

## Fe-N-C catalysts - Investigating the degradation induced by PEM fuel cell vs. room temperature conditions

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Polymer-Electrolyte-Membrane (PEM) Fuel Cells (FC) are of large interest for automotive application. Due to the high costs of platinum-based catalysts; however, the production of FC cars is expensive. Most of the platinum is needed on the cathodic site because of the limited kinetic of the oxygen reduction reaction (ORR). Therefore, the utilisation of an alternative non noble metal catalyst (NNMC) for the oxygen reduction is desired to reduce costs. In this purpose, Fe-N-C catalysts are the most promising candidates [1-3].

When Fe-N-C catalysts are synthesised according to our oxalate-supported pyrolysis of porphyrins a porous carbon matrix is formed during the heat-treatment [4]. No additional carbon support is needed [4] and, as a consequence, active site densities (SD) of up to  $12 \cdot 10^{19}$  sites  $\text{cm}^{-3}$  can be reached [5]. These catalysts exhibit a high activity towards the ORR. We have recently demonstrated that  $^{57}\text{Fe}$  Mössbauer spectroscopy is a powerful tool for the characterisation of active sites in Fe-N-C catalysts [5-7]. It was found that ferrous low-spin  $\text{FeN}_4$ -centres catalyse the ORR [5-7], whereas the turn-over frequency (TOF) depends on the electron density on the iron centre [7] and on the gas atmosphere used during the catalyst's synthesis [5]. While TOF and SD of Fe-N-C catalysts are quite promising, the stability has still to be improved. In this respect, possible degradation might be induced either by a disintegration of  $\text{FeN}_4$ -centres or an oxidation of the carbon as it is found for Pt/C, as well.

In the present work, we have investigated the degradation behaviour of our standard Fe-N-C catalyst. Long-term stability tests were performed in (i) 0.5M sulphuric acid and (ii) under standard PEM FC conditions. Structural changes of the iron sites were followed by  $^{57}\text{Fe}$  Mössbauer spectroscopy. In order to study a possible degradation of the carbon matrix, Raman spectroscopy was also performed. These techniques were supplemented by bulk elemental analysis and scanning electron microscopy.

It will be shown that the stability strongly depends on the chosen measurement conditions. A possible degradation mechanism will be discussed that might enable a better stabilisation of this type of catalyst in the future.

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