

Supporting Information

Analyzing Structural Changes of Fe-N-C Cathode Catalysts in PEM Fuel Cell by Mößbauer Spectroscopy of Complete Membrane-Electrode-Assemblies

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Experimental methods:

Catalyst A. Typically, each batch of catalyst A was prepared by dry mixing 800 mg of MOF (ZIF-8, Basolite Z1200, Aldrich, produced by BASF), 200 mg of 1,10 phenanthroline ($\geq 99\%$, Aldrich), and 32 mg of iron^{II} acetate (Triportech, where iron was enriched at $\geq 95\%$ in ⁵⁷Fe as required for Mößbauer spectroscopy). This mixture was introduced under N₂ in a ca 65 cm³ hardened stainless steel crucible with 20 chrome steel balls of 0.25 inch diameter. Then it was ballmilled (FRITSCH Pulverisette 7) at 400 rpm for 3h. The resulting powder was pyrolyzed for 1h at 1050°C under a constant flow of Ar. This synthesis procedure yielded about 450 mg of catalyst powder (the typical mass lost during pyrolysis under Ar was roughly 70 %).

The catalyst powder was then leached for 24h in an HCl solution (a mixture of 1 volume of concentrated HCl and 2 volumes of de-ionized (DI) water). The resulting material was thoroughly rinsed with DI water. This acid leaching step was repeated twice. The final product was then dried under vacuum at 80°C for 1h, before being reactivated at 500°C under Ar for 1h.

This synthesis procedure, which yielded about 400 mg of a powder labeled cat A, was performed several times in order to get enough catalyst for this work. All individual batches were mixed together previous to the preparation of the cathodes.

Preparation of the cathodes. For all the cathode layers in this work, we used an ionomer-to-catalyst mass ratio of 1.5. The ink was prepared according to the following formula: 10 mg of catalyst was mixed in a glass vial with 326 μ L of Nafion 5 wt% dispersion solution (Aldrich), 163 μ L of ethanol and 136 μ L of DI water. Several steps were used to produce a homogeneous ink: 1) the corresponding volume of ethanol and DI water were added to the measured quantity of cat A and this solution was dispersed for 15 min in an ultrasonic bath; 2) glass beads and the Nafion dispersion were added, then the whole mixture was mixed for 15 more minutes in an ultrasonic bath followed by 30 min in a vortex mixer and again for 15 min

using ultra-sonication. To prevent overheating during ultra-sonication, ice was added to the ultrasonic bath to keep it cool. After the ink homogenization steps, an aliquot of 330 μl of this ink contained about 5.3 mg of catalyst and 8.6 mg of ionomer. Hence, 4 such volumes (330 μl) of this ink were deposited consecutively on a gas diffusion layer - GDL (Sigracet 25BC, square shape having a surface of 5.29 cm^2 covered by a microporous layer (as purchased) to obtain a final loading of catalyst of about 4 mg/cm^2 . After deposition and just before the surface of the catalyst/Nafion mixture completely dried, the electrode was covered with a Kapton film in order to minimize surface cracking. The catalyst-coated GDL was then let to dry in a vacuum oven at 80 $^{\circ}\text{C}$ for 1 h. To obtain a smooth electrode surface, after drying, the gas diffusion electrode (GDE) loaded with the catalyst/Nafion mixture was hot-pressed for 40 seconds at 120 $^{\circ}\text{C}$ under a load of 2000 lb. Then the Kapton film was removed leaving a smooth electrode surface.

Preparation of the anodes. Using the same type of GDL as for the cathode catalyst layer (Sigracet 25BC, square 5.29 cm^2), a volume of 209 μL of a solution containing the platinum catalyst (47 wt% Pt/Vulcan from Tanaka Kikinzoku Kogyo) was deposited and dried in order to obtain 0.5 $\text{mg Pt}/\text{cm}^2$. In the latter case, the ionomer-to-catalyst mass ratio was 2.

Preparation of Membrane-Electrode-Assemblies. Membrane-electrode-assemblies (MEAs) were obtained by hot-pressing 5.29 cm^2 square anode and cathode GDEs against either side of a Nafion membrane NRE 211 (thickness of ca. 25 μm and EW of 1100) at 120 $^{\circ}\text{C}$ for 40 seconds using a load of 2000 lb. Prior to applying the load, the MEA reached thermal equilibrium at the set temperature with the hot press plates.

