



Experiment title: **Post-mortem analysis of Fe-N-C catalysts for the oxygen reduction reaction (ORR) in proton exchange fuel cells - a synchrotron-based Mößbauer spectroscopic study**

Experiment number:
MA-3722

Beamline:	Date of experiment: from: Oct 31 st 2017 to: Nov 3 rd 2017	Date of report: 2018-02-20
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Report:

The proton exchange membrane fuel cells (PEMFC) are a very promising technology for energy supply in automotive propulsion. In a PEMFC, water is formed by catalysing the respective half-cell reactions, namely the hydrogen oxidation reaction on the anode and oxygen reduction reaction on the cathode. Today, state-of-the-art catalysts are platinum-based. While they achieve good performance, they are expensive and contribute to 25 % to an overall FC stack! Due to economic reasons; however, costs need to be reduced. The replacement of platinum on the cathode by Fe-N-C catalysts is a promising strategy as Fe-N-C catalysts can reach ORR activities close to platinum but are prepared from earth abundant and cheap elements. One mayor drawback is the poor stability of Fe-N-C catalysts. On the basis of structure-activity correlations, we were able to identify that specific FeN₄ centers catalyse the ORR¹⁻⁵. In our precious work we used post-mortem analysis of membrane electrode assemblies (MEAs) that were degraded during fuel cell operation⁶. By analysing this data it became clear that under strong oxidizing conditions the activity loss correlates with a leaching of ORR active FeN₄ centers in parallel to the burn-off of carbon. Recently, we were able to show, that up to 0.8 V the degradation of one of today's most active Fe-N-C catalysts is potential independent, but related to Le Chatelier's principles and the disintegration of active sites hosted in micropores⁷.

While such integral studies give already important insights on the overall degradation, the mechanistics related to the deactivation of Fe-N-C catalysts might be better followed by local studies in which local changes are compared to local profiles (temperature, water, current density). With this motivation, this work was a proof of concept study to figure out to what extend indeed the degradation is a local phenomenon, also for Fe-N-C catalysts.

In contrast to the first planned measurement concept, the orientation of the samples relative to the beam had to be adapted in order to maximize the absorption effect and therefore lower the measurement time. In this proof of concept study we focussed on the investigation of three MEAs, an as-prepared MEA, a MEA that was treated at about 0.6 V in a low-temperature (LT-) PEMFC for 24 h and a MEA treated at 0.6 V in a high-temperature (HT-) PEMFC for 12 h. As expected the loss in peak power density was higher for HT-PEM (-40 %) compared to LT-PEM (-25 %) even though the time of operation was only half.

The following questions we wanted to answer, in order to do so, the Figures given in parenthesis for each point helped in clarification.

a) Is the degradation of Fe-N-C catalysts homogeneously distributed, or does it depend on the local position within the flow-field? As shown in Figure 1a, while there are no changes for the as-prepared MEA, the measurements in LT-PEM and HT-PEM indicate that the relative absorption area (related to iron content) and – more important – the shape of the spectra (related to changes of iron species) varies for both treated MEAs. The insert gives schematically the flowfield with the investigated positions in the indicated color code similar to the spectra.

