	PDC	ZIF-8	FeAcac	CoAcac	MnAcac
Fe-N-CNT/PDC	23.6	23.6	47.2	5.7	-	-
MnFe-N-CNT/PDC	21.4	21.4	42.7	5.1	-	9.4
CoMnFe-N-CNT/PDC	21.4	21.4	42.7	5.1	4.7	4.7
CoFe-N-CNT/PDC	21.4	21.4	42.7	5.1	9.4	-
CoFe-N-CNT	42.7	-	42.7	5.1	9.4	-
CoFe-N-PDC	-	42.7	42.7	5.1	9.4	-



Scheme S1. Pictorial description of the preparation route used for the CoFe-N-CNT/PDC catalyst.

S2. ICP-MS measurements

For the Fe-N-C (Pajarito Powder, LLC), the sample is placed in a rolled rim tube and 2 mL of concentrated HNO_3 is added together with 3 boiling beads, followed by 5 minutes of ultrasonication, and later boiled for 1 hour. The tube is filled to 50 mL with ultrapure water and then filtered, obtaining a 1:5 dilution. The sample is diluted again to the volume required for the analysis. An ICP-MS Thermo Fisher Scientific iCap Q device with autosampler ESI SC2 DX was used for measuring the Fe content in Fe-N-C samples. The iCapQ was tuned with an autotune and performance test prior to the measurement.

For CoFe-N-CNT and all the PDC-containing catalysts, ca. 0.2 g of dried sample was weighed into a PTFE vessel and pre-digested in an open vessel on a hot plate at 80 °C using 3 mL of ultrapure water and 3 mL of concentrated HNO_3. After cooling, 3 mL of concentrated HCl was added and allowed to react until effervescence subsided, followed by the addition of 2 mL of concentrated HNO_3. Subsequently, 1 mL of concentrated $HClO_4$ and 2.5 mL of HF were added, and the vessels were heated at 80 °C for 1 h, then the temperature was increased to 110 °C and maintained until incipient dryness. The temperature was further raised to 160 °C to achieve complete dryness. An additional 1 mL of concentrated $HClO_4$ was added and evaporated to dryness. After cooling, 1 mL of concentrated HNO_3 and three drops of H_2O_2 were added and allowed to react. Finally, 9 mL of 2% HNO_3 was added, the vessels were capped, and the solutions were heated at 100 °C for 30 min to ensure complete dissolution. The digests were then diluted to the required volume for analysis. For the analysis, Agilent 8900 ICP-MS/MS device was used.

S3. RRDE and GDE half-cell studies

The rotating ring-disc electrode (RRDE) half-cell studies were performed in Ar-saturated or O_2-saturated 0.5 M H_3PO_4 solution (85%, Carl Roth) at 23 °C with a catalyst-coated glassy carbon (GC, 5 mm disc diameter) tip-Pt ring working electrode (RRDE Pt-GC, Metrohm), a standard double junction mercury sulfate (Hg/Hg_2SO_4) reference electrode (sat. K_2SO_4, RREF0026, Pine Research Instrumentation), and a Pt-wire counter electrode. The potential values are reported to the reversible hydrogen electrode (RHE) and were converted using the equation $E_{\mathrm{RREF0026}} + 0.718(\pm 0.001)$ V.[1] The RRDE measurements were performed using the Nova 2.1 software, Autolab potentiostat/galvanostat PGSTAT204 with RRDE Rotator and Motor Controller (Metrohm). The cathodic direction polarisation curves for ORR were compensated for iR-drop using ohmic resistance values obtained by the current interruption method. The catalyst ink was prepared in 2-propanol with Nafion® solution (5%, Sigma-Aldrich) and pipetted onto the working electrode according to the published route.[1] In the case of all studied M-N-C materials 0.4 mg cm^{-2} catalyst loading was used, including the comparison Fe-N-C (PMF-014401, Pajarito Powder, LLC). The electron transfer number (n) and H_2O_2 yield (%) were calculated from RRDE ring (collection efficiency (N) of 23%)[1] and disc current and the corresponding equations.[2] The reported mass activity values at 0.80 V (MA@0.80V) from the RRDE disc curves have been calculated with respect to the M-N-C loading (0.4 mg cm^{-2}) using the equation from earlier work.[3]

Furthermore, an accelerated durability test (ADT) protocol for RRDE measurements was implemented with 10,000 CV cycles (100 mV s^{-1}) from 1.0 to 0.6 V vs RHE and an *I-E* ring and disc curve at 1600 rpm before and after the CV cycling. The M-N-C coated disc of the RRDE electrode was analysed before and after the ADT using the scanning electron microscopy (SEM) with a Helios Nanolab 600 (FEI) microscope operated at 10 kV. Also, the bulk elemental composition was studied using an INCA Energy Dispersive X-ray Spectrometer (EDX, Oxford Instruments), which was operated at an accelerating voltage of 15 kV.

The gas diffusion electrode (GDE) half-cell measurements were carried out according to the reported route and conditions.[1] The ink was prepared via sonication of 10 mg M-N-C in 776 µl 2-propanol, 234 µl Milli-Q water, and 7.5 µl polytetrafluorethylene (PTFE, 60%, Sigma-Aldrich) solution and drop-cast onto a 2.4 cm^2 gas diffusion layer (GDL, Freudenberg H23C2) to prepare the GDE. The GDE (M-N-C loading of 4.2 mg cm^{-2}, confirmed by ICP-MS) was hot-pressed (TRG-2, P/O/Weber) with a pre-soaked phosphoric-acid doped polybenzimidazole membrane (PA-PBI, Celtec®-P, TRIGONA Fuel Cell Components GmbH) to 80% of the total thickness. For application in the FlexCell® PTFE (Gaskatel) setup, the PA-PBI/GDE assembly was sandwiched between the stainless steel (SS 216L) plate current collector and PTFE shield, which limited the geometric active area to 0.5 cm^2 for both sides of the PA-PBI/GDE. The measurements were performed at 160 °C using 40 mL of 85 % H_3PO_4 electrolyte, a Pt coil counter electrode, a commercial RHE (Gaskatel) reference electrode, 150 ml min^{-1} O_2 gas flow, and silicone gaskets. The experiments were controlled by the potentiostat Modulab 2100 A (Ametek) equipped with a 12 V/20 A external booster (Ametek). The three-part measurement protocol consisting of “begin of test” (BoT) and “end of test” (EoT) cyclic voltammograms (CV) with galvanostatic steps and electrochemical impedance spectroscopy (EIS) measurements (iR-drop correction 95%) were performed according to the published route.[4]

