



# Iron porphyrin-based cathode catalysts for PEM fuel cells: Influence of pyrolysis gas on activity and stability

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## ABSTRACT

Fe-based catalysts for the O<sub>2</sub> reduction in acidic medium were prepared by impregnating chloro-iron tetramethoxyphenylporphyrin (Cl-FeTMPP) on a non-microporous carbon black and heat-treating the resulting material at 950 °C either in NH<sub>3</sub> (Mode 1) or in Ar (Mode 2). The most active catalyst using Mode 1 has a Fe bulk content of 0.4 wt% and an activity of 17 mA mg<sup>-1</sup> at 0.8 V in fuel cell. This activity is controlled by the microporous surface area of the catalyst. The most active catalysts using Mode 2 has an Fe bulk content of 3.7 wt% and an activity of 1.9 mA mg<sup>-1</sup> at 0.8 V in fuel cell. In Mode 2, the nitrogen and/or the iron surface concentrations control the activity. Concerning stability, Mode 1-catalysts are unstable while Mode 2-catalysts show stability for at least 15 h when at least 66 wt% Cl-FeTMPP is impregnated onto N330 and heat-treated at 950 °C in Ar. The catalyst made with 66 wt% Cl-FeTMPP has a bulk Fe content of 5.2 wt% and an activity of 1.3 mA mg<sup>-1</sup> at 0.8 V in fuel cell. Thus, in the present study, pyrolysis in NH<sub>3</sub> gives active but unstable catalysts while pyrolysis in argon gives less active but more stable catalysts at high Cl-FeTMPP loading. Graphitization of Cl-FeTMPP during pyrolysis in argon seems to impart stability. Mode 2-catalysts are stable in spite of a high peroxide yield of 26% while Mode 1-catalysts are unstable in spite of a low 5% peroxide yield.

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## 1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are efficient and clean electrochemical power generation devices that produce electricity from H<sub>2</sub> and O<sub>2</sub> gases. Due to their low temperature of operation (~80 °C), catalysts are required to facilitate H<sub>2</sub> oxidation at the anode and O<sub>2</sub> reduction at the cathode. Platinum remains the catalyst of reference for the oxygen reduction reaction (ORR) in PEMFCs [1]. Its high cost and poor availability makes the development of non-noble metal catalysts highly desirable.

After the discovery by Jasinski that the cobalt phthalocyanine reduces O<sub>2</sub> in alkaline medium [2], other Co- and Fe-N<sub>4</sub> macrocycles were also found to catalyze the ORR in acid medium. It was then found that the activity and stability of these macrocycles adsorbed onto a carbon support could be improved by a heat-treatment in an inert atmosphere and at high temperature [3]. Later, it was discovered that catalysts with similar activities could be synthesized using metal and nitrogen precursors less expensive than the Co- or Fe-N<sub>4</sub> macrocycles [4]. From these results, it was concluded that

three components are needed to form catalytic sites at high temperature: (i) nitrogen (ii) Fe or Co ions and (iii) carbon. Catalytic sites are formed only if these three components are simultaneously present [5–9]. Such catalysts are labeled Fe/N/C or Co/N/C.

Fe/N/C catalysts can be produced using iron acetate and NH<sub>3</sub>. Using these inexpensive precursors, our group has focused on improving the activity by increasing the number of catalytic sites on the carbon black support. It was discovered that two parameters govern the number of catalytic sites per mass of carbon (the site density); (i) the nitrogen content of the catalyst and (ii) the microporous surface area of the catalyst. The latter parameter is often the one restricting the site density for catalysts resulting from a heat-treatment in pure NH<sub>3</sub> [10–13]. At  $T > 750$  °C, NH<sub>3</sub> reacts with the carbon support [12]. This reaction preferentially gasifies the disordered carbon of a carbon black, creating porosity inside the carbon black particles but also leaving N-bearing functionalities on the newly created surface [14,15]. For such Fe/N/C catalysts, a higher content of disordered carbon in the initially non-microporous carbon support results in a higher microporous surface area in the catalyst, and hence in a higher catalytic activity [16–18].

