

Supporting Information

On an easy way to prepare Metal-Nitrogen doped Carbon with exclusive presence of MeN₄-type sites active for the ORR

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1. Experimental details

1.1 Preparation of catalysts

Preparation of porphyrin-based catalysts under addition of iron oxalate and sulfur. For the preparation of the Fe-N-C catalysts (Fe,Fe)₁ and (Fe,Fe)₂ 0.3 g sulfur were grounded in a mortar, in a first step. Then 1.07 g FeTMPPCl (TriPorTech, 95 % purity) and 5,145 g iron-oxalate dihydrate (Riedel de Häen) were added and everything was mixed until a homogeneous colour of the precursor was achieved. The precursor of (Co,Fe)-N-C catalyst (Co,Fe) was similarly prepared but utilizing 1.07 g CoTMPP instead of the FeTMPPCl. All three precursors were pyrolyzed at 800 °C. The heating ramp was 7.5 °C/min. At 450 °C the samples were held for 10 min before the heating process was continued to 800 °C where the temperature was maintained for 45 min. The complete heat-treatment processes were performed in nitrogen atmosphere. After quenching to room temperature (RT), the samples were acid-leached (1 M HCl) for about 5 hours, with 1 h US treatment. These suspensions were then filtrated and washed with distilled water until the filtrate exhibited a pH value of 5. The filter cakes were dried at 80 °C. For the preparation of (Fe,Fe)₁ the iron oxalate was previously grounded in an Achat Pulverisette (Fritsch, Germany).. This Pulverisette is located on a shaker that was continuously vibrated with 3000 vibrations min⁻¹ for 24 h in order to reduce the particle size of the as-received iron oxalate. During this process 20 g of iron oxalate were filled in the mortar together with the achat ball of 493 g and a diameter of 70 mm.

Preparation of porphyrin-based catalysts under addition of tin oxalate. The (Fe,Sn)-N-C precursor was prepared by mixing 0.57 g FeTMPPCl with 3.88 g tin oxalate in the mortar. For the (Co,Sn)-N-C precursor instead of the FeTMPPCl the same molar fraction of CoTMPP was utilized. These precursors were pyrolyzed at 750 °C in nitrogen atmosphere. Therefore, a heating ramp of 5 °C/min was applied. The samples were maintained at 450 °C for 15 min and at 750 °C for 45 min. After cooling down to room temperature the samples were similarly acid-leached as described for the catalysts prepared under iron oxalate and sulfur addition.

Purification treatment. The purification treatment includes a second heat-treatment of each catalyst in forming gas (10 % H₂ in N₂) with a heating ramp of 10 °C/min to the end temperature of the first heat-treatment (750 °C for porphyrins with tin oxalate, 800 °C for porphyrins with iron oxalate and sulfur), were the catalysts were maintained for 30 min. After cooling down, the samples were transferred to a second acid-leaching step in 1M HCl that was assisted by an ultrasonic treatment for 1h. Filtration and drying processes were similarly performed to the first acid-leaching.

1.2 Electrochemical characterization

Catalyst inks have been prepared by suspending 2 mg of catalyst in 400 μl of a 1:1 water-ethanol mixture containing 0.2 % Nafion. This suspension was treated 30 min in an ultrasonic bath and for about 10 s with an US homogenizer. 5 μl of the catalyst ink were dropped onto a 0.1963 cm^2 glassy carbon disk (RDE) obtaining a catalyst load of 0.13 mg/cm^2 . The experiments were carried out at room temperature in a three-electrode-system with a platinum wire as counter electrode and $\text{Hg}/\text{Hg}_2\text{SO}_4/0.5 \text{ M H}_2\text{SO}_4$ as reference electrode (0.68 V vs. SHE).

Prior to the determination of the oxygen reduction current the working electrode with our catalyst was cycled in a potential range from 1.0 V to 0.0 V with a scan rate of 50 mV/s in nitrogen-saturated 0.5 M H_2SO_4 . Typically 15-20 scans were required until a steady state was reached.