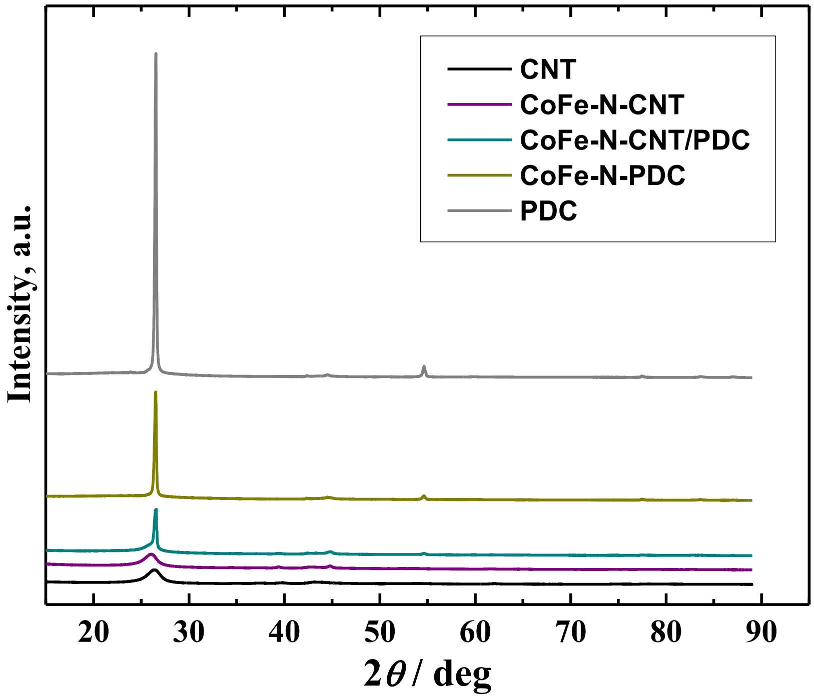


Fig. S1 XRD patterns for different catalyst materials and their backbone precursors.

Table S2 Elemental composition (wt%) of transition metals and S determined from ICP-MS analysis for different nanocarbon backbone CoFe-N-C catalysts.

Element	**CoFe-N-CNT**	**CoFe-N-CNT/PDC**	**CoFe-N-PDC**
S	0.111	0.061	0.005
Fe	2.159	1.353	0.962
Co	1.054	1.001	0.774
Mo	1.388	0.658	0.010
Zn	0.003	0.008	0.069

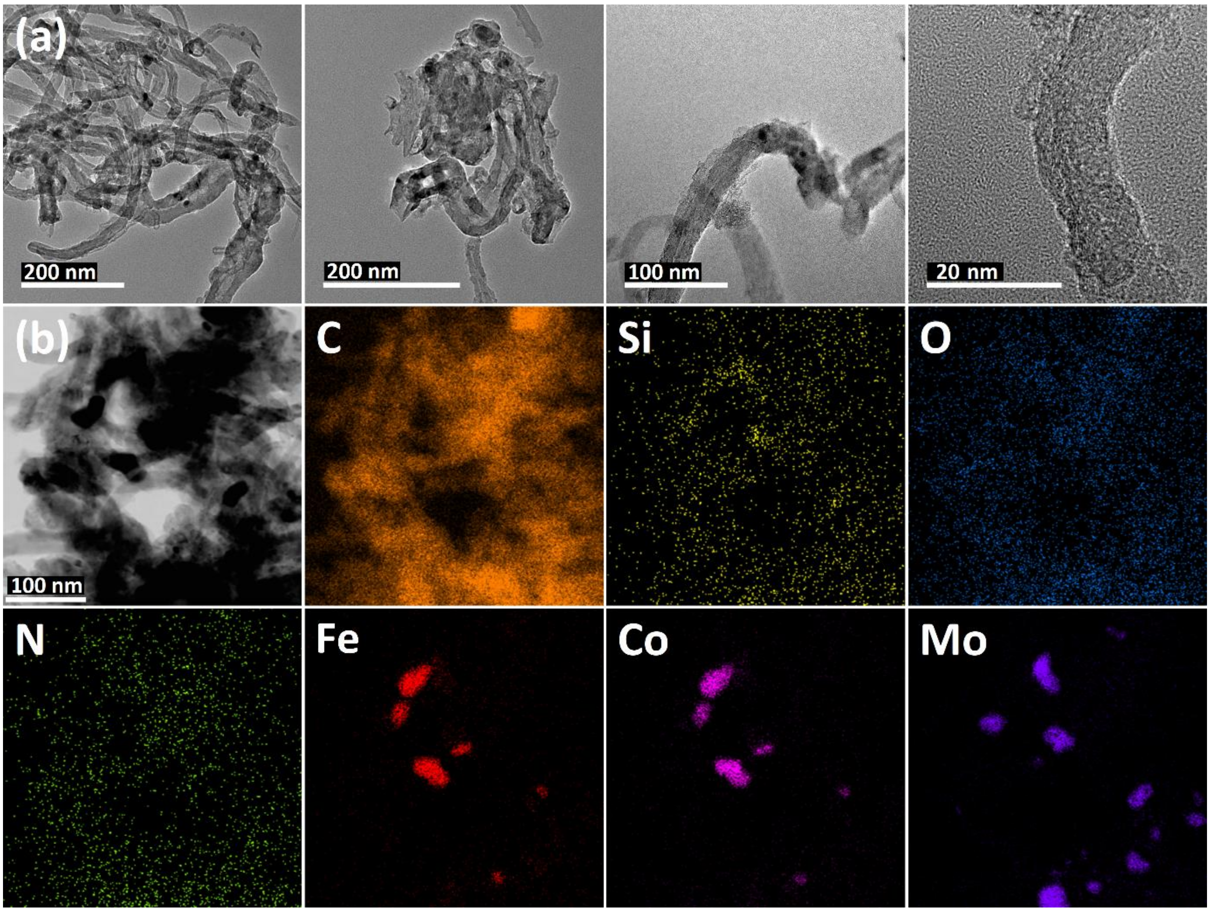


Fig. S2 Bright-field HR-TEM images for CoFe-N-CNT catalyst from (a) different magnifications and locations, (b) with TEM-EDS elemental maps.