While Fe/N/C catalysts made using iron acetate, ammonia and carbon black are active for the ORR, they do not sustain stable currents in fuel cells. The decrease in current can be observed even after only a few hours. We therefore set out to investigate if Fe/N/C catalysts obtained from Fe-N<sub>4</sub> macrocycles would show better stability in fuel cells. Ten-hour-experiments previously carried out on a cat-

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alyst obtained from iron tetraphenylporphyrin loaded on a carbon support and heat-treated at 900 °C in Ar suggest that short-term stability in fuel cell is achievable [19,20]. The activity and active-site identification of catalysts made from the heat treatment of FeN<sub>4</sub>- and CoN<sub>4</sub>-macrocycles have been the object of many publications ([5] and references therein [20–41]). Some stability data for Fe or Co/N/C catalysts in acid solution has been reported [42], but little data is available on their stability in fuel cells. Stability over 15 h is reported for a Co/N/C catalyst prepared by loading cobalt porphyrin on a carbon black pre-treated with H<sub>2</sub>O<sub>2</sub> and heat-treating the mixture at 900 °C in Ar [43]. Stability, but low activity, was reported by the group of Atanasoski for a Fe/N/TiC catalyst [44] that was prepared similarly to the Fe/N/C catalyst described by the same authors in Ref. [45]. Finally, Popov and coworkers report on catalysts synthesized by impregnating ethylene diamine and iron or cobalt salt on ketjenblack followed by a heat treatment in argon [46]. Low activity but quasi-stability for 500 h in fuel cells was reported. Two other works report on the stability in fuel cell of Fe/N/C or Co/N/C catalysts without heat treatment [47,48]. Bashyam and Zelenay [47] report on a catalyst composed of a cobalt–polypyrrole–carbon composite. Stability over 100 h in fuel cell was reported. A synthesis similar to that of Ref. [47] was used by Reddy et al. who replaced the carbon black support with single-wall carbon nanotubes. Stability in fuel cell over 50 h was reported [48].

However, the possible reasons for the stability or instability of Co/N/C or Fe/N/C catalysts have not been investigated in depth previously. In this paper, the focus is not on the activity but on the stability and/or instability of Fe/N/C catalysts. The present study explores possible factors governing the stability. It is shown that, using Cl-FeTMPP and a given carbon support, stable or unstable Fe/N/C catalysts are synthesized depending on the pyrolysis gas (NH<sub>3</sub> or argon) and also depending on the Cl-FeTMPP nominal loading on the carbon. Stability in fuel cell is observed only for catalysts prepared with a Cl-FeTMPP nominal loading >60 wt% and heat-treated in argon. All catalysts heat-treated in NH<sub>3</sub> are unstable but they are initially more active than those heat-treated in argon. Experimental data supports the hypothesis that stability is brought on by the graphitization of the carbon due to Cl-FeTMPP.

## 2. Experimental

### 2.1. Catalyst synthesis

#### 2.1.1. Mode 1: using NH<sub>3</sub> as the main nitrogen precursor

A given mass of chloro-iron tetramethoxyphenylporphyrin (Cl-FeTMPP) purchased from Porphyrin Systems was weighed and dispersed in acetone. The mass of carbon black support required to reach the desired nominal wt% loading of Cl-FeTMPP on the carbon was weighed and added in the porphyrin-acetone dispersion. The nominal loading is defined as the expected loading of the powder before pyrolysis. The carbon black support was a commercial carbon black of grade N330 (BET area 74 m<sup>2</sup> g<sup>-1</sup>, other characteristics can be found in Ref. [17]) from Sid Richardson Carbon Corporation. In Mode 1, the target for the nominal iron loading on the carbon was either 0.2 wt% (3.5 wt% of Cl-FeTMPP loading on carbon) or 0.4 wt% (7 wt% Cl-FeTMPP). The suspension was stirred for 2 h. Then acetone was evaporated. The powder was placed in a quartz boat (10 cm long, 1 cm wide). The initial mass was weighed. The quartz boat containing the powder as well as a glass rod/magnet assembly was placed in a quartz tube (*D* 3.5 cm, *L* 120 cm) that was itself fitted in a split hinge tube furnace. The boat was initially placed outside the furnace heating zone. The tube was purged with Ar at 1000 sccm for 30 min. The furnace was then turned on and let to stabilize to its set temperature (950 °C) for 100 min under Ar/H<sub>2</sub> flows of 1000/100 sccm.

