Supporting information:

**Influence of Iron Precursor Hydration State on Performance of Non-Precious Metal Fuel Cell Catalysts**

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**Experimental parameters**

Electrochemical evaluation of the prepared catalyst materials was done by single cell fuel cell measurements using a commercial 5 cm² PEMFC from Scribner Assoc. with an electrode area of 2.25 cm². A commercial Pt/C catalyst (10 wt% Pt with 0.5 mg Pt/cm² from FuelCell Inc.) was used at the anode side, while the discussed catalyst materials were used as cathode catalysts. A commercial ionomer (NRE-212 Nafion membrane from Sigma) was completing the MEA. Detailed parameters for the MEA preparation are given in. All measurements discussed here were done at 80 °C. The cell was fueled by fully humidified 100% H₂ (instrumental grade from AGA) and using synthetic air (instrumental grade from AGA) as a fully humidified oxidant. A back-pressure of 1.5 bar was applied at both the anode and cathode side of the cell. Electrochemical impedance measurements were done in the single cell at 0.7 V between 100 kHz and 0.01 Hz with 10 measurement points per decade. Rotating disk electrode (RDE) measurements were carried out using a three electrode RDE setup from Gamry Instrument in 0.1M HClO₄ solution. Ag/AgCl ref. and graphite rod (6 mm diameter) served as reference and counter electrode, respectively. The catalyst inks were prepared by ball milling the catalyst for 40 min (15 Hz), followed by mixing 10 mg catalyst, 95μL Nafion solution (5 wt% in lower aliphatic alcohols and water, Sigma-Aldrich) and 350μL ethanol (99.5% Solvesso). After sonication (30 min) 5μL of the ink was deposited on a polished glassy carbon rotating disk electrode (5 mm diameter, Gamry Instrument) and dried in room temperature for 30 min. The ORR polarization curves were recorded stepwise, every 30mV, with a hold time of 60s, starting at 1V to -0.25V (versus RHE) in oxygen saturated electrolyte. The potential was held at the open circuit potential for 120 s before every polarization experiment. A polarization curve was measured for each catalyst at four different rotation speeds (100, 400, 900 and 1600 rpm). To achieve the Koutecky-Levich plots the Koutecky-Levich equation presented below was used:

\[
\frac{1}{i} = \frac{1}{i_L} + \frac{1}{i_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{i_K}
\]

\[
B = 0.62nFACD_0^{2/3}\nu^{-1/6}
\]

Here, \(i_L\) is the diffusion limited current and \(i_K\) the kinetic current. The coefficient used to calculate the number of electron transfer mechanism for each catalyst was obtained from the Faraday constant (\(F=96485 \text{ mol}^{-1}\)), the electrode area (\(A=0.196 \text{ cm}^2\)), the bulk concentration of \(O_2\) in 0.1M HClO₄ (\(C_{O_2}=1.2x10^{-3} \text{ mol L}^{-1}\)), the diffusion coefficient of \(O_2\) in 0.1M HClO₄ (\(D_{O_2}=1.93x10^{-5} \text{ cm}^2 \text{s}^{-1}\)), and the kinetic viscosity in HClO₄ (\(\nu=0.00893 \text{ cm}^2 \text{s}^{-1}\)).

Nitrogen physisorption measurements were done on the powder catalyst using a TriStar3000 instrument after degassing the samples at 225 °C for 4 h. The specific surface area was calculated from the first adsorbed monolayer of nitrogen using the Brunauer-Emmett-Teller (BET) method while the pore size and pore size distribution was calculated with the Barrett–Joyner–Halenda (BJH) method.

\(^1\)H-NMR spectroscopy measurements were conducted using a Varian 400 MHz spectrometer on the furfurylamine/iron chloride precursor solutions with an iron to furfurylamine molar ratio of 1:250. Deuterated DMSO, contained in glass capillaries and inserted in the NMR-tubes, were used for reference.

Transmission electron microscope (TEM) analysis was performed on a JEOL 1200EX II (120kV) microscope. The sample powders were dispersed on a C/Cu grid by evaporating 5 μL of the sample suspended in ethanol.

Small angle X-ray scattering (SAXS) was done on powder catalyst samples at beamline I1711 at the MAX II ring of the MAX-lab national synchrotron laboratory (Lund, Sweden). The data were analyzed using the BioXTAS RAW program.
X-ray Diffraction (XRD) measurements were conducted on powder samples using a Bruker D8 Advance instrument operated in Bragg-Brentano geometry using Cu Kα radiation.

Additional Tables

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Table S1 Integrated ¹H-NMR peak areas of furfurylamine and furfurylamine/FeCl₃ hexahydrate mixtures after 0 days, 7 days and 14 days.

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Table S2 Integrated ¹H-NMR peak areas of furfurylamine and furfurylamine/anhydrous FeCl₃ mixtures after 0 days, 7 days and 14 days.

Additional Graphs

SAXS:

Fig. S1 SAXS data of Fe-OMC catalysts prepared with precursor solutions using various iron sources (anhydrous FeCl₃ – magenta, FeCl₃ hexahydrate – light green, anhydrous FeCl₃ + FeCl₃ hexahydrate (molar ratio 50%) – black.
**Fig. S2** SAXS data of Fe-OMC catalysts prepared with precursor solutions of various age (freshly prepared – blue, 24h after preparation – green, 1 week after preparation – purple).

**Fig. S1** SAXS data of Fe-OMC catalysts prepared with precursor solutions using various FeCl₃·6H₂O to furfurylamine molar ratios in the precursor solution (1 : 3 – black, 1 : 8 – red, 1 : 16 – light green, and 1 : 32 – blue).

**XRD:**

**Fig. S2** XRD data of Fe-OMC catalysts prepared with FeCl₃·6H₂O precursor solutions of various age (freshly prepared – yellow, 24h after preparation – light green, 1 week after preparation – dark green) and of Fe-OMC catalysts prepared with 24 h old precursor solutions with various hydration states (hexahydrate – light green, anhydrous – magenta, 50/50 ratio of hexahydrate and anhydrous - black).

**Fuel cell tests:**
Fig. S5 Polarization curves (a) and Nyqvist plots (b) of Fe-OMC catalysts prepared with precursor solutions using anhydrous FeCl₃ (pink) and hydrated FeCl₃ (blue) with iron to furfurylamine molar ratio 1:250.

References