Unveiling the Influence of Different Experimental Parameters on the Degradation Kinetics of Fe–N–C Oxygen Reduction Reaction Catalysts

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M-N-C catalysts have emerged as highly efficient electrocatalysts for the cathodic oxygen reduction reaction (ORR) in proton exchange membrane fuel cells (PEMFC).¹ Current efforts to further improve their mass activity (MA) towards the ORR consist in maximizing their active site density and/or their turnover frequency.^{2,3} Despite these advances, the catalytic performance of M–N–C materials, and in particular of Fe-N-C, decreases rapidly in operating conditions.² Several degradation mechanisms have been described: (i) carbon surface and/or bulk oxidation, (ii) protonation of the N-groups, (iii) demetallation and (iv) carbon corrosion. High electrode potential and presence of O_2 in the cathode gas feed seem to accelerate the degradation of Fe-N-C catalysts.^{3,4} To shed fundamental light into their combined influence, in this work, we investigated the durability of a Fe-N-C aerogel catalyst synthesized using a "one-pot" sol-gel method described in our previous work.⁵ Various accelerated stress tests (ASTs) were performed using a Load-Cycle (LC) protocol (alternation of high and low cathode potentials) and different (i) temperature, (ii) gas atmosphere (Ar or O₂) and (iii) upper limit potential. Figure 1 shows the normalized ORR mass activity at 0.80 V (vs. RHE) after different ASTs. A high temperature and presence of O_2 in the gas feed represent the most detrimental conditions to the Fe–N–C aerogel,³ due to the formation of H_2O_2 and reactive oxygen species (ROS). However, even in the absence of O_2 , a high electrode potential and temperature also contribute to MA loss. In contrast, exposure to air at high temperature mildly affects their ORR performance. To prevent the undesirable effects of ROS, the addition of minute amounts of Pt is underway in our laboratories.



Figure 1: Variation of the mass activity towards the ORR of a model Fe-N-C aerogel catalysts in different accelerated stress test conditions.

References

- 1. Mehmood, A. et al. Nat. Catal. 5, 311-323 (2022).
- 2. He, Y., Liu, S., Priest, C., Shi, Q. & Wu, G. Chem. Soc. Rev. 49, 3484-3524 (2020).
- 3. Kumar, K. et al. Angew. Chem. Int. Ed. 59, 3235–3243 (2020).
- 4. Zhang, H. et al. Nat. Catal. 5, 455-462 (2022).
- 5. Ge, H. et al. ACS Catal. 13, 1149–1163 (2023).