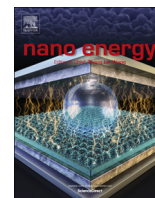




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Is iron involved in the lack of stability of Fe/N/C electrocatalysts used to reduce oxygen at the cathode of PEM fuel cells?

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ABSTRACT

NC_Ar+NH₃ is a Fe/N/C electrocatalyst developed by our group to reduce oxygen. It is obtained from the pyrolysis in Ar, then in NH₃, of a mixture of ZIF-8 (a metal-organic-framework) and the complex made between iron^{II} acetate and 1,10 phenantroline. In terms of activity and performance, NC_Ar+NH₃ is becoming a serious contender to Pt, but it is still unstable in a H₂/O₂ PEM fuel cell. Its current density recorded at 0.6 V and 80 °C decreases, first quickly during about 15 h, then more slowly for several tens of hours. The aim of this work is to verify if iron in the catalyst could be at the origin of the first rapid decay of NC_Ar+NH₃ through a Fenton reaction with some H₂O₂ generated by an incomplete reduction of O₂ in fuel cell. To do so, the strategy was simple: produce a MOF_Ar+NH₃ catalyst using the same ZIF-8, but without deliberate addition of iron precursor, and compare its stability to that of NC_Ar+NH₃. However, this has been impossible to achieve since there is a native iron impurity in ZIF-8 leading to an increase of Fe content after each pyrolysis step. In order to circumvent this problem, we produced several MOF_Ar+NH₃ (t) catalysts, varying (t), the pyrolysis time in NH₃ (and therefore also the Fe content). This enabled us to determine, by extrapolation to 50 ppm Fe on a log *i* vs log Fe content, the initial current density at 0.6 V of a catalyst (MOF_CN_x_Ar+NH₃) for which the current density would essentially be attributable to CN_x catalytic sites. From the similarity of the normalized instability curves for MOF_CN_x_Ar+NH₃, all MOF_Ar+NH₃ (t) and NC_Ar+NH₃ catalysts, we are able to conclude that neither iron (through a Fenton reaction) nor H₂O₂ alone are responsible for the first rapid decay of these Fe/N/C catalysts in fuel cells, but that a slow electro-oxidation of the carbonaceous support of all NC_Ar+NH₃ and MOF_Ar+NH₃(t) catalysts, occurring in about 15 h in H₂/O₂ fuel cell, is transforming the initially hydrophobic catalyst layers into hydrophilic ones. It is proposed that this phenomenon, causing micro-pore flooding, is at the origin of the first quick decay at 0.6 V of all the catalysts studied in this work. The slow electro-oxidation of the carbonaceous support during the durability test at 0.6 V also affects the mass activity of the catalysts. This was demonstrated for NC_Ar+NH₃. We also determined what would be the initial polarization curve, the initial maximum power of MOF_CN_x_Ar+NH₃ (0.150 W cm⁻²; 22% of that of NC_Ar+NH₃), the initial mass activity at 0.9 V of MOF_CN_x_Ar+NH₃ (0.3 A g⁻¹; 3% of that of NC_Ar+NH₃) and its initial Tafel slope (56 mV decade⁻¹). The Tafel slope similarity for MOF_CN_x_Ar+NH₃ and for NC_Ar+NH₃ (60 mV decade⁻¹) indicates that the ORR kinetics on both types of catalysts, and therefore on CN_x and FeN_x catalytic sites, is also similar.

