Identification of catalytic sites in non-precious metal electrocatalysts for PEM fuel cells

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Among the different energy conversion devices in the framework of a H_2 economy, low temperature polymer-electrolyte-membrane fuel cells (PEMFC) are envisioned as a power source for electric vehicles and as distributed energy sources. A major drawback that might prevent the large scale implementation of PEMFC devices is the current use of platinum and platinum-based alloys to speed up the oxygen reduction reaction (ORR) at the cathode.

Metal-nitrogen-carbon Me-N-C (Me=Fe, Co) catalysts, prepared from the pyrolysis of Fe or Co, N and C elemental precursors, represent today promising non-precious substitutes to traditional platinum-based catalysts. Despite great advances in the activity of heat-treated earth-abundant catalysts, difficulties arise from the typical highly heterogeneous nature of these materials due to pyrolysis-based synthesis during which a complex matrix of different species is formed, including both graphitic and amorphous carbon, and metal-based nanoparticles presumably inactive or poorly active for the ORR, thus preventing the clear spectroscopic identification of the active sites. This presentation addresses the limits and advantages of EXAFS and XANES modelling approaches in deciphering the active sites geometry of Me-N-C electrocatalysts that are entirely free of metallic particles, and in elucidating the structural basis of their activity. In particular, an accurate XANES analysis involving the optimization of several model structures revealed a porphyrinic-like arrangement of N and C atoms around the central Fe and Co ions. These results strongly contrast with the pyridinic nitrogen structure often assumed till now. However, in contrast to Fe-based sites, defective porphyrinic cobalt sites are also viable candidates. The *in-situ* XANES signatures performed in the ORR potential region show a distinct behavior of CoN_xC_y and FeN_xC_y moieties, highlighting differences in the way how such sites catalyze the ORR. The active sites formation mechanism probed by quick-EXAFS will also be presented.