Previous to the RDE experiments, the electrolyte was purged with oxygen and the open circuit potential (OCP) was measured. RDE experiments were performed with a sweep rate of 5 mV/s in oxygen-saturated electrolyte at 200, 400, 576, 729 and 900 rpm (in this sequence). During the measurement, oxygen was only passed over the surface of the electrolyte. Tafel-plots have been calculated by the Levich-approach. All potentials are given in reference to the standard hydrogen electrode (SHE).

For catalysts prepared under tin oxalate addition the measurement conditions were slightly different as these samples belonged to a different project. In this case a catalyst load of 0.35 mg/cm^2 was obtained as the RDE disk had an area of 0.071 cm^2 . For the RDE experiments the rotation rates were 200, 400, 900, 1600 and 2500 rpm (in this sequence).

Therefore, the linear sweep voltammograms obtained for rpm900 are compared in this work. The mass-related kinetic current density is obtained by dividing the kinetic current density (in mA/cm^2) with the catalyst loading (in mg/cm^2).

1.3 Structural characterization

^{57}Fe Mößbauer spectroscopy. Mößbauer measurements were made to characterize the iron compounds within the catalysts prepared under iron oxalate and sulfur addition. The spectra was recorded at room temperature with a CMCA-550 (Wissel) equipped with a constant electronic drive system with a triangular reference waveform (Halder Electronics). A $^{57}\text{Co}/\text{Rh}$ -source was used, velocity scale and isomer shift δ_{iso} were calibrated with natural iron (α -Fe-foil, 25 μm thick, 99.99 % purity). An assignment of the iron species was made by a comparison of the Mößbauer parameters to literature data.

X-band Electron Paramagnetic Resonance Spectroscopy (EPR). For the X-band EPR spectroscopic measurements (9.5 GHz) a defined quantity of the (Fe,Fe)1 samples before and after purification treatment was filled into a quartz tube designed for X-band EPR. This tube was evacuated and purged with nitrogen three times. Finally, the tubes were brought to normal pressure in N_2 atmosphere before closing them. The EPR spectra were recorded at 5 K with a modulation amplitude of 1 mT and a modulation frequency of 100 kHz. The spectra shown in Figure 3a were corrected for the EPR spectrum of just the quartz tube.

X-ray absorption near edge spectroscopy. X-ray absorption spectroscopy of the iron edge was performed at beamline KMC-2 of BESSY II, Helmholtz-Zentrum Berlin für Materialien und Energie (HZB). The measurements were performed simultaneously in transmission and fluorescence mode. In transmission geometry a Fe foil, placed after the sample, was used to establish a reference signal I_{Ref} . The fluorescence signal was measured rectangular towards the incoming beam. Measurements were made with a step width of 0.5 eV with a holding time of 2 s between ± 50 eV of the iron edge (7112 eV) and a step width of 5 eV for 3 s for higher energies (> 50 eV above the edge).

X-ray diffraction. For the identification of crystalline phases, XRD measurements of all standard catalysts were carried out employing a Bruker diffractometer D8 Advance in Bragg-Brentano Θ - 2Θ coupling using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) and a silicon disk as sample holder. Samples were rotated during the measurements. Spectra were recorded in a range of $15^\circ < 2\Theta < 60^\circ$. The measured diffractograms were analyzed using the database of the Joint Committee on Powder Diffraction Standards (JCPDS).

Neutron Activation analysis. Neutron activation analysis was performed at the reactor BER II of the Helmholtz-Center Berlin in the group of D. Alber.

Transmission electron microscopy. TEM images were taken using a Philips CM 12 electron microscope at 120 kV. Small amounts of the catalyst were suspended in H_2O and then placed on a grid before drying.