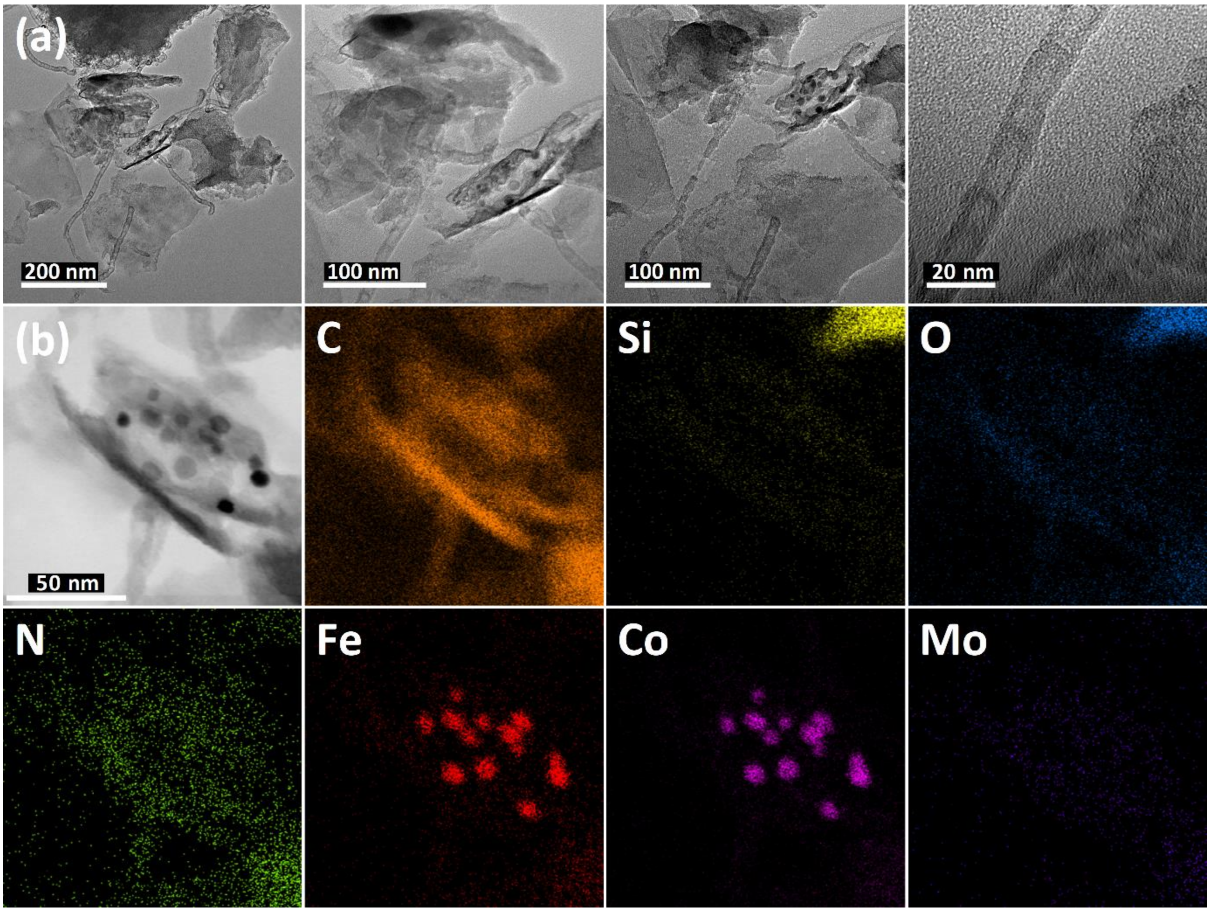


Fig. S3 Bright-field HR-TEM images for CoFe-N-PDC catalyst from (a) different magnifications and locations, (b) with TEM-EDS elemental maps.

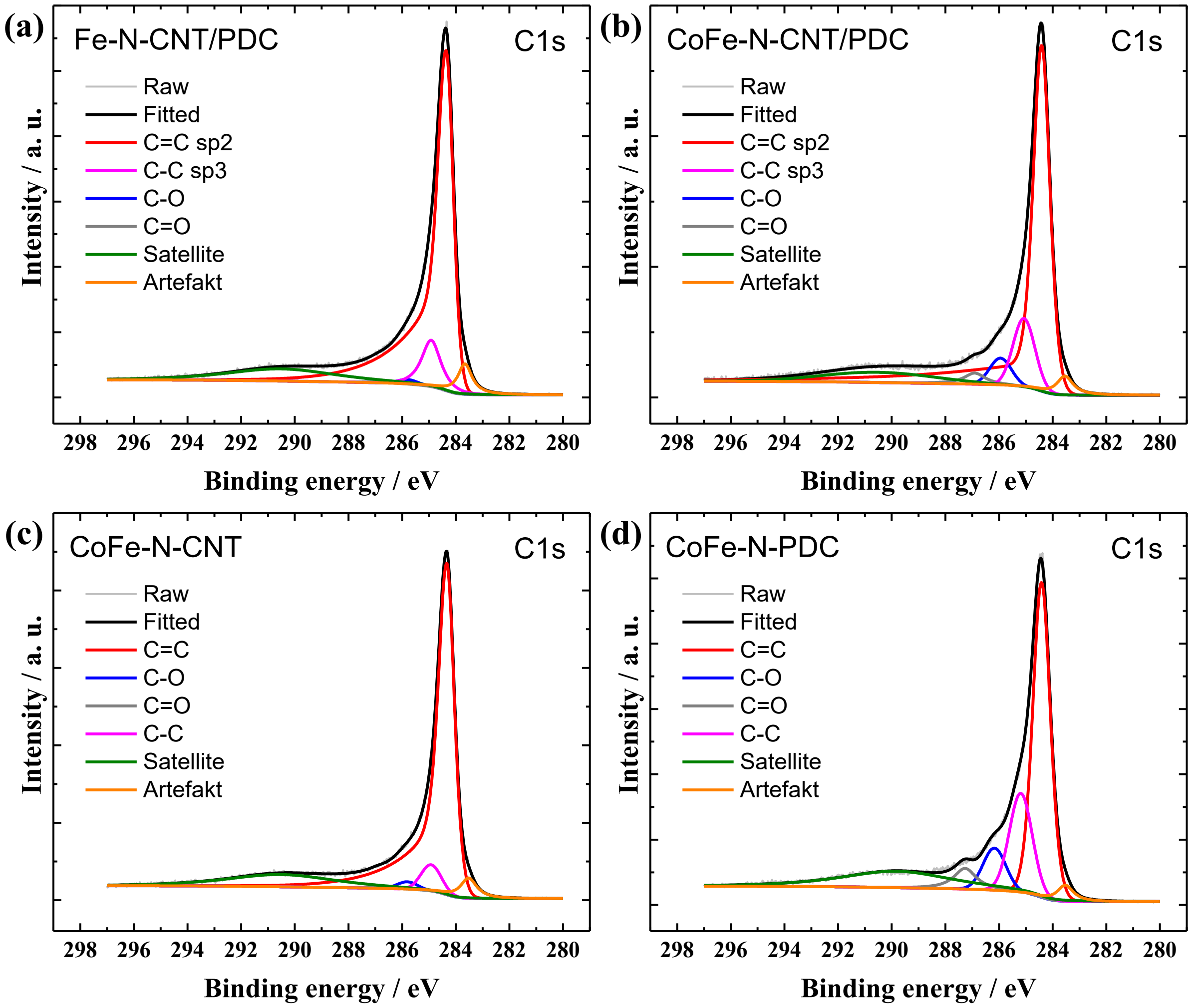


Fig. S4 Deconvoluted high-resolution XP-spectra of C1s of the determined carbon species for different catalyst material powders.

