

Unravelling the Influence of Oxygen on the Degradation Mechanisms of Fe-N-C Oxygen Reduction Reaction Catalysts in PEMFC Cathode

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Pyrolyzed iron-nitrogen-carbon materials (Fe-N-C) comprising mostly atomic Fe-N_x moieties are the most mature class of noble metal free catalysts for the oxygen reduction reaction (ORR) in acidic media. Such catalysts show excellent performance in proton exchange membrane fuel cell (PEMFC) device, approaching that of platinum-based catalysts.^[1] However, an important performance loss is observed under realistic PEMFC conditions.^[2] To shed fundamental light into the degradation mechanisms at stake, two different Fe-N-C materials were prepared, one using a metal organic framework (MOF) and the other a sacrificial support method (SSM), and are labelled Fe-N-C_MOF and Fe-N-C_SSM, respectively. These materials were characterized before and after two different accelerated stress tests (ASTs: 10 k cycles, 0.6-1.0 V vs. RHE, 3s-3s, 0.1 M H₂SO₄, 80°C) under Ar or O₂ atmosphere. Stronger degradation and higher ORR mass activity loss were observed when the AST is performed in O₂ vs. Ar-saturated acidic electrolyte. For AST under Ar condition, physicochemical characterisations revealed a demetallation process and eventually the occurrence of a clustering mechanism whereas for AST performed in O₂ atmosphere, a decrease of the Fe content and the formation of Fe oxide particles was observed (**Figure 1**).

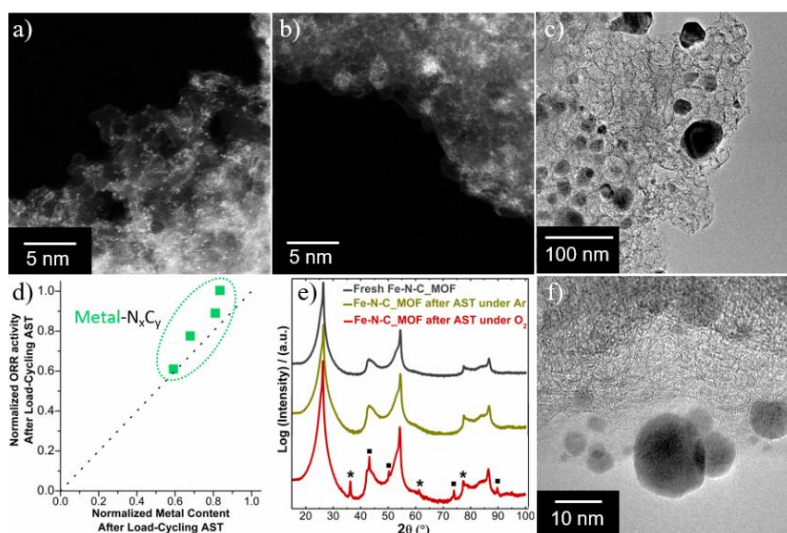


Figure 1. HR-STEM-HAADF images of a) Fe-N-C_SSM before and b) after AST under Ar atmosphere and c) TEM image after AST under O₂.^[3] d) Linear correlation between the normalized ORR mass activities and the residual Fe content after AST under Ar atmosphere for Fe-N-C_MOF materials,^[4] e) X-ray diffraction patterns of Fe-N-C_MOF materials before and after different AST. (■) and (*) indexed Fe cubic Fm-3 m (PDF 04-002-3692) and Fe_{0.9}O wüstite Fm-3 m (PDF 04-001-9267) phases, respectively, f) TEM image of Fe-N-C_MOF material after AST under O₂ atmosphere.^[5]

Keywords: Electrocatalysis, Fe-N-C, Oxygen Reduction Reaction, Durability, PEMFC

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