Supplementary information

Degradation of Fe/N/C catalysts upon high polarisation in acid medium

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Experimental

Catalyst synthesis

Preparation of the catalyst precursor for the Fe/N/C catalyst involved the weighing of Fe^{II}Ac, phen and ZIF-8 (31.45 mg Fe^{II}Ac / 200 mg phen / 800 mg ZIF-8), followed by the rapid complexation of Fe^{II} by phen in a ethanol/water solution (1:2, v/v), dispersion of ZIF-8 into the iron-phen complex solution that was then stirred for 1h. The dispersion was then heated mildly to evaporate 3/4 of the water and ethanol and transferred in a vacuum oven for overnight drying at 80°C. The collected dry powder (ca 1 g) was then placed in a zirconium oxide crucible (ca. 45 cm³) filled with 100 zirconium oxide balls of 5 mm diameter (0.4 g each). The crucible was sealed under air and placed in a planetary ball-miller (FRITSCH Pulverisette 7 Premium) to undergo 4 cycles of 30 min of ball-milling at 400 rpm. The resulting catalyst precursor was then transferred into a quartz boat (10-15 cm long) and inserted into a quartz tube (1 inch diameter) and shock-heated within ca 2 minutes up to 1050 °C in a flowing Ar atmosphere (flow rate *ca*. 650 sccm) and held at this temperature for 1 h. The pyrolysis was stopped by opening the split hinge oven and directly removing the quartz tube from the oven. A second catalyst, labelled Fe/N/C-dry, was synthesized absolutely identically to Fe/N/C except that the wet complexation of Fe^{II} by phen and subsequent addition of ZIF-8 in the solution was bypassed, and the dry powders of Fe^{II}Ac, phen and ZIF-8 (31.45 mg Fe^{II}Ac / 200 mg phen / 800 mg ZIF-8) were weighed and directly inserted in the zirconium oxide crucible for ballmilling. After pyrolysis, catalysts were acid-washed via immersion and stirring in a pH 1 H₂SO₄ aqueous solution at room temperature, filtered and then copiously washed with de-ionized water.

Rotating-disk electrode measurements

Electrochemical activity of the catalysts towards the ORR was determined using the rotating disk electrode (RDE) technique. A catalyst ink including 10 mg of catalyst, 109 μ l of a 5 wt. % Nafion[®] solution, 300 μ l of ethanol and 36 μ l of de-ionized water was sonicated and mixed using a vortex. An aliquot of 7 μ l was deposited on the glassy-carbon disk (0.196 cm²) resulting in a catalyst loading of *ca*. 800 μ g·cm⁻². The working electrode with the deposited catalyst layer was used in a three-electrode cell setup connected to a potentiostat (Versastat 3, AMETEK) and rotator (MSR, Pine Instruments). The counter electrode and reference electrode were a gold wire and a reversible hydrogen reference electrode, respectively. The latter comprised a Pt wire immersed in a H₂-saturated 0.1 M H₂SO₄ electrolyte volume filling

a separate compartment connected to the cell electrolyte through a narrow fritted glass section. The electrolyte in the main cell was an O₂-saturated aqueous solution of 0.1 M H₂SO₄. For measurements at 40-80°C, the entire glass cell, including the reference electrode compartment, was immersed in an oil bath heated with a hot plate and regulated by a thermocouple immersed in the electrolyte. A RDE glassy-carbon tip shrouded in polyether ether ketone (Pine Instruments) and designed for high temperature was used as a working electrode. The RDE polarization curves were recorded with a scan rate of 10 mV·s⁻¹ at 1500 rpm and corrected for the background current measured in the N₂-saturated electrolyte.

MEA preparation

Cathode inks were prepared using the following formulation: 20 mg of catalyst, 652 μ l of a 5 wt. % Nafion[®] solution, 326 μ l of ethanol and 272 μ l of de-ionized water. The inks were alternatively sonicated and agitated with a vortex mixer every 15 min, for a total of 1h. Then, three aliquots of 400 μ l of the catalyst ink were successively deposited on the microporous layer of an uncatalysed 4.84 cm² gas diffusion layer (GDL, Sigracet S10-BC) to reach a catalyst loading of 4 mg cm⁻². The cathode was then placed in a vacuum oven at 90 °C to dry for 1 h. The anode used for all PEMFC tests performed in this work was 0.5 mg_{Pt}·cm⁻² on a Sigracet S10-BC GDL. MEAs were prepared by hot-pressing 4.84 cm² anode and cathode against either side of a Nafion[®] NRE-211 membrane at 125 °C for 2 min. The cathode had previously been smoothed by pre-pressing it at 125 °C for 40 s in order to minimize the risk of puncturing the membrane during MEA hot pressing.