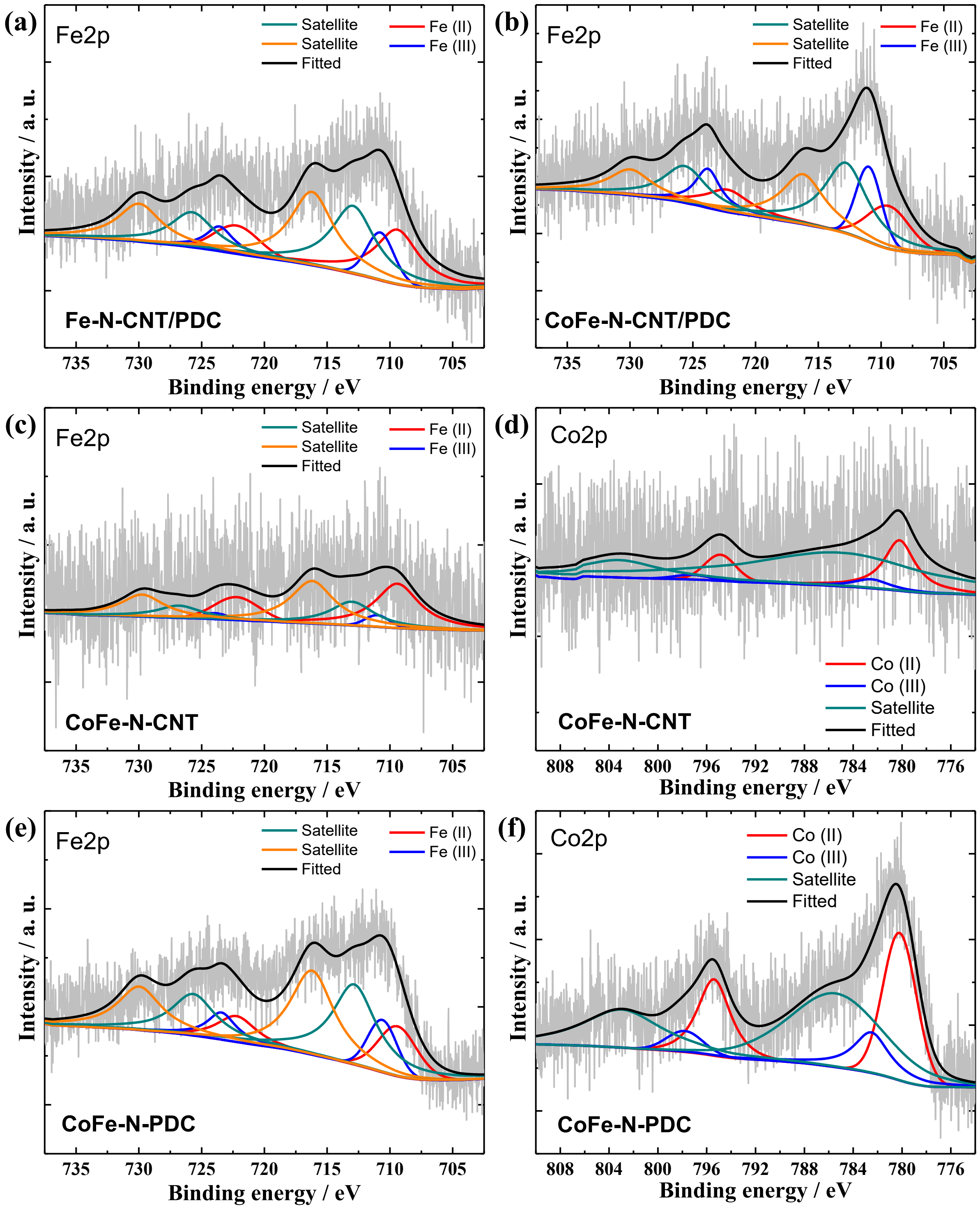


Fig. S5 Deconvoluted high-resolution XP spectra recorded in (a, b, c, e) Fe2p and (d, f) Co2p region for different catalyst materials. The deconvolution has been carried out according to the previously published procedures.[1-3]

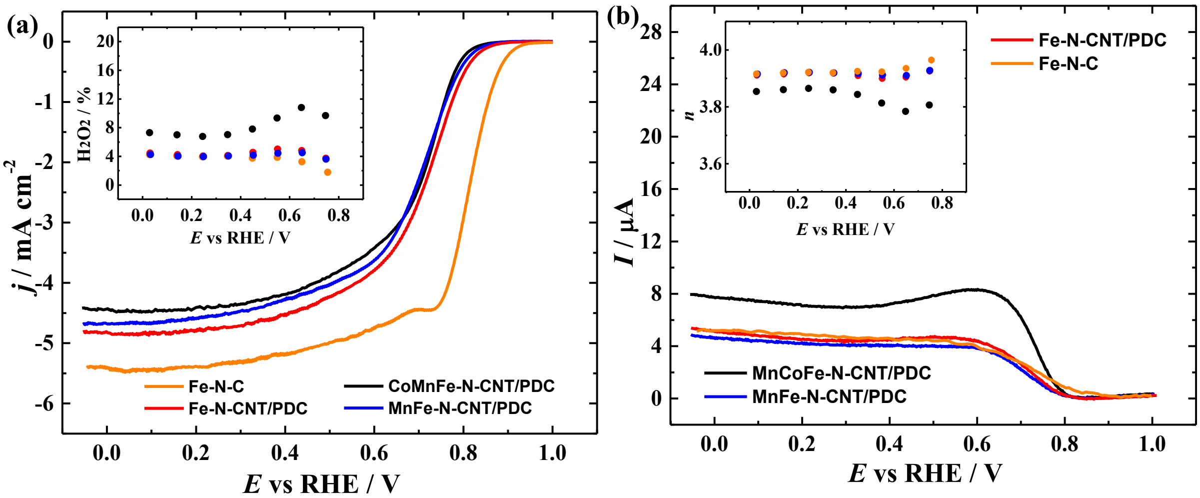


Fig. S6 Polarisation curves recorded with RRDE method for (a) oxygen reduction at disc, (b) H_2O_2 oxidation at ring on different M-N-C coated GC-disc with Pt-ring electrode in O_2-saturated 0.5 M H_3PO_4 at 1600 rpm and 10 mV s^{-1}. The insets show (a) peroxide yield (%) and (b) electron transfer number (*n*) as a function of potential. Catalyst loading 0.4 mg cm^{-2}.