2. Comparison of XANES and Möbbauser profiles for three different preparation approaches

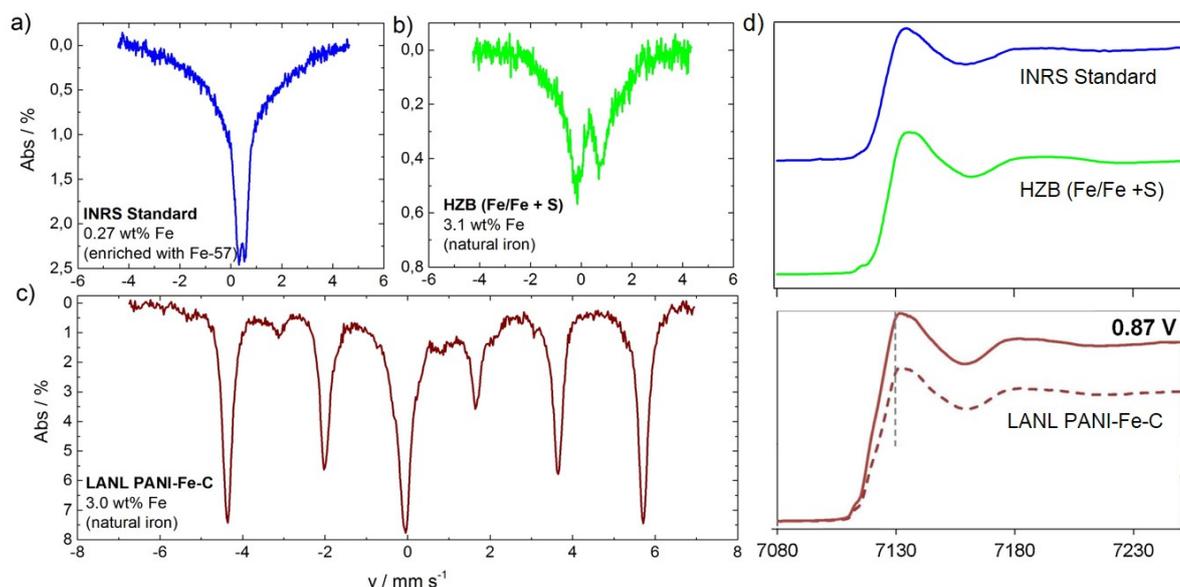


Figure S1: Comparison of the Möbbauser spectra (a-c) and XANES profiles (d) of three catalysts that are differing significantly in their preparation process. The Möbbauser spectra of INRS standard and HZB (Fe/Fe + S) shown in a) and b), respectively, are reproduced from Kramm et al., *Phys. Chem. Chem. Phys.* (2012) and Kramm et al., *J. Mater. Chem. A* (2014). The Möbbauser spectrum of LANL (PANI-Fe-C) is reproduced from Ferrandon et al., *J. Phys. Chem. C* (2012). The XANES profiles of INRS standard and HZB (Fe/Fe + S) are own measurements as performed at the KMC-2 beamline from BESSY II, whereas the image of the XANES profile of LANL (PANI-Fe-C) was taken and modified from literature, namely Ferrandon et al., Figure 1 *Electrochim. Acta* (2013).

Table S1: Summary of the precursor composition and preparation steps for the three catalysts compared in Figure S1 as well as reference to literature data.

	Precursors	Preparation steps	References
INRS Standard	FeAc, carbon black	HT1: 950 °C in NH ₃ (-35 wt%)	1
HZB (Fe/Fe + S)	FeTMPPCl, Fe oxalate dihydrate, Sulfur	HT1: 800 °C in N ₂ , 45 min AL1: 1M HCl, > 1h at room temp.	2
LANL PANI-Fe-C	FeCl ₃ , carbon black, aniline, APS	HT1: 900 °C in N ₂ , 1 h AL1: 0.5 M H ₂ SO ₄ , 80°C, 8h HT2: 900 °C in N ₂ , 3 h	3,4