PEMFC testing

PEMFC tests were performed with a single-cell fuel cell with serpentine flow field (Fuel Cell Technologies Inc.) using an in-house fuel cell bench and a Biologic Potentiostat with a 50A load and EC-Lab V10.19 software. Teflon gaskets were used at both the anode and cathode sides. The gasket thicknesses were chosen to achieve 15-20 % compression of the gas diffusion electrodes. For the tests, the fuel cell and humidifier's temperatures were 80 °C, and the inlet pressures were set to 1 bar gauge for both anode and cathode sides. Thus, the absolute pressure for both H₂ and O₂ was 1.5 bars (with *ca*. 0.5 bar partial pressure attributed to the water vapour at 80 °C with 100% relative humidity). The flow rates for humidified H₂ and O₂ were *ca* 50-70 sccm downstream of the fuel cell. Polarization curves were recorded by scanning the cell voltage from open circuit voltage down to 0.3 V at a scan rate of 0.5 mV·s⁻¹.

SEM-EDX analysis of the MEA cross section

A small piece of an MEA was embedded in an Agar low viscosity resin (LV R1078) that, after polymerization, allowed an easy sectioning with a quartz blade and a satisfactory surfacing with a Diatom[™] knife. The MEA cross section was analyzed with a SEM (Quanta 200F from FEI) equipped with an Energy Dispersive X-ray system for chemical analysis (X-max, Oxford Inca)

Mössbauer spectroscopy

In order to obtain enough signal with 4 mg cm⁻² cathode loadings, a catalyst was synthesized using a 50/50 mix of ⁵⁷Fe acetate and natural Fe^{II} acetate, thereby increasing the content of ⁵⁷Fe in the catalyst by a factor 25. The synthesis procedure was otherwise unmodified. ⁵⁷Fe Mössbauer spectra were measured with a source of ⁵⁷Co in rhodium metal. The measurements were performed keeping both the source and the absorbers at room temperature. Pristine or *post mortem* cathode layers of *ca* 5 cm² geometric area and with a loading of 4 mg_{FeNC} cm⁻² were cut in four pieces and stacked for the transmission Mössbauer experiments. The spectrometer was operated with a triangular velocity waveform, and a NaI scintillation detector was used for the detection of the gamma rays. Velocity calibration was performed with an α -Fe foil. The spectra were fitted with appropriate combination of Lorentzian lines. In this way, spectral parameters such as the isomer shift (IS), the electric quadrupole splitting (QS), the linewidth at half maximum (LW) and the absolute resonance areas (A) of the different components of the absorption patterns were determined.

For the fitting of the six experimental spectra, the following fitting strategy was applied: 1) the parameters (IS, QS, LW) for D* and for the singlet were obtained from the fitting of the spectrum of the Fe/N/C cathode after 600 cycles, 2) the parameters for D1 were obtained from the fitting of the spectrum of the pristine Fe/N/C-dry cathode, 3) the fitting of the pristine Fe/N/C cathode was performed with the parameters for the singlet and for D1 found in steps 1-2 being constrained, 4) the fitting of the Fe/N/C cathode after 150 and 600 cycles was reperformed with the parameters for singlet, D*, D1 and D2 found in steps 1-2-3 being constrained, 5) the fitting of the Fe/N/C dry cathode after 150 and 600 cycles was performed with the parameters for singlet, D*, D1 and D2 performed, while those for D2 were not constrained in this series.

Identical-location STEM and EDS

For Identical Location Scanning Transmission Electron Microscopy investigations, the catalyst suspension was prepared by diluting a small amount of the catalyst in de-ionized water. About 5 µl of the diluted solution was deposited on a TEM gold finder grid (NH7) coated with a Lacey carbon film and then dried in air. High-resolution STEM and EDS investigations were performed with a JEM-2200FS (Jeol, Japan) transmission electron microscope, operated at an acceleration voltage of 200 kV. The electrochemical treatment was carried out by immobilizing the gold grid on top of a glassy carbon tip. The tip was then connected to a rotating disk electrode (Radiometer Analytical, France) and inserted in a three compartment Teflon cell, with a graphite rod, as counter electrode, and a saturated Ag/AgCl electrode (Metrohm), as a reference electrode. The Ohmic drop was compensated by means of positive feedback. The degradation investigation included three steps, namely, observation of the catalyst at the pristine stage (0 cycle), after 300 and 900 cycles of 3s/3s at 0.9/1.4 V vs. RHE. Further details concerning the Identical Location technique can be found in Ref. (1).

