Non-Noble Metal-based Catalytic Sites for the Electroreduction of Oxygen

J. P. Dodelet, M. Lefèvre
INRS-Énergie et Matériaux, C. P. 1020, Varennes, Québec, Canada, J3X-1S2

P. Bertrand
PCPM, Université Catholique de Louvain, 1348 Louvain-la-Neuve, Belgium

Non-noble metal catalysts for the reduction of oxygen in polymer electrolyte membrane fuel cells are a subject of current interest. It has been known for several decades that N_4-Metal macrocycles (like Fe porphyrins or phthalocyanins) adsorbed on carbon and heat treated at various temperatures are catalysts for O_2 reduction in acidic medium. The best electrocatalytic activities have been shown to occur in the pyrolysis range comprised between 500 and 700°C. In that temperature range, it has been proposed [1] that the catalytic site is N_4-Metal (Fe) bound to the carbon support. This site has been labeled: the low temperature catalytic site.

Another catalytic site has also been detected at pyrolysis temperatures $\geq$ 800°C. The entire structure of this second catalytic site, also labeled the high temperature catalytic site, is not yet known. However, some information about its formation and its composition has been collected. So far, it is known that:

(i)   C, N, Fe are necessary to obtain that catalytic site [2]. C is either carbon black or activated carbon or a carbon precursor as perylene tetracarboxylic dianhydride (PTCDA). The precursor of N is usually NH_3 or N-containing molecules (like N_4-Fe) chelates. The precursor of Fe is either an N_4-Fe chelate, but it may also be a salt like Fe acetate.

(ii)   From XPS experiments [3], it is known that the nitrogen atoms on the carbon support have to be of the pyridinic type (N contributes one π electron to the conjugation and has two other electrons in an n orbital) in order to obtain a catalyst.

(iii)   From Time of Flight Secondary Ion Mass spectrometry (ToF SIMS) [4], it is also known that the pyridinic nitrogens have to be in a structure of the phenanthroline type, in order to be able to coordinate the Fe ion in the catalytic site (see Fig. 1).
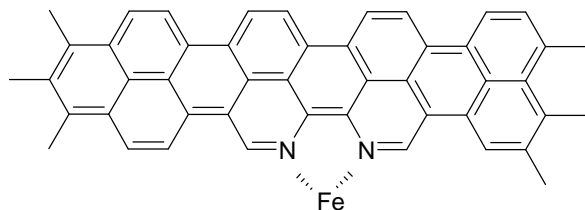

Figure 1: Part of the proposed structure for the high temperature catalytic site, at the edge of a graphene plane. The complete coordination of Fe is still unknown.

When such nitrogen atoms exist on the carbon support, adding Fe ions (even 50 ppm) induces catalytic activity. Increasing the Fe content increases the concentration of the catalytic sites until all nitrogens of the phenanthrolinic type are used. This happens around 0.5 wt% Fe, when Fe acetate is used as Fe precursor and around 2 wt% when a porphyrin like Cl-FeTMPP is used as Fe precursor. Increasing the Fe content further produces Fe metal (or carbide) particles that induce graphitization around them. These particles are catalytically inactive.

ToF SIMS experiments correlated with Rotating Disk Electrode (RDE) experiments have been performed to obtain more information about the structure of both catalytic sites. These experiments have been performed on two types of catalysts using pyrolyzed PTCDA at 900°C in H_2:NH_3:Ar ambient as carbon support. The first type of catalysts uses Fe acetate as Fe precursor with a Fe content of 0.2 wt%. The second type of catalysts uses Cl-FeTMPP as Fe precursor with also 0.2 wt% as Fe content. The two Fe precursors, which are adsorbed on pyrolyzed PTCDA, are pyrolyzed a second time in H_2: NH_3: Ar ambient at various temperatures ranging from 500 to 1000°C in order to obtain a range of catalytic activities.

From the comparison, at various pyrolysis temperatures, between the relative intensities of the $FeN_xC_y^+$ ions obtained by ToF SIMS and the catalytic activity of each catalyst determined by RDE measurements in O_2 saturated H_2SO_4 at pH = 1, the following conclusions have been obtained:

(i)   Two different catalytic sites exist simultaneously in both types of catalysts at all pyrolysis temperatures. Therefore, what was previously labeled as low and high temperature catalytic sites exist simultaneously and not independently at all pyrolysis temperatures.

(ii)   One of the catalytic sites (labeled FeN_4/C) is characterized by the $FeN_4C_y^+$ family of ions and ions coming from the fragmentation of these precursors. They may have their origin from what was previously labeled the low temperature catalytic site. The other catalytic site (labeled FeN_2/C) is characterized by the $FeN_2C_y^+$ family of ions, with $FeN_2C_4^+$ being the main ion in that family. These ions may have their origin from what was previously labeled the high temperature catalytic site, whose part of the structure is illustrated in Fig.1.

(iii)   The occurrence of the FeN_2/C catalytic site goes through a maximum in the pyrolysis temperature range between 700 to 900°C, depending upon the Fe precursor. This maximum of occurrence for FeN_2/C corresponds to a minimum of occurrence for FeN_4/C and is particularly important for catalysts made from a Fe acetate precursor for which the FeN_2/C catalytic site may represent up to 80% of the two catalytic sites present in the material. When the porphyrin is used as Fe precursor, the maximum occurrence of FeN_2/C drops to about 50%.

(iv) FeN_2/C catalytic sites are much more active than FeN_4/C catalytic sites.

References:

(1) J. A. R. van Veen, H. A. Colijn , J. F. van Baar, Electrochim. Acta 33, 801 (1988).

(2) G. Lalande, R. Côté, D. Guay, J. P. Dodelet, L. T. Weng, P. Bertrand, Electrochim. Acta 42, 1379 (1997).

(3) G. faubert, R. Côté, J. P. Dodelet, M. Lefèvre, P. Bertrand, Electrochim. Acta 44, 2589 (1999).

(4) M. Lefevre, J. P. Dodelet, P. Bertrand, J. Phys. Chem. B104, 11238 (2000).