SPECTROELECTROCHEMICAL EPR AND MÖSSBAUER METHODS FOR IDENTIFYING REVERSIBLE REDOX ACTIVE IRON OXIDE STRUCTURES IN FENC CATALYSTS

Kaltum Abdiaziz[a], Lingmei Ni[b], Sonia Chabbra[a], Hendrik Haak[b], Edward Reijerse[a], Pascal Theis[b], Derya Demirbas[c], Ulrike I. Kramm[b], Alexander Schnegg[a]

[a]Max-Planck-Institute for Chemical Energy Conversion, Mülheim (Ruhr), Germany
[b]Technische Universität Darmstadt, Darmstadt, Germany
[c]Max-Planck-Institute for Coal Research, Mülheim (Ruhr), Germany

FeNC, featuring FeN_4, are considered prime candidates for replacing noble metals like Pt for the oxygen reduction reactions (ORR) in fuel cells. However, FeNC catalysts suffer from pyrolysis-induced inhomogeneity, containing various iron species, some of which are accessible to electron paramagnetic resonance (EPR) spectroscopy [1]. Separately, in-situ Mössbauer and EPR spectroscopy effectively identify iron species by their oxidation and spin states, crucial for understanding catalytic mechanisms, though not without some ambiguity. Therefore, we present a combinational in-situ MS and EPR spectroscopy study of FeNC catalysts in order to shed much-needed light on the ambiguity surrounding the assignment of Fe sites in FeNC materials. Correlation of in-situ MS and EPR spectroscopy identifies redox active strongly and weakly magnetically coupled high-spin Fe(III) in oxygenic coordination environment or superparamagnetic clusters, high-spin Fe(II) six-coordinated in iron oxides and intermediate-spin Fe(II) in square-planar coordination with no indication of the presence of Fe(III)N_4 sites (Figure 1).

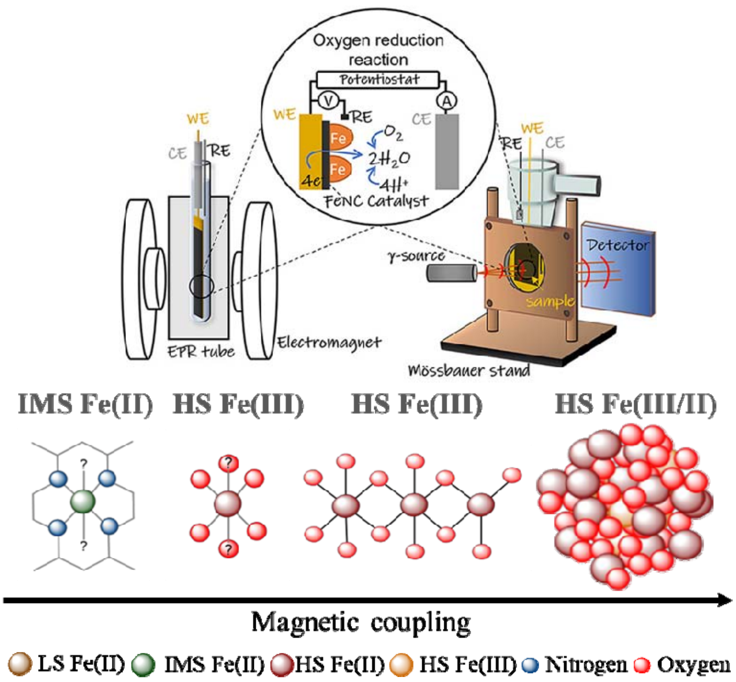

Figure 1: (top) Scheme of the *in situ* SEC-EPR and MS setup, schematic diagram of ORR on the WE as a possible electron transfer process (bottom) Summary of the electrochemically active Fe structures identified in the FeNC catalysts.

[1] Abdiaziz, Kaltum, et al. JACS 148. 4 (2026): 3995–4007