High frequency resistance measured with electrochemical impedance spectroscopy

The HFR-value of an MEA usually represents the sum of the membrane resistance and contact resistances occurring at the interface between the different components.² This lump resistance is labelled R. However, for a thick porous electrode (in our case, the cathode) an additional component to the overall HFR may arise. The analytical expression for the HFR of a porous electrode of thickness L and having effective ionic and electronic conductivities σ_e and σ_i is L/($\sigma_e + \sigma_i$).³ In that case, the total HFR of the MEA (neglecting the HFR of the thin Pt/C anode) is given by the equation HFR = $R + L/(\sigma_e + \sigma_i)$, where L is the cathode thickness. It can be deduced that, for a fixed cathode thickness L, the cathode HFR component is negligible if only one of the two conductivities is large enough. Usually, in PEMFC electrodes, the electronic conductivity is at least *ca* 100 S m^{-1.4} According to the equation, an additional resistance of 10 m Ω cm² is expected from the 100 µm-thick cathode (typical for the Fe/N/C loading of 4 mg cm⁻²). The initial HFR-value of the MEA before cycling is 85 m Ω cm² (Fig. 5D), as expected for a humidified Nafion 211 membrane, contact resistances and an HFR component of 10 m Ω cm² due to the thick cathode. From Fig.5D, and assuming that the lump membrane & contact resistance R is 85 - $10 = 75 \text{ m}\Omega \text{ cm}^{-2}$ (constant with cycling), an initial value for the cathode-specific HFR-value (*i.e.* L/($\sigma_e + \sigma_i$)) of 10 m Ω cm^{-2} is found for the pristine MEA, but increases to 165 m Ω cm⁻² after 300 cycles. From the

HFR expression and assuming a cathode thickness of 100 μ m, one may then calculate that the sum ($\sigma_e + \sigma_i$) is 100 S m⁻¹ initially but only 6 Sm⁻¹ after 300 cycles. Since the effective proton conductivity σ_i in such Nafion-carbon based porous active layers is typically 1-2 S m⁻¹ in these experimental conditions,⁵ one may estimate that the effective electron conductivity within the cathode layer was *ca* 100 and 5 S m⁻¹ initially and after the 300 high-voltage cycles, respectively.

Supplementary references

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Figure S1. Cyclic voltammogram of the Fe/N/C catalyst at 20 (A), 40 (B), 60 (C) and 80°C (D) after 0 and 300 square wave cycles from 0.9 to 1.4 V vs. RHE for 3s/3s (see inset of Fig. 1).



Figure S2. PEMFC test experiments on membrane and identification of the Fe-band

A) Lack of effect of replacing the anode and membrane after 300 cycles at 0.9/1.4 V. The solid black line is the initial polarization curve while the other two curves (superimposed) correspond to the cycled MEA and to the cycled cathode with a new anode + membrane.
B) SEM image of a cross-section of the MEA after 300 cycles at 0.9/1.4 V. The image shows only the membrane since electrodes had delaminated. The milky band corresponds to iron.
C) Relative iron concentration across the membrane after 300 cycles at 0.9/1.4 V. The iron analysis was performed with EDX and corresponds to the location shown in B.

D) Effect of re-hot-pressing a degraded MEA. The solid black line is the initial polarization curve of the MEA (initial anode and membrane, hot-pressed together, plus separate cathode), the red curve is the curve after a potential hold at 1.3 V for 1800 s, and the green curve corresponds to the MEA comprising the degraded cathode and a new anode and new membrane, all hot-pressed together at 125 °C.

For the initial MEA, only the anode was hot-pressed onto the Nafion membrane while the cathode was simply squeezed between the membrane and the cathode current collector during cell assembly.



Figure S3. Comparison between computed & experimental PEMFC polarisation curves The model used to compute the polarisation curves involves a Tafel kinetics with a 90 mV decade⁻¹ Tafel slope for the ORR, calculation of the local overpotential across the cathode active layer according to Ohm's law applied to the electron and proton conductive phases, and oxygen diffusion and consumption within spherical agglomerates. The agglomerate size and oxygen diffusion coefficient were kept constant for all calculations, as well as the effective proton conductivity in the cathode. Table S1 summarizes the important parameters and how they were modified to compute the three curves in Fig. S3. The mathematical equations for the cathode porous layer were solved numerically, and an additional external Ohmic drop iR was then added to the cathode polarisation curve with $R = 75 \text{ m}\Omega \text{ cm}^2$, which corresponds to the lump resistance R deduced from Fig. 4.

Computed curve	normalized ORR	Effective electron	Effective proton
label in Fig. S3	activity at 0.9 V	conductivity, σ_e	conductivity, σ_i
	/ a.u.	/ S m ⁻¹	/ S m ⁻¹
c. Initial	1.000	100	1
d. 300 cycles	0.025	5	1
e. 300 cycles	0.025	100	1

Table S1. Principal parameters used to compute the polarisation curves of Fig. S3



Figure S4. Relative decrease in current density at 0.7 V for Fe/N/C and Pt/C as a function of the time spent at 1.4 V vs. RHE.

The initial current densities at 0.7 V were 588 and 116 mA cm⁻² for Pt/C and Fe/N/C, respectively. Pure H₂ and O₂ were fed at a flow rate of 50-70 sccm into the humidifiers held at 80°C, the cell temperature was 80°C, and the gas inlet pressure was 1 bar gauge. For the MEA with Fe/N/C, the anode and cathode catalyst loading were 0.5 mg_{Pt} cm⁻² and 4 mg_{FeNC} cm⁻² and the membrane was NafionTM NRE-211. For the Pt/Pt MEA, the anode and cathode catalyst loadings were 0.5 mg_{Pt} cm⁻² and the membrane was NafionTM NRE-211.