Fuel cell testing. Fuel cell tests were performed in a single-cell test fuel cell using a custom-built fuel cell test bench and a BioLogic SP-150 Potentiostat equipped with a VMP3B-20 Booster and an EC-Lab V9.98 software. The mass loading of the catalyst was kept constant to have always the same electrode thickness in fuel cell tests. Teflon gaskets were used at both

the anode (135 μm thick) and cathode sides (185 μm thick). The gasket thicknesses were chosen to achieve about 30% total compression of the gas diffusion + catalyst layers. For all tests, the fuel cell temperature was kept at 80°C. Back pressures were set to 15 psig (1 barg) at the anode and cathode gauges, meaning that the absolute pressures at both electrodes were 30 psi or 2 bar, when the back pressure at each electrode is combined with the atmospheric pressure. H₂ and O₂ (or Air) flow rates were 0.3 slpm using fully humidified gases. The temperature of the O₂ (or Air) humidifier was set at 75 °C with their gas lines to the cell heated at 85 °C; the temperature of the H₂ humidifier was set at 90 °C with its gas line to the cell heated at 95 °C.

⁵⁷Fe Mößbauer experiments. ⁵⁷Fe Mößbauer spectroscopy was performed in standard transmission geometry with a ⁵⁷Co/Rh source of an initial activity of 50 mCi and a proportional counter as detector at room temperature. The source was moved backwards and forwards with a triangular waveform to apply slight changes in energy (expressed as Doppler velocity). Calibration of the velocity scale was made with respect to α -Fe. Mößbauer spectra were fitted with a Lorentzian size analysis provided by the software recoil 1.05. This allows the identification of the Mößbauer parameters and the relative absorption area of each iron site ($\text{Abs}_{\text{SiteX}}$). The assignment of iron species was made by comparing the obtained Mößbauer data to values published in literature for (non-pyrolyzed) FeN₄ macrocycles and/or inorganic iron species.

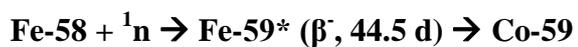
For detailed analysis of the changes of iron species with time of fuel cell operation the content of iron assigned to each site was calculated,

$$(\text{Fe}_{\text{SiteX}})_{\text{catA}} = (\text{Fe}_{\text{total}})_{\text{catA}} \cdot (\text{Abs}_{\text{SiteX}})_{\text{catA}}$$

assuming similar Debye-Waller factors for the different iron species.

For the investigation of structural changes at the Fe-N-C cathode catalysts in PEM fuel cells, two MEAs that were similarly treated were investigated at the same time to obtain enough signal and meaningful Mößbauer spectra.

Neutron Activation Analysis. Neutron Activation Analysis was performed at the reactor BER II of the Helmholtz-Center Berlin. During the analysis exclusively the Fe-58 isotopes are activated:



The radioactive decay of Fe-59* provides information on the content of Fe-58 within the sample. With the known fraction of Fe-58 isotopes in the samples also the overall content of iron can be determined.

Please note: Due to the requirements for ^{57}Fe Mößbauer Spectroscopy all investigated samples were prepared with Fe-57 enriched precursors. Hence, in order to take into account the changed isotopic distributions in our samples (induced by the Fe-57 enrichment) the Fe-57 enriched precursors were used as standards.

Energy Dispersive X-ray analysis. EDX mapping was performed on the cross sections of MEAs that were subjected to $t = 0$, $t = 1\text{h}$, and $t = 24\text{h}$ of oxidizing treatment. The conditioned MEAs were cut with a scalpel from the cathode to the anode, to get the cross sections of the MEA. EDX was made with respect to O, F, and Pt.