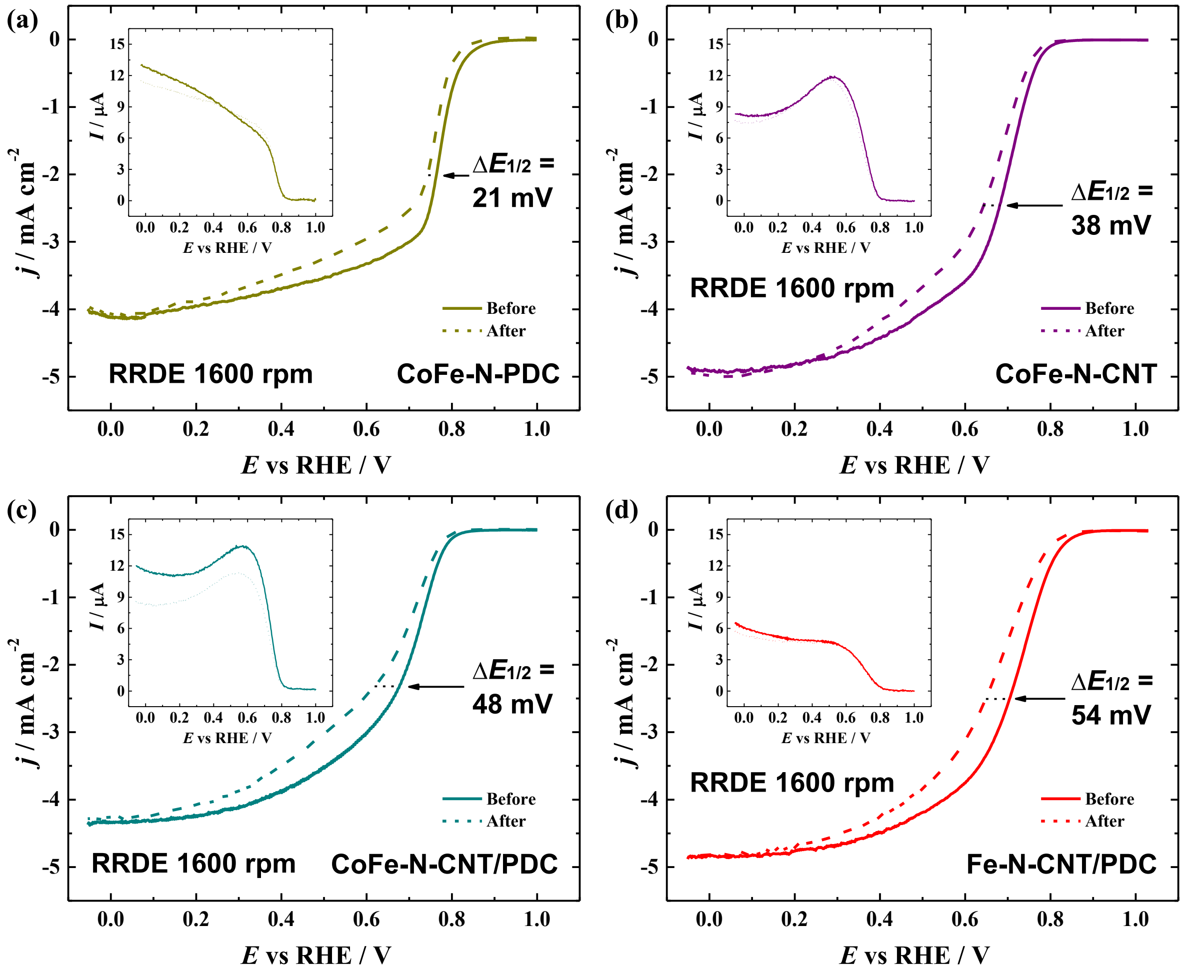


Fig. S7 RRDE voltammetry disc electrode curves for oxygen reduction at disc and (insets) H_2O_2 oxidation at ring before (solid line) and after (dashed line) 10 000 CV cycles recorded in 0.5 M H_3PO_4 at 1600 rpm (v = 10 mV s^{-1}) for different catalyst material coated GC electrodes. Catalyst loading 0.4 mg cm^{-2}.

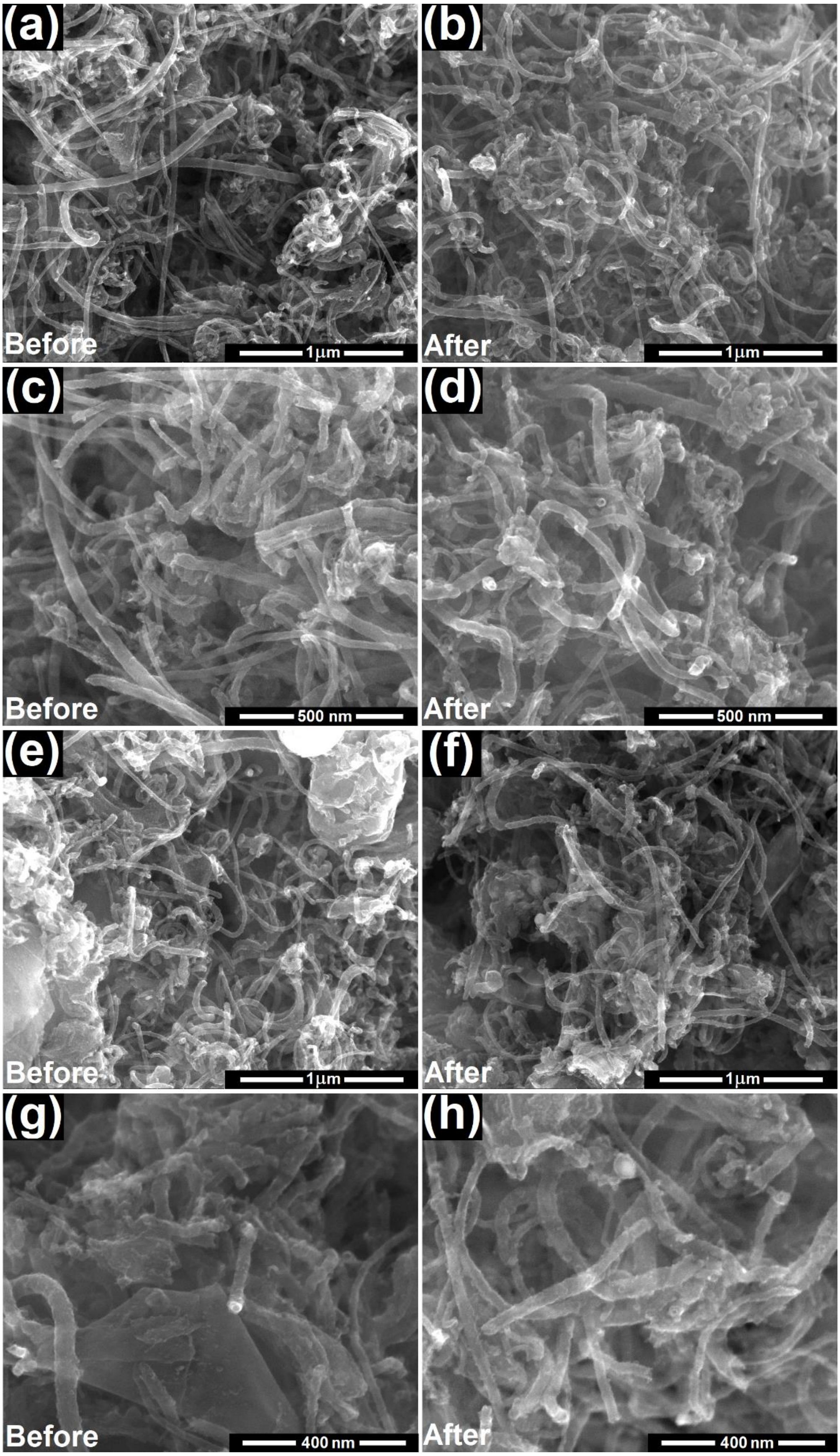


Fig. S8 SEM images before and after long-term stability testing of 10 000 CV cycles recorded in 0.5 M H_3PO_4 (Fig. S7) for (a-d) CoFe-N-CNT and (e-h) CoFe-N-CNT/PDC catalysts.