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1. Introduction

Proton exchange membrane (PEM) fuel cells are clean and efficient electrical power sources for mobile and stationary

applications. They run on two electrochemical reactions: the oxidation of hydrogen into protons at the anode and the reduction of oxygen (Air) at the cathode, where the desired final reaction product is water. Electrocatalysts are necessary at both electrodes to obtain useful power. Presently, all H₂/O₂ (Air) fuel cell prototypes use Pt or its alloys to perform both electrochemical reactions [1]. However, Pt is an expensive metal and there are worldwide efforts either to lower its content or to replace it at the fuel cell electrodes. In particular, its replacement is highly desired at the cathode where most Pt electrocatalyst is located, due to the

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sluggish character of the oxygen reduction reaction (ORR) in acid medium [2]. Today, the best non-noble alternatives to Pt are Fe- or/and Co/N/C catalysts obtained by the high temperature pyrolysis of Fe- or/and Co precursor(s) on carbon (or on a carbon precursor) in the presence of a nitrogen precursor. This synthesis requirement led to a large variety of preparation procedures for ORR catalysts. Several reviews, discussing the synthesis of these catalysts as well as their catalytic sites have been recently published [3–7].

Presently, some of the best Fe- or/and Co/N/C electrocatalysts have shown high mass (or volumetric) activity at 0.9 V vs RHE [8] and high performance at 0.6 V in H_2/O_2 PEM fuel cells [9]. They have also shown stability at 0.4 V in H_2 /Air fuel cells [10]. Long term durability of the most performing catalysts at potentials ≥ 0.6 V (the potential range used in automotive application [11]) has however not been reached without somewhat compromising the mass activity and the performance of these catalysts. This is a definite constraint that limits these catalysts into becoming serious contenders to Pt (at least for automotive applications).

Durability tests measured in PEM fuel cells are not very often reported for non-noble catalysts. When they are reported, comments are often lacking or the resulting instabilities are sometimes explained by additional hypotheses. Examples of this include: (i) an electro-oxidation of the carbonaceous catalyst support causing the loss of catalytic sites which are integrated in the carbonaceous structure [12]; (ii) the loss of metallic Fe- or/and Co ions from the Metal-Nx sites (MeNx sites) releasing free metallic ions that will either exchange for protons in the Nafion ionomer (increasing therefore the membrane-electrode-assembly resistance) or will react with some peroxide released by the catalysts upon incomplete reduction of oxygen (generating therefore the highly oxidizing Fenton's reagent [13], able to chemically oxidize the carbonaceous support and its embedded catalytic sites), or the loss of metallic ions will transform a MeNx site in several pyridinic CNx sites that remain on the carbon support [14,15]; (iii) the reaction of protons with the basic pyridinic CNx catalytic sites [16], which are also present with MeNx sites in Me/N/C catalysts [15,17]; (iv) water flooding of the catalyst pores impeding the transport of oxygen into the cathode [18]; etc. An excellent review about stability and durability of non-noble catalysts for ORR in fuel cells has been recently published [19].

Our group has produced one of the most performing Fe/N/C catalysts so far displaying an initial peak power up to 0.91 W cm^{-2} in H_2/O_2 PEM fuel cell [9]. The catalyst was labeled NC_Ar+NH₃ (or sometimes NC_Phen_Ar+NH₃). It is made by first ball-milling a mixture of ZIF-8 (a metal organic framework containing zinc nodes and 2 methylimidazole ligands) and the complex formed between Fe^{II}acetate and 1,10 phenanthroline (Fe^{II} [Phen]₃·2Ac-). The resulting material is first pyrolyzed in Ar at 1050 °C, then in pure NH₃ at 950 °C. Although NC_Ar+NH₃ is very performing initially at 0.6 V in H_2/O_2 fuel cell, it loses its initial high performance within less than 100 h (see Fig. 1). What is more important to note in Fig. 1 is that two decay rates may be observed on the curve representing the current density decay at 0.6 V: a fast decay lasting about 15 h, followed by a much slower decay lasting up to the end of the chronoamperometry experiment.

