

***In situ* Mössbauer spectroscopy for the active site identification in non precious metal catalysts for fuel cells**

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Fuel cells are electrochemical devices that convert chemical energy directly into electricity. This environmental friendly technology plays an important role in the future energy landscape. Especially proton exchange membrane fuel cells are attractive energy devices for automotive propulsion due to their high-energy efficiency. Today, platinum-based catalysts are the state-of-the art but they contribute to a huge extent to the overall costs of a fuel cell system. Platinum and other precious metals represent an economical roadblock for a wide spread use of PEMFCs. Most of the platinum is required for the sluggish oxygen reduction reaction (ORR). In the past decades, iron and nitrogen doped carbon catalysts (Fe-N-C) archived high current density and emerged as a promising alternative to platinum-based catalysts.

A typical Fe-N-C catalyst is prepared by at least one heat-treatment at 800 – 1100 °C of iron, nitrogen and carbon precursors, often also followed by an acid leaching. The iron contents of < 5 wt% are relatively low compared to precious metal catalysts. Furthermore, in an ideal case the catalysts behave x-ray amorphous without any periodically arranged inorganic contributions. In contrast, molecular FeN_x sites are embedded in an amorphous carbon framework. Thus, several standard techniques are not suited for the characterization of Fe-N-C, but X-ray absorption and Mössbauer spectroscopy became important. Both techniques give indeed strong evidence for the participation of FeN_x sites to the ORR. However, the exact coordination environment remains elusive but is important for a basic understanding of the reaction mechanism and of possible degradation scenarios.

In this work, in-situ and operando Mössbauer spectroscopy are used to identify the iron species that are formed during electrochemical conditioning, in order to identify the exact coordination environment and possible intermediates of the ORR.

The talk consists of three parts: In a first part structural changes induced by applied potential will be discussed for three differently prepared Fe-N-C catalysts to identify differences and similarities. Then, measurements under ORR conditions will be used to identify the iron species which is formed prior to the rate determining step. The third part will be used in order to correlate the as measured Mössbauer parameters to concrete structural motifs that were used as model systems in density functional theory calculations of theoretical Mössbauer parameters. On the basis of this, we make a suggestion for a reduction cycle on Fe-N-C catalysts and will highlight the main difference between our model and the current status discussed in literature.