



# Probing active sites in iron-based catalysts for oxygen electro-reduction: A temperature-dependent $^{57}\text{Fe}$ Mössbauer spectroscopy study



Moulay Tahar Sougrati, Vincent Goellner, Anna K. Schuppert, Lorenzo Stievano\*, Frédéric Jaouen\*\*

UMR-5253, CNRS, Université de Montpellier, Institut Charles Gerhardt, Agrégats, Interfaces et Matériaux pour l'Energie, CC1502, place Eugène Bataillon, 34095 Montpellier cedex 5, France

## ARTICLE INFO

### Article history:

Received 17 July 2015

Received in revised form 15 October 2015

Accepted 16 October 2015

Available online 2 November 2015

### Keywords:

Mössbauer spectroscopy

Electrocatalysis

Iron catalysts

Fuel cells

Oxygen reduction reaction

Carbon

## ABSTRACT

Two Fe-N-C electrocatalysts for oxygen reduction were studied by  $^{57}\text{Fe}$  Mössbauer-spectroscopy between 300 and 5 K. The first catalyst contains almost exclusively  $\text{FeN}_x\text{C}_y$  moieties while the second contains additional crystalline phases, *i.e.* metallic iron and iron carbide. The Mössbauer parameters of two quadrupole doublets named D1 and D2, attributed to low and medium spin  $\text{FeN}_4/\text{C}$  moieties, respectively, do not change with temperature down to 5 K. This indicates that such moieties do not undergo phase transition or magnetic ordering, supporting the view that the active sites are localized on isolated iron atoms. At room temperature, the Lamb-Mössbauer factors of doublets D1 and D2 are 0.46 and 0.52, smaller than those of  $\alpha\text{-Fe}$  (0.67) and  $\gamma\text{-Fe}$  (0.78). These values allow for the first time a precise Mössbauer quantification of Fe species in Fe-N-C catalysts. The ORR activity is best correlated with the absolute content of the  $\text{FeN}_4/\text{C}$  moiety associated with doublet D1, assigned to a  $\text{Fe}^{\text{II}}\text{N}_4/\text{C}$  moiety in low-spin state. The ORR turnover frequency of such moieties is however known to depend on chemical and electronic properties of the carbon matrix, which will require additional descriptor(s) than the site density in order to precisely interpret the ORR activity of such materials.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

While important examples of past electrochemical developments are corrosion mitigation as well as industrial electrolytic processes [1], electrochemistry is currently strongly tied with the development of novel technologies for energy production and storage [2]. Electrochemical energy conversion devices offer the advantages of (i) a higher theoretical energy efficiency compared to heat engines and (ii) connectivity to the electric power grid. The latter advantage may be used to recharge a fleet of battery-driven vehicles but also for peak-shaving of the intermittent electric power produced by solar and wind energies through the reversible storage of electrical energy [3]. Among the electrochemical systems with high energy density under intense development, the hydrogen/air Polymer Electrolyte Membrane Fuel Cell (PEMFC) is today

perceived as one of the best contenders to replace internal combustion engines in the near future [2]. While PEMFC-powered automobile fleets with 400 km driving range have now been demonstrated, remaining challenges are increased durability and reduced cost [4]. Related to cost, but also impacting the long term viability of this technology, the replacement of the rare-element platinum presently used as a catalyst at both the anode and the cathode is a longer-term challenge [3–5]. The investigation of alternative catalysts based on Earth-abundant elements is of particular importance for the cathode, which accounts for about 90% of Pt in PEMFCs [6]. This asymmetric platinum loading is due to the notoriously sluggish oxygen reduction reaction (ORR) at the cathode, which contrasts with the fast hydrogen oxidation reaction at the anode. While several classes of ORR catalysts based on Earth-abundant transition metals have been investigated, one of the most promising classes of non-precious metal catalyst is today the Metal-Nitrogen-Carbon (Me-N-C) system, with iron or cobalt being the most active metal centres [7–16].

While Me-N-C catalysts may be synthesized from a variety of carbon, nitrogen and metal precursors, a necessary feature for designing highly active Me-N-C catalysts is the simultaneous

\* Corresponding author. Tel.: +33 4 67 14 33 46; fax: +33 4 67 14 33 04.