Recently, by replacing the iron phenanthroline complex with an iron porphyrin one in the synthesis of a catalyst now labeled NC_Por_Ar+NH₃, we were able to propose a working hypothesis based on water filling the micropores, followed by flooding the catalytic sites located in these micropores in order to explain the occurrence of the first fast decay in the stability of these types of NC catalysts [18]. Indeed, such NC catalysts are known to be highly microporous [9] and we also know that most of the active sites in these catalysts are hosted in these micropores [20]. Filling these micropores with water will dramatically decrease the mass

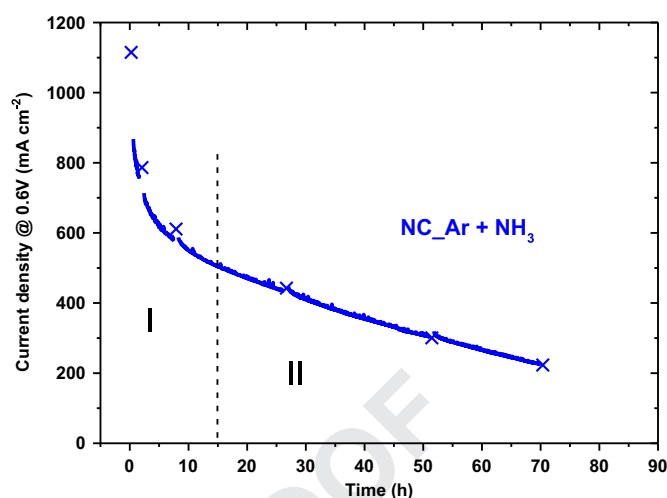


Fig. 1. Chronoamperometry curves showing two decay rates (I and II) for the current density at 0.6 V and 80 °C in H_2/O_2 fuel cell for NC_Ar+NH₃. The cathode catalyst loading is 4 mg cm^{-2} and the MEA membrane is Nafion 211.

transport of oxygen to the most active catalytic sites, drastically reducing at 0.6 V the contribution of these sites to the total current. As this is a working hypothesis, it is important now to see whether the first rapid decay in the stability curve of Fig. 1 may have alternative explanations. This paper investigates and disproves the possibility that a Fenton's reaction would initiate the first decay by chemically oxidizing the carbonaceous catalyst and its FeNx and CNx catalytic sites. At the same time, we will also show that removing all FeNx sites from a Fe/N/C catalyst is a difficult task even when a Fe precursor is not deliberately added to the other precursors of the catalyst. This is particularly true when ZIF-8 is used to obtain an N-doped carbonaceous material upon high temperature pyrolysis.

2. Experimental

2.1. Synthesis of catalysts

Two types of catalysts were used in this study: (i) catalysts with deliberate addition of some iron precursor, and (ii) catalysts without deliberate addition of any iron precursor.

Catalysts of type (i) were made according to the optimized conditions prevailing for the NC catalysts synthesis described in reference [9]. For these NC catalysts, three types of precursors were used: a zinc-imidazolite framework (ZIF-8, here also labeled MOF, and purchased under the name of Basolite Z1200 from Aldrich), which is used as a carbon and a nitrogen precursor; 1,10 phenanthroline (labeled Phen and purchased from Aldrich: purity $\geq 99\%$), which is another carbon and nitrogen precursor; iron^{II} acetate (labeled FeAc and purchased from Aldrich: purity 95%), which is the iron precursor. Phen is used to form a complex with the iron^{II} ion. The optimum nominal composition of the catalyst precursors is: MOF/Phen=80/20 (in weight), while the optimum nominal iron loading is 1 wt%.

For the synthesis of NC_Ar, 1600 mg of MOF, 400 mg of Phen and 64 mg of FeAc were first mixed for 2 h at room temperature in 100 ml of ethanol and 20 ml of de-ionized (DI) water. Then the mixture was heated to 60–80 °C for 2–3 h until about 50 ml of a thick slurry was obtained. The slurry was placed in a drying oven at 95 °C and in air where it was left overnight. The resulting dry powder was then transferred under N₂ in a 65 cm³ steel vial containing 20 chrome-steel balls of 0.25 in. diameter. After sealing the vial under N₂, it was placed in a planetary ball-miller

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