Table S3 Bulk elemental composition (wt%) determined from EDS analysis before and after long-term stability testing of 10 000 CV cycles recorded in 0.5 M H_3PO_4 (Fig. S7) for CoFe-N-CNT and CoFe-N-CNT/PDC catalysts with Nafion® solution coated on GC electrodes.

Element	CoFe-N-CNT Before	CoFe-N-CNT After	CoFe-N-CNT/PDC Before	CoFe-N-CNT/PDC After
C	86.2	85.2	77.9	77.4
N	3.4	3.4	2.8	2.4
O	2.0	3.2	7.2	9.0
F	5.1	5.0	7.2	5.7
Si	0.0	0.0	3.1	3.7
S	0.2	0.2	0.1	0.1
Fe	1.0	0.8	0.6	0.5
Co	1.0	0.9	0.6	0.5
Zn	0.0	0.0	0.0	0.0
Mo	1.2	1.3	0.6	0.7

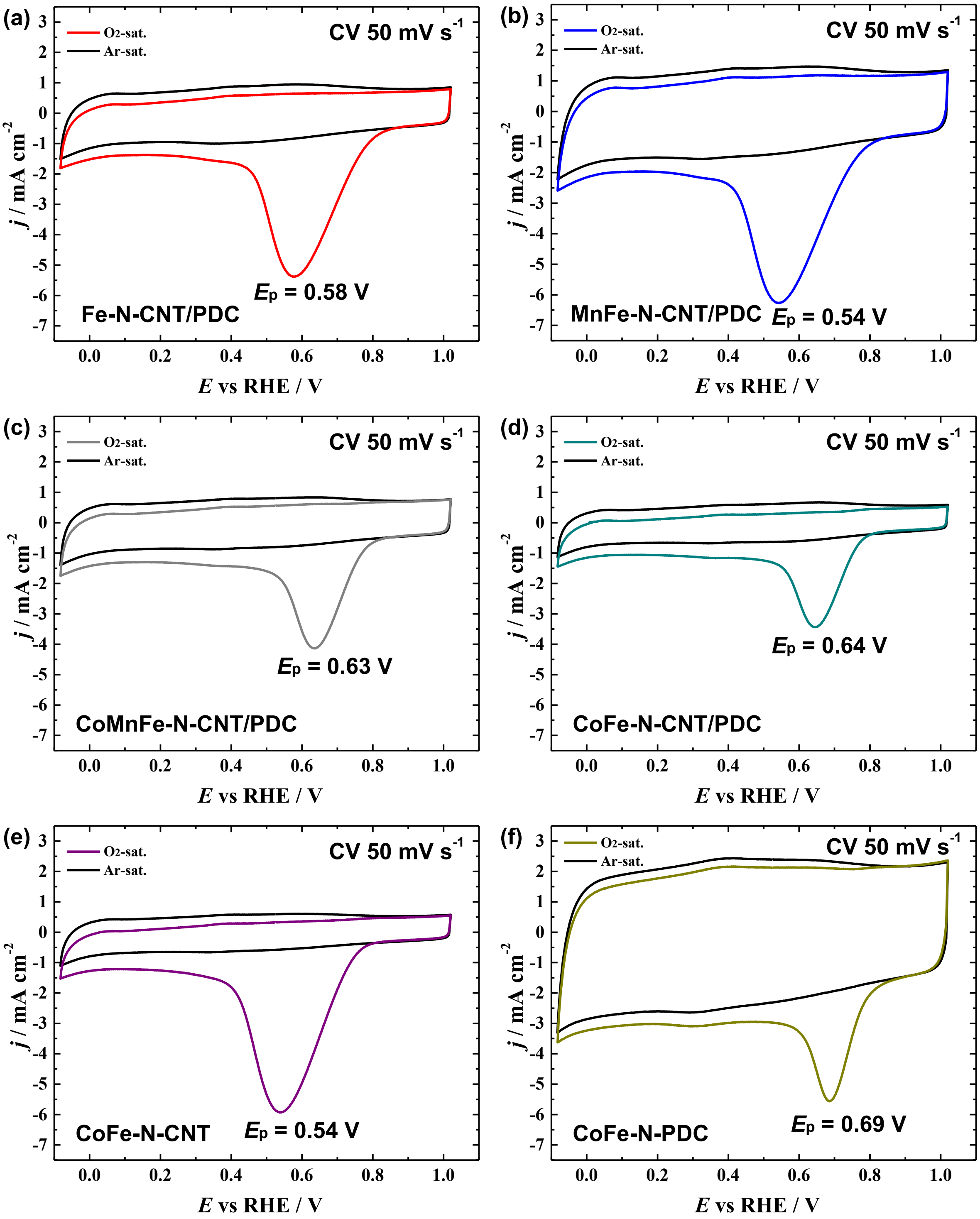


Fig. S9 Cyclic voltammograms of disc electrode recorded with different M-N-C functionalised catalyst material coated GC-disc with Pt-ring electrode in O_2- or Ar-saturated 0.5 M H_3PO_4. Catalyst loading 0.4 mg cm^{-2}.