After 100 min of furnace stabilization, the Ar/H<sub>2</sub> flow was switched to pure NH<sub>3</sub> with a flow rate of 2000 sccm. After 20 min under pure NH<sub>3</sub>, the boat was moved slowly to the middle of the furnace by dragging the glass rod/magnet assembly using an outer magnet. Once the boat was positioned, timing for the heat-treatment was initialized. Once the desired heat-treatment duration had expired, the tube was removed from the furnace and let to cool down under NH<sub>3</sub> flow. After 10 min, the NH<sub>3</sub> flow was replaced with an Ar flow for 20 min. The mass of the powder was measured again. The percentage of mass that was lost during the heat-treatment, *W*, was calculated as follows:

$$W = 100 \cdot \frac{\text{initial mass} - \text{final mass}}{\text{initial mass}} \quad (1)$$

#### 2.1.2. Mode 2: using Cl-FeTMPP as the only N precursor

Several catalysts were synthesized by impregnation of various Cl-FeTMPP loadings on N330 (7–90 wt% Cl-FeTMPP on carbon). Cl-FeTMPP was impregnated on the carbon black as described in Section 2.1.1. The pyrolysis procedure was the same as in Section 2.1.1 except that the gas during the pyrolysis was pure argon (flow 1000 sccm). The cooling down was as in Section 2.1.1. The mass loss during pyrolysis was measured as in Section 2.1.1. Pure Cl-FeTMPP was also pyrolyzed in the same conditions.

### 2.2. Physical characterization of catalysts

Pore size measurements were performed with a Quantachome Instruments Autosorb-1. The samples were first degassed at 200 °C for 2 h under vacuum. Adsorption and desorption isotherms were measured at 77 K with N<sub>2</sub> as adsorbate. The adsorption data was analyzed with the Brunauer–Emmett–Teller theory to give the BET surface area and with the non-local density functional theory (NLDFT, slit-pore geometry model from Autosorb software, Quantachrome Instruments) to give the pore size distribution. The macroporous area was estimated by subtracting from the BET area, the micro- and mesoporous areas obtained by the NLDFT analysis. Micropores are pores having a size <2 nm, mesopores have a size comprised between 2 and 50 nm and macropores have a size >50 nm [49].

Surface elemental analysis was performed by X-ray photoelectron spectroscopy (XPS) using a VG Escalab 200i instrument and the Al K $\alpha$  line (1486.6 eV) as the X-ray source. Narrow scans were recorded for C<sub>1s</sub>, N<sub>1s</sub>, O<sub>1s</sub> and Fe<sub>2p</sub>. The quantification was performed using Casa software.

The bulk Fe content was measured by neutron activation analysis (NAA) at École Polytechnique de Montréal.

Bragg–Brentano X-ray diffraction (XRD) was performed with a Bruker D8 diffractometer using Cu K $\alpha$  radiation. This allows determination of the lattice spacing between the graphene layers  $d^{002}$  and the mean stacking height of the graphitic crystallites,  $L_c$ . The  $d^{002}$ -value was determined using Eq. (2).

$$d^{002} = \frac{\lambda}{2 \sin \theta} \quad (2)$$

where  $\lambda$  is the X-ray wavelength of the Cu K $\alpha$  radiation, 1.541874 Å, and  $\theta$  the position of the 002 diffraction line in degrees.  $L_c$  is obtained from Eq. (3) [16,50]:

$$L_c = \frac{K \cdot \lambda}{\beta \cdot \cos \theta} \quad (3)$$

where the form factor *K* is 0.91,  $\beta$  is the full width at half maximum (in radians) of the 002 diffraction peak in the graph of intensity vs.  $2\theta$ , and  $\theta$  is as defined under Eq. (2).

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