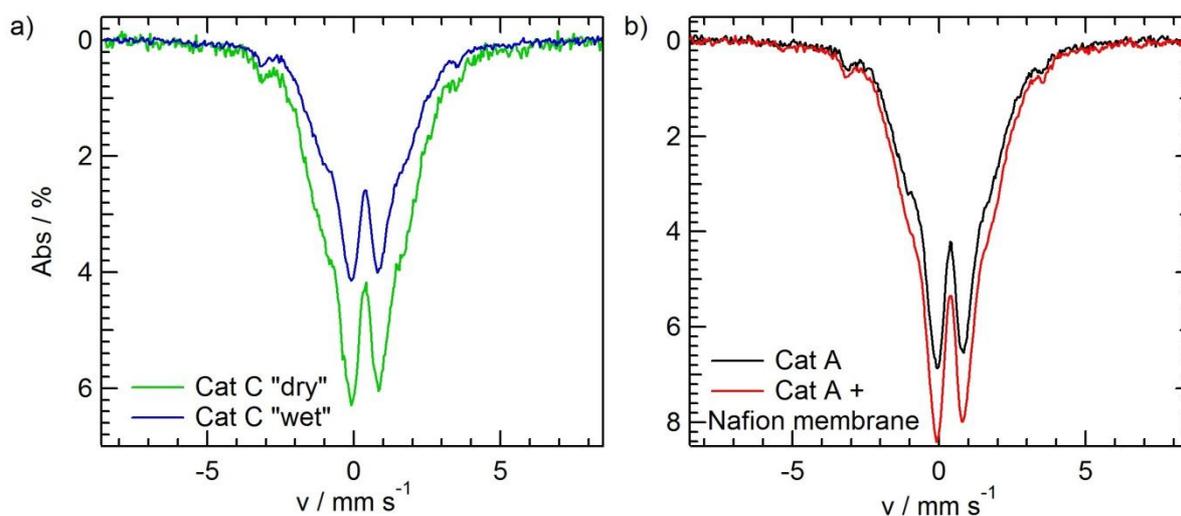


Figure S1: (a) Comparison of the Mößbauer spectra of Cat C, a “dry” catalyst powder similar to Cat A and the same catalyst labeled Cat C “wet”, after storage in water vapor. To wet “dry” Cat C, a glass ($V = 600$ ml) was first filled with 300 ml of boiling water. Then, a Petri dish filled with 120 mg of the powder of “dry” Cat C was placed above the water level and kept there for 1.5 hours whereas the glass was covered during this time. After this treatment, the mass of “wet” Cat C was 122 mg. It corresponds to an uptake of $2 \mu\text{l}$ of water by the powder of “dry” Cat C. (b) Comparison of the Mößbauer spectrum of Cat A with that of the same catalyst, but with a Nafion membrane NM-212 (Quintech) placed between the source of γ rays and the powder of Cat A.

Explanation details for a decreasing absorption probability observed when the catalyst powder is mixed with Nafion.

With respect to Figure 1b of the main text, the most significant change that appears in the Mößbauer spectra during the preparation of the MEA is related to a drastic reduction in the Mößbauer absorbance of the catalyst after mixing it with Nafion+ EtOH. As a consequence, after evaporation of EtOH, the Mößbauer absorbance of the remaining Cat A, mixed with Nafion on a Cathode or in a MEA, is much smaller than the absorbance of a powder of Cat A. This is to be compared with the effect of EtOH on the powder of Cat A that resulted in an enhancement of the Mößbauer absorbance.

The recoil is proportional to the reciprocal of the mass of the iron-containing solid. By considering that for samples containing catalyst and Nafion the recoil is taken by the overall mass ($m_{\text{cat+Nafion}}$), one would expect a larger recoilfree fraction and therefore a higher absorption probability in comparison to the Nafion-free sample (where the recoil is taken only by m_{cat}). Obviously, this is not observed experimentally and Nafion cannot be considered as solid in terms of recoil.

To explain the observed behavior and the drastic decrease of the Mößbauer absorbance, we have to consider two effects: (i) a hindering effect for each catalyst particle surrounded by Nafion in the ink that prevent the catalyst particles to form large aggregates of catalyst (and therefore large masses) onto the GDE of the Cathode or in the MEA after ink drying; (ii) the fact that dry (recast) Nafion may be considered as a viscous liquid rather than a rigid ionomer. The Mößbauer absorbance of small particles of Cat A surrounded by a viscous thin layer of recast Nafion becomes therefore smaller than that of the original powder of Cat A.