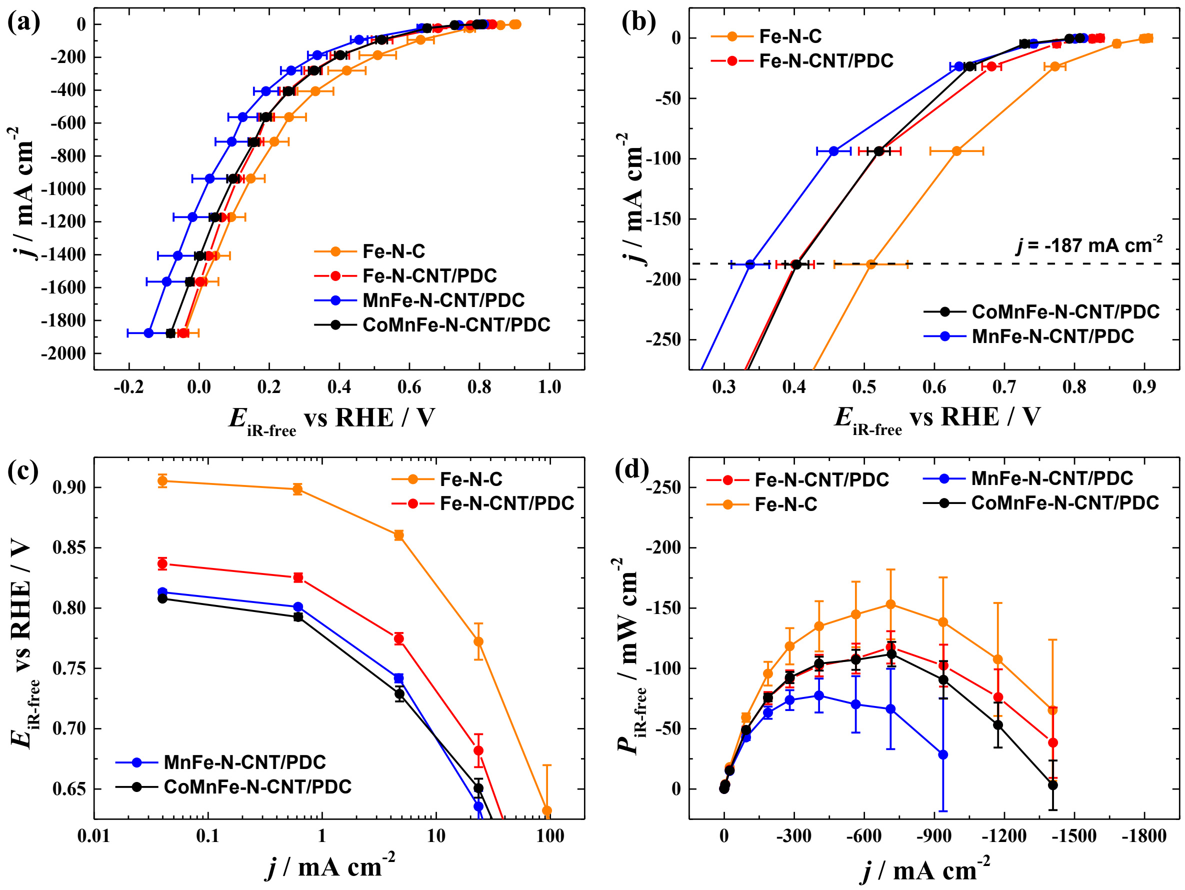


Fig. S10. (a, b) HT-GDE half-cell polarisation curves of M-N-C coated (4.2 mg cm^{-2}) GDEs for ORR measured using the O_2 flow rate 0.15 L min^{-1}, 160 °C, conc. H_3PO_4, PA-PBI membrane. (c) Semi-logarithmic plots of the polarisation curves and (d) calculated power density curves.

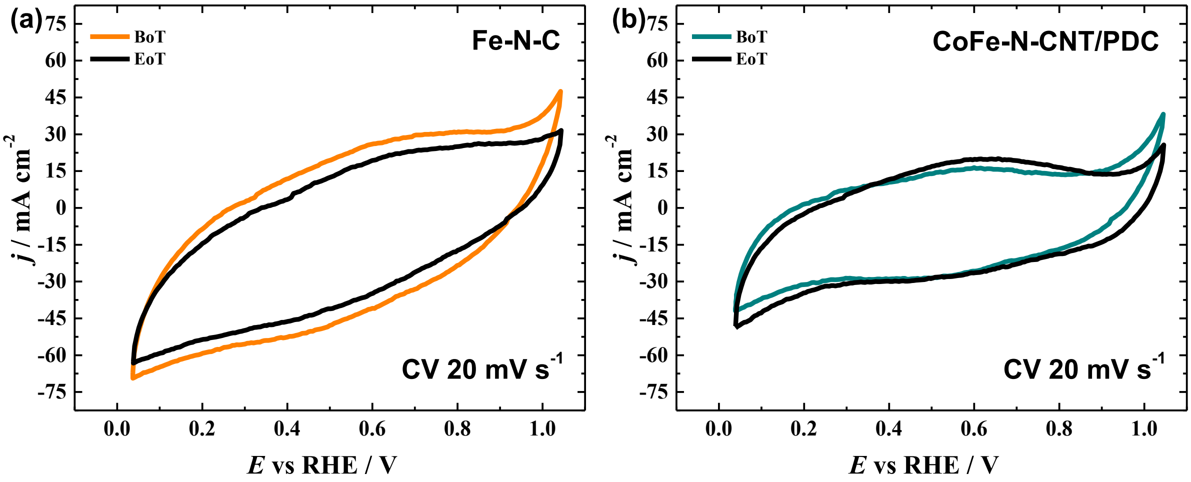


Fig. S11 CVs recorded before (BoT) and after (EoT) recording of the data for HT-GDE polarization curve of different catalysts shown in Fig. 7. The measurement was performed in a HT-GDE half-cell at 160 °C, conc. H_3PO_4, nitrogen flow rate of 120 mL min^{-1} and N_2 purge of the electrolyte, scan rate 20 mV s^{-1}. Catalyst loading 4.2 mg cm^{-2}.