3. RDE experiments on catalysts prepared by a pyrolysis of porphyrin plus tin oxalate

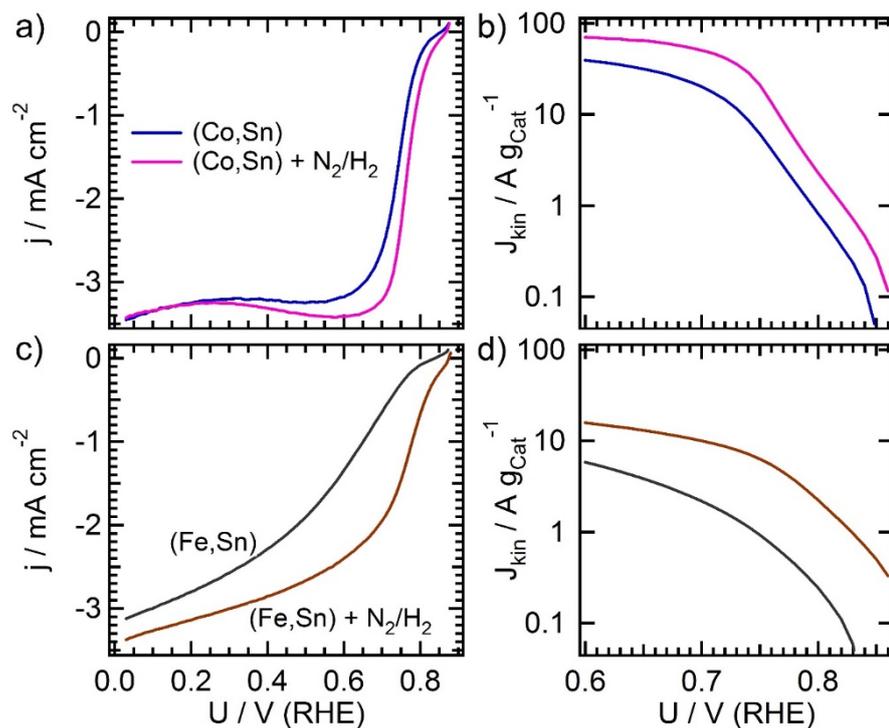


Figure S2: Effect of a forming gas treatment with subsequent acid leaching on the ORR activity of Me-N-C catalysts prepared from (a,b) cobalt porphyrin and (c,d) iron porphyrin with tin oxalate. Measurements performed in 0.5 M H_2SO_4 , with a N/C ratio of 0.4, area of the glassy carbon disk of 0.071 cm^2

4. Change in Metal content induced by the purification treatment

Table S2: Metal contents of some of the catalysts before and after the purification treatment. Values were obtained from Neutron Activation Analysis. The relative change is calculated as $(M_{\text{after}} - M_{\text{before}}) / M_{\text{before}} \cdot 100 \%$.

Catalyst label	(Fe,Fe) ₁	(Co,Fe)	(Co,Sn)
Before	3.1 wt% Fe	6.7 wt% Fe / 0.7 wt% Co	3.3 wt% Co / 9.0 wt% Sn
After (+ N ₂ /H ₂)	2.4 wt% Fe	2.9 wt% Fe / 0.3 wt% Co	2.8 wt% Co / 4.0 wt% Sn
Rel. change / %	-23 %	-57 % (Fe) / -57 % Co	-15 % (Co) / -56 % (Sn)

