Fe/N/C - catalysts: probing the spin state of iron using X-ray Emission Spectroscopy

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The needed improvements for a successful implementation of non-noble metal catalysts of the Fe/N/C-type in polymer electrolyte fuel cells require a fundamental understanding of their active site structure, which is currently still lacking. Specifically, the spin state and local configuration of the N-coordinated, atomically dispersed Fe-ions that are believed to constitute the active sites in these materials remain under vivid debate [1, 2]. With this motivation, non-resonant X-ray emission spectra of several catalysts prepared with a variety of synthesis methods were acquired using the von Hamos X-ray emission spectrometer at the SuperXAS beamline (Swiss Light Source) (see Fig. 1a), and their corresponding, average spin number was quantified with the help of reference compounds with a similar N-coordination environment and a well-known spin state (cf. Fig. 1b). Complemented with other spin-sensitive techniques including Mössbauer spectroscopy, these results provide unprecedented insights into the spin state of the active sites in these Fe/N/C-type catalysts both under *ex* and *in situ* conditions, as well as on the relation between these sites' electronic configuration and their contribution to the catalysts' O_2-reduction activity.

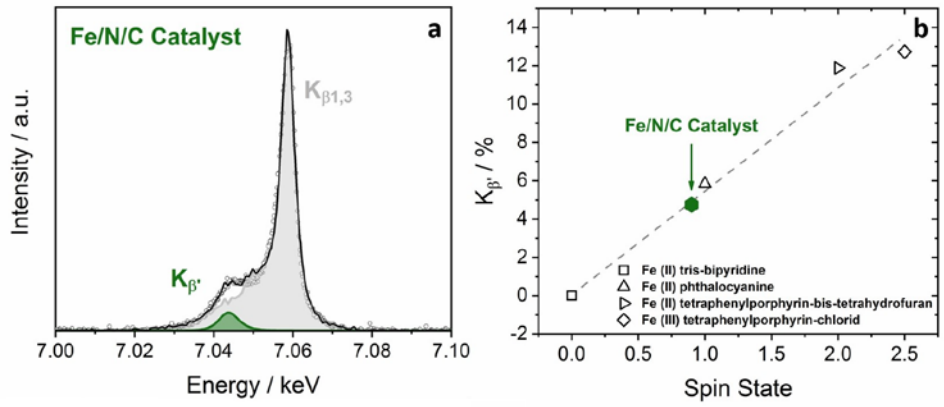

Figure 1: a) exemplary K_β-XE spectrum of an Fe/N/C catalyst fitted with two components ($K_{\beta1,3}$ and $K_{\beta'}$) ; b) correlation between the $K_{\beta'}$-contribution derived from the fitted XE spectra and the spin state of Fe in various reference compounds (empty symbols), alongside the interpolation for an Fe/N/C catalyst from which an average spin number of 0.9 is estimated.

References

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