\*\* Corresponding author. Tel.: +33 4 67 14 32 11; fax: +33 4 67 14 33 04.

E-mail addresses: [lorenzo.stievano@umontpellier.fr](mailto:lorenzo.stievano@umontpellier.fr) (L. Stievano), [frederic.jaouen@univ-montp2.fr](mailto:frederic.jaouen@univ-montp2.fr) (F. Jaouen).

presence of these three elements during a pyrolytic step at or above  $\sim 700^\circ\text{C}$  [17–19]. In contrast to Pt-based catalysts, the ORR activity of Fe(Co)/N/C catalysts increases with increased metal loading only in the range of 0.3–3.0 wt% [12,20–24]. This observation has been explained on the basis of a saturation effect: the nitrogen-doped carbon matrix may only host a restricted number of Fe- or Co-based active sites. While the nitrogen content was initially thought to be the main factor limiting the density of active sites [25,26], the microporous surface area was later shown to be even more limiting [11,13,18,27,28]. On the basis of the importance of micropores and of the knowledge on the Fe coordination obtained from X-ray absorption spectroscopy [29–31],  $^{57}\text{Fe}$  Mössbauer spectroscopy [32–34] and time-of-flight secondary ion mass spectroscopy [21,35], the most active site for catalysing the ORR in such microporous Fe-N-C catalysts was proposed to be a  $\text{FeN}_{2+2}$  moiety forming a molecular bridge over two graphitic nano-crystallites separated by a distance of 10–20 Å and involving two ligating nitrogen atoms from each graphene sheet [27]. However, several structurally-distinct  $\text{FeN}_x\text{C}_y$  moieties most probably coexist in Fe-N-C catalysts, each having a distinct ORR activity. Various edge, inter-edge and intra-sheet  $\text{FeN}_x\text{C}_y$  or  $\text{Fe}_2\text{N}_x\text{C}_y$  moieties have been proposed and their energy of formation and ability to interact with dioxygen computed with density functional theory [36–42]. Along with the  $\text{FeN}_x\text{C}_y$  or  $\text{CoN}_x\text{C}_y$  moieties integrated in graphene sheets and centred about a single metal atom, or at the most two ( $\text{Fe}_2\text{N}_x\text{C}_y$ ) metal atoms, the above-mentioned saturation effect almost systematically results in the formation of undesired Fe- or Co-based crystalline phases such as reduced metal, metal nitrides or carbonitrides. Such secondary structures are inert or poorly active towards ORR and can be easily spotted by X-ray diffraction, or by  $^{57}\text{Fe}$  Mössbauer spectroscopy in the case of iron. In a first attempt to synthesize Fe-N-C catalysts comprising only  $\text{FeN}_x\text{C}_y$  moieties and free of undesired Fe-based crystalline phases, a series of catalysts with Fe contents in the range of 0.03–1.55 wt% was synthesized [23]. However, a  $^{57}\text{Fe}$  Mössbauer study of this series of catalysts revealed that undesired crystalline Fe-containing phases had formed even at very low Fe contents [43]. In fact, the coexistence of secondary iron phases along with  $\text{FeN}_x\text{C}_y$  moieties is ubiquitous in the Fe-N-C catalysts that have to date been investigated with either X-ray absorption spectroscopy or  $^{57}\text{Fe}$  Mössbauer spectroscopy [28,44–49]. The Mössbauer spectrum of one of the purest catalyst reported before 2015 was recorded for a catalyst synthesized *via* the pyrolysis of a chloro- $\text{Fe}^{\text{III}}$ -porphyrin, iron oxalate and elemental sulfur. It showed an overwhelming majority of doublets assigned to various  $\text{FeN}_x\text{C}_y$  moieties and only a very weak singlet assigned to  $\gamma$ -Fe particles [50,51]. While the magnetic ordering of  $\alpha$ -Fe and of most iron carbides produce a Zeeman splitting of their Mössbauer spectra into magnetic sextets, nano-sized particles of such structures may undergo superparamagnetic relaxation at room temperature, leading to singlets or quadrupole doublets instead of magnetic sextets [52].

The presence of metallic iron and iron carbides in Fe-N-C catalysts strongly complicates the spectroscopic identification of  $\text{FeN}_x\text{C}_y$  moieties and consequently the precise determination