5. Mößbauer spectroscopy on (Co,Fe) and (Co,Fe) + N₂/H₂

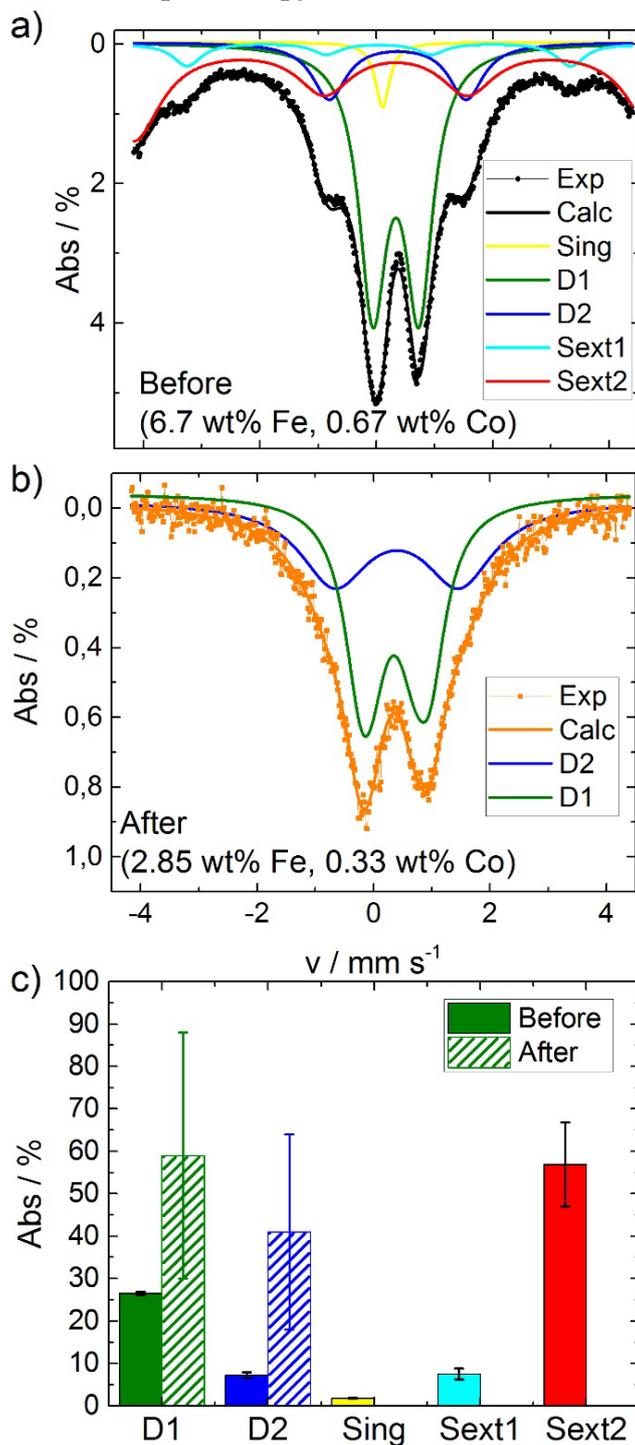


Figure S3: Mößbauer spectra of the (Co,Fe) catalyst before (a) and after (b) purification treatment. In c the relative absorption areas of iron species are compared. Mößbauer parameters and assignment to iron species are listed in Table 2 of the main manuscript. The overall metal contents given in part a) and b) were determined by Neutron Activation Analysis.

6. X-ray diffraction and TEM of (Co,Sn) catalysts

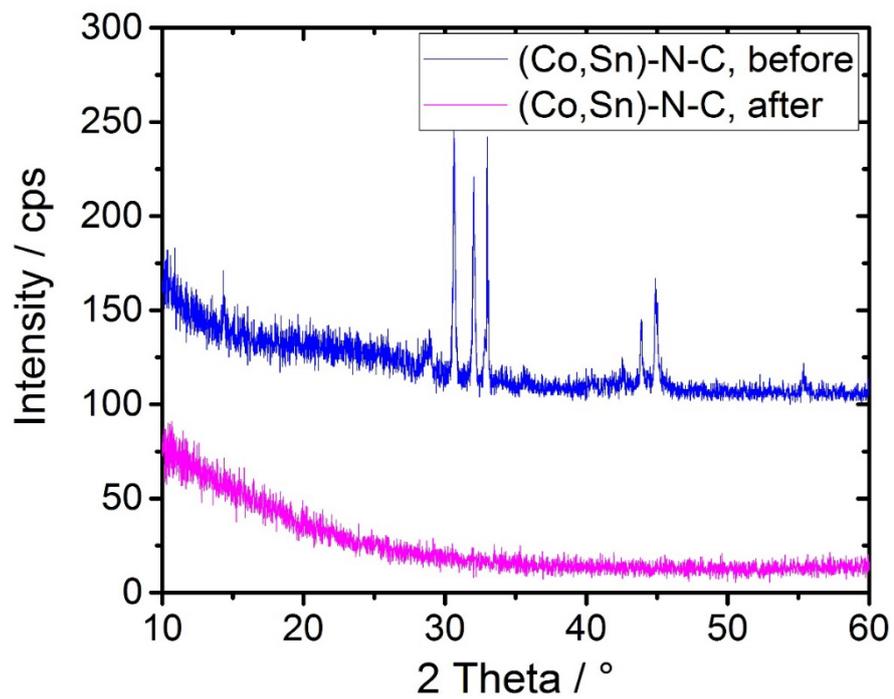


Figure S4: X-ray diffractograms of the (Co,Sn) catalyst before and after purification treatment.