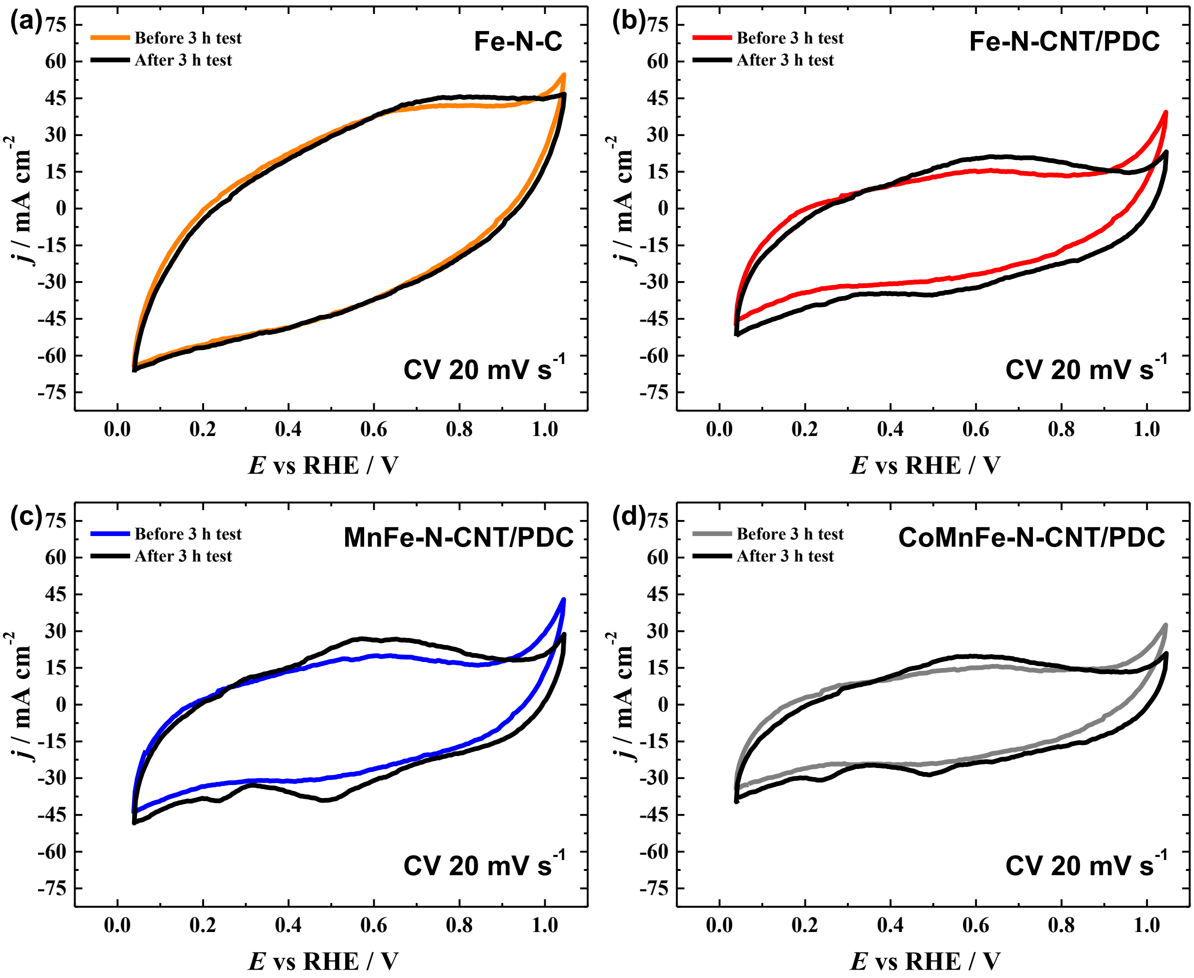


Fig. S12 CVs recorded with Fe-containing or Mn with multiple metals-based M-N-C catalysts before and after chronopotentiometry 3 h measurements at 0.1 A cm^{-2} with EIS measurements after every 20 minutes in HT-GDE half-cell at 160 °C, conc. H_3PO_4, nitrogen flow rate of 120 mL min^{-1} and N_2 purge of the electrolyte, scan rate 20 mV s^{-1}. Catalyst loading 4.2 mg cm^{-2}.

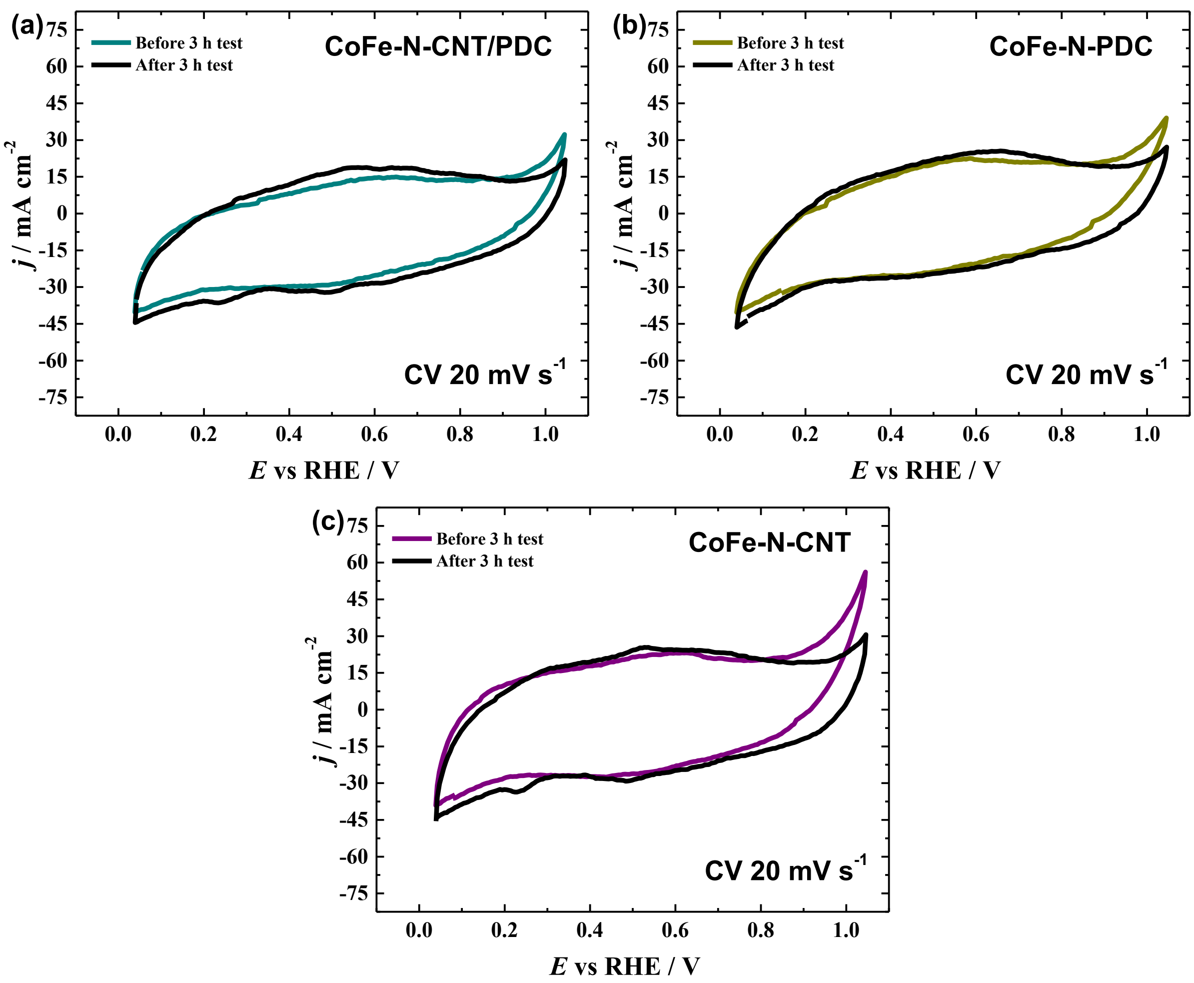


Fig. S13 CVs recorded with various CoFe-N-C catalysts before and after chronopotentiometry 3 h measurements at 0.1 A cm^{-2} with EIS measurements after every 20 minutes in HT-GDE half-cell at 160 °C, conc. H_3PO_4, nitrogen flow rate of 120 mL min^{-1} and N_2 purge of the electrolyte, scan rate 20 mV s^{-1}. Catalyst loading 4.2 mg cm^{-2}.

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