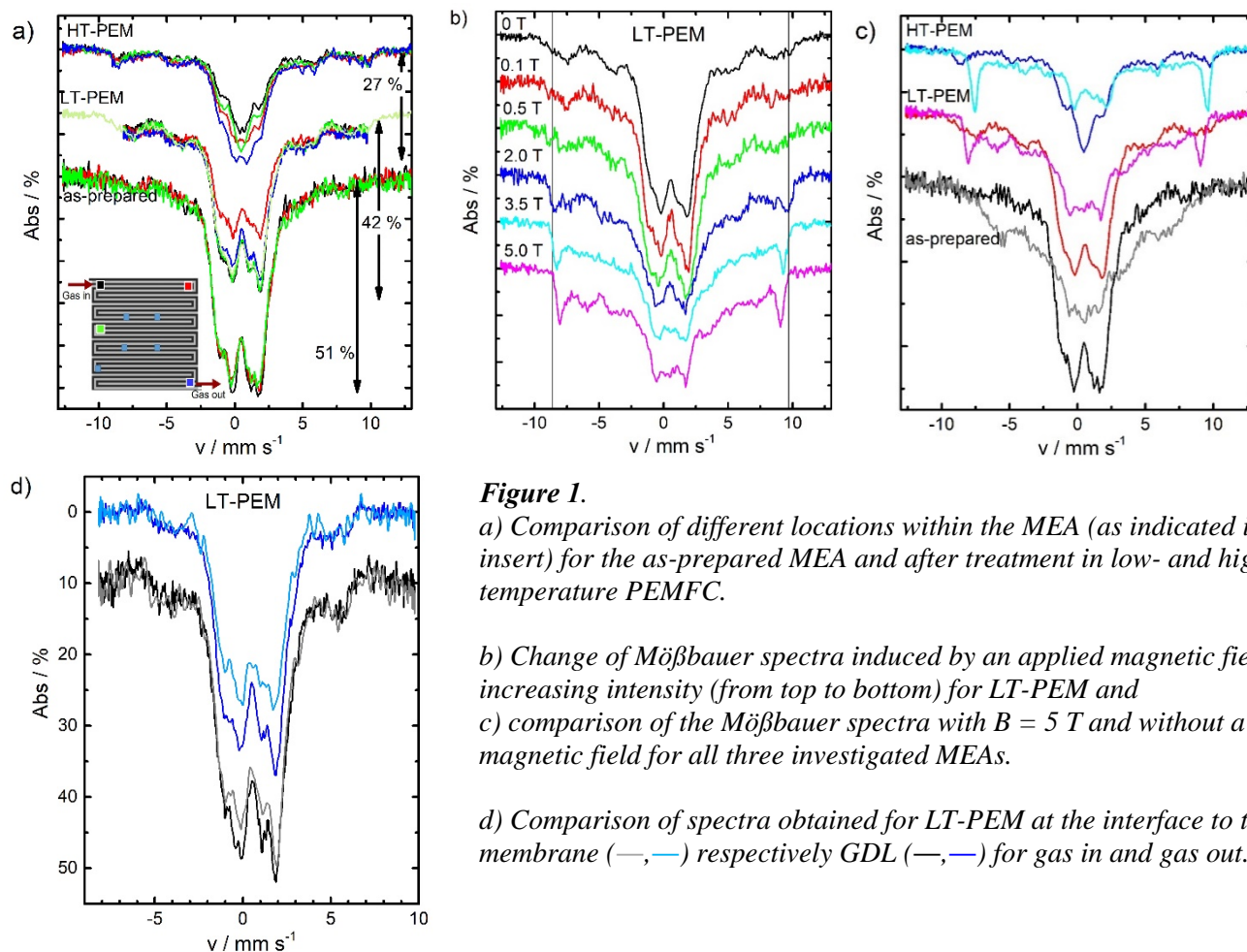


Figure 1.

a) Comparison of different locations within the MEA (as indicated in the insert) for the as-prepared MEA and after treatment in low- and high-temperature PEMFC.

b) Change of Möbbaauer spectra induced by an applied magnetic field of increasing intensity (from top to bottom) for LT-PEM and c) comparison of the Möbbaauer spectra with $B = 5$ T and without a magnetic field for all three investigated MEAs.

d) Comparison of spectra obtained for LT-PEM at the interface to the membrane (—, —) respectively GDL (—, —) for gas in and gas out.

b) When the FeN_4 sites get demetallized, is iron removed from the MEA or iron oxide / hydroxide formed during operation? In order to answer this question, Figure 1b gives the Möbbaauer spectra of LT-PEM measured always at the same position with an applied field of $B = 0$ to 5 T. In addition, Figure 1c gives just the comparison of $B = 0$ T and $B = 5$ T for all three MEAs. All measurements focussed on the spot highlighted in green in the insert of Figure 1a. The maximum magnetic field that was obtained within the fits is about 52 T ($\delta_{\text{iso}} = 0.57 \text{ mm s}^{-1}$). Such values are typical for ferric iron in octahedral coordination of oxygen ($\delta\text{-FeOOH}$)⁸. It becomes apparent that with applying a magnetic field of ~ 3.5 T or larger, the sextet lines get more resolved with somehow split-up into a high field sextet with small linewidth and a more broaden sextet with lower magnetic field. Hence, the results show that indeed iron hydroxide is formed as decomposition product.

c) Is there a difference in change for the catalyst at the membrane vs. GDL interfaces? In order to answer this question we performed at the gas inlet and gasoutlet of the LT-PEM measurements at both interfaces. It becomes apparent that indeed for the membrane interface in both cases a smaller absorption is obtained in comparison to the GDL interface.

In conclusion, we were able to proof our idea of locally resolved degradation for Fe-N-C catalysts applied in fuel cells. It will now be necessary to move a step forward to go from model catalysts (with a relatively homogeneous composition but less relevant in terms of achieved activity) to high-performance catalysts.

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