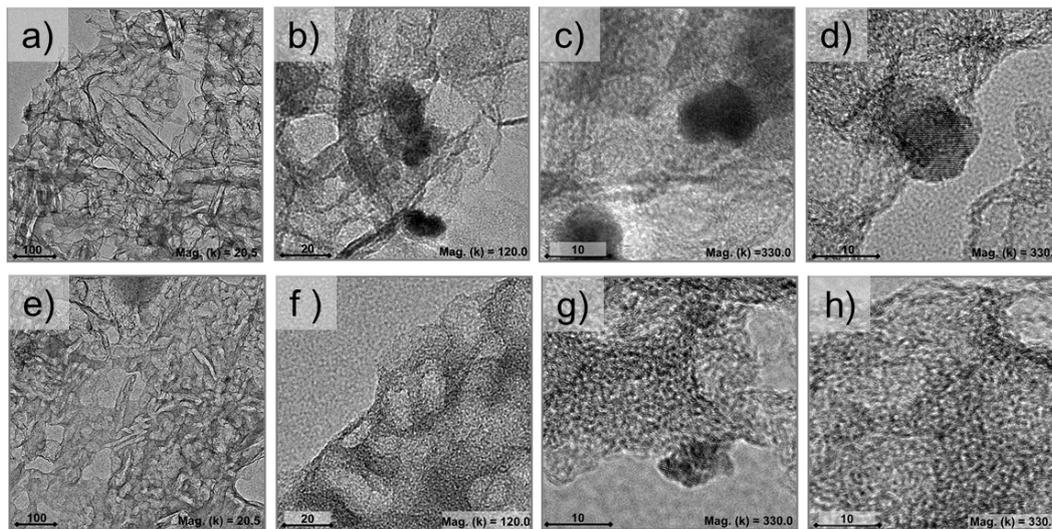


Figure S5: Comparison of TEM images of the (Co,Sn) catalyst before (a-d) and after (e-h) purification treatment.

7. Comparison of our particle-free catalysts to the ones described by Zitolo and Jaouen et al. in Nature Materials

In Nature Materials Zitolo and Jaouen et al. prepared two catalysts free of inorganic iron particles. Both catalysts were prepared from precursor containing ZIF-8, phenanthroline and iron acetate. The iron loading was 0.5 wt%.

The first catalyst, assigned as **0.5Fe** in that work was prepared by a heat treatment in Argon for 1 hour at 1050 ° C. In similarity to the weight loss obtained for catalysts prepared from a similar precursor for the same heat treatment conditions (Kramm et al., J.Am.Chem.Soc. 2014), we assume a weight-loss of 65 % for this catalyst. Consequently, the iron content after pyrolysis of this catalyst is assumed as ~ 1.5 wt% Fe.

For the second catalyst, assigned as **0.5Fe-900**, a pyrolysis in ammonia at 900 °C for 5 min was performed. Based on the weight loss obtained for carbon black in the same temperature range and based on the TG curve provided for a precursor composition close to the one described in the Nature Materials paper (Proietti et al., Nature Commun. 2011), we assume about 60 % weight-loss during this short pyrolysis. Therefore, the iron content after pyrolysis of this catalyst is assumed as ~ 1.2 wt% Fe.

For the Mößbauer spectra the exact absorption areas of the doublets D1 and D2 are not reported in the Nature Materials publication. Due to the high similarity to our spectra, however, we estimate the contribution of D1 in both spectra to ~ 50 %.

Supporting References

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- (2) Kramm, U. I.; Herrmann-Geppert, I.; Fiechter, S.; Zehl, G.; Zizak, I.; Dorbandt, I.; Schmeißer, D.; Bogdanoff, P. *Journal of Materials Chemistry A* 2014, *2*, 2663.
- (3) Ferrandon, M.; Wang, X.; Kropf, A. J.; Myers, D. J.; Wu, G.; Johnston, C. M.; Zelenay, P. *Electrochimica Acta* 2013, *110*, 282.
- (4) Ferrandon, M.; Kropf, A. J.; Myers, D. J.; Artyushkova, K.; Kramm, U.; Bogdanoff, P.; Wu, G.; Johnston, C. M.; Zelenay, P. *Journal of Physical Chemistry C* 2012, *116*, 16001.