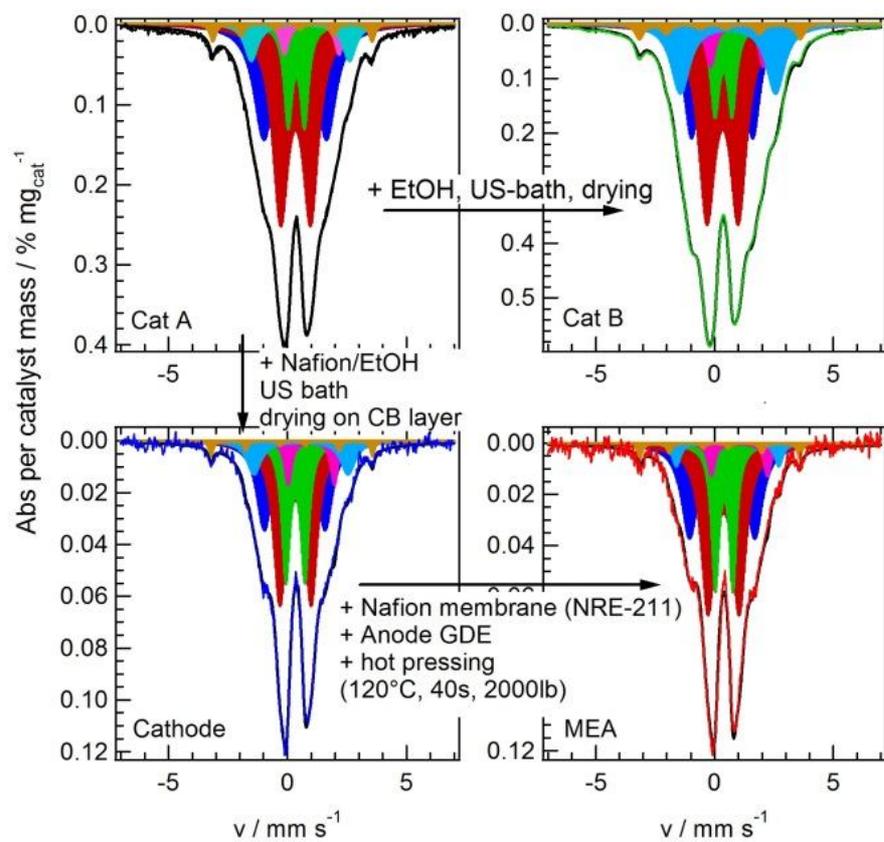


Figure S2: Deconvolution of the Möbbaauer spectra of Cat A, Cathode, MEA, and Cat B of Figure 1b. It is important to note the difference in these four absorbances normalized to the same mass of catalyst.

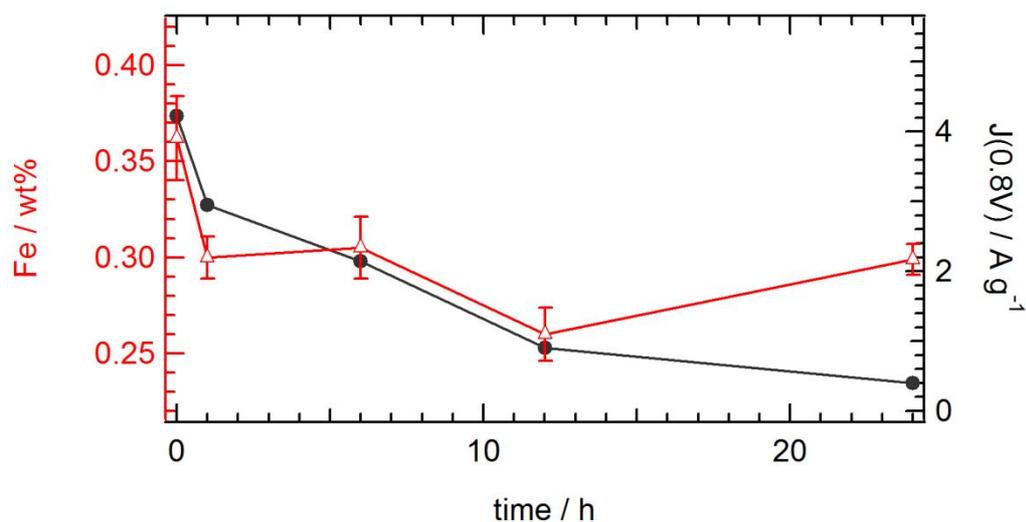


Figure S3: Superimposition of the change in mass activity of the catalyst measured electrochemically at 0.8V in one MEA submitted to the oxidizing treatment depicted in Figure 2c and the change in the experimental iron content measured by NAA before and after 1, 6, 12, and 24h in the several MEAs used to obtain the Mößbauer spectra of Figure 3a.

Table S1: Determined concentration of iron in iron carbide ($\text{Fe}_{\text{Sext.}}$) and correction factors $f(t)$ to calculate the corrected iron concentrations of each FeN_4 site in Figure 4 from the determined iron concentrations of these sites. For correction the average value of the first two measured points (0.0085 wt%) was related to the as determined iron concentration of the sextet.

	0h	1h	6h	12h	24h
$\text{Fe}_{\text{Sext.}}$ / wt%	0.0098	0.0073	0.0117	0.0147	0.0275
$f(t)$	0.867	1.16	0.77	0.57	0.31