

Atomic Imaging of Fe, N-doped Carbon Electrocatalysts' Active Sites and Their Stability .

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Fe, N-doped carbon electrocatalysts (*i.e.* Fe – N – C) are of interest for the oxygen reduction reaction because they can solve the geological and economic constraints associated with the use of Pt-based electrocatalysts. However, the nature and the stability of their active sites is yet to be fully understood. The presence of nitrogen and atomically dispersed Fe is believed to result in the presence of various moieties, *i.e.* Fe-N_x, N-pyridinic, N-pyrrolic, *etc.* Such assumptions are based on the fitting of the N1s peak observed by X-ray photoelectron spectroscopy (XPS)^{1,2} and, for the Fe-N_x moieties, extended X-ray absorption fine structure (EXAFS)³. Imaging a non-model Fe – N – C electrocatalyst at an atomic scale could provide additional insights onto the exact structure of those moieties, and, in combination with electrochemical ageing, ease the assessment of their stability. Here, we discuss the multiplicity of actives sites in an Fe – N – C electrocatalyst synthesized by the sacrificial support method. We use a combination of XPS, EXAFS, scanning transmission electron micrographs (STEM) and electron energy loss elemental mapping (EELS – see **Figure 1**) to unveil the presence, additional to Fe-N_x, of other active sites, *e.g.* Fe-N_xC_y or nitrogen moieties. Then, we investigate the stability of said moieties (with a focus onto Fe-N_x) using a combination of step-cycles (10,000 cycles; 0.6 – 1.0 V vs. RHE, 3s – 3s, in Ar-saturated 0.1 M H₂SO₄, T = 80°C) and STEM (see **Figure 1**), showing that, in these experimental conditions and for this specific family of Fe – N – C electrocatalysts, the atomically dispersed Fe forms clusters – but not nanoparticles – during the ageing process.

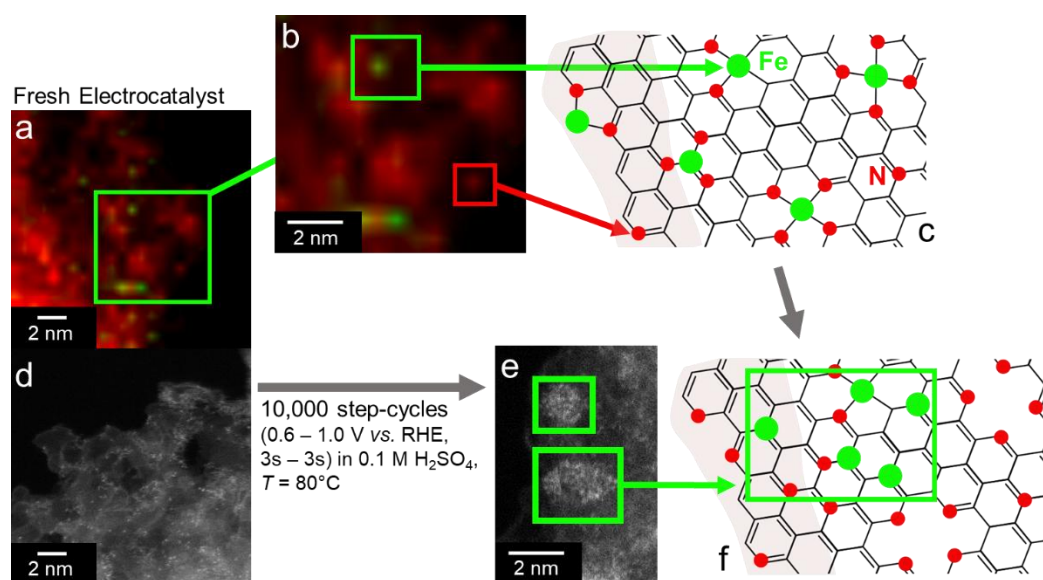


Figure 1. (a, b) electron energy loss elemental mapping; (d, e) scanning transmission electron micrographs (c, f) schematic representation of the Fe – N – C electrocatalyst synthesized by the sacrificial support method (a – d) before and (e, f) after ageing (10,000 step-cycles; 0.6 – 1.0 V vs. RHE, 3s – 3s, 0.1 M H₂SO₄, T = 80°C).

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- (3) Zitolo, A.; Goellner, V.; Armel, V.; Sougrati, M.; Mineva, T.; Stievano, L.; Fonda, E.; Jaouen, F. *Science* (80-.) **2015**, *14* (September), 937–942.

