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

Kavita Kumar, 1 Tristan Asset, 2 P. Atanassov, 2 Frédéric Jaouen, 3 Laetitia Dubau, 1 Frédéric Maillard 1

1 Univ. Grenoble Alpes, CNRS, Grenoble-INP, Université Savoie-Mont-Blanc, LEPMI, 38000 Grenoble, France

2 Department of Chemical & Biomolecular Engineering, Nacional Fuel Cell Research Center (NFCRC), University of California, Irvine, CA 92697, USA

3 CNRS, Université de Montpellier, ENSCM, UMR 5253 Institut Charles Gerhardt Montpellier, 1919 route de Mende, F-34293 Montpellier, France

Pyrolyzed iron-nitrogen-carbon materials (Fe-N-C) comprising mostly atomic Fe-Nx 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 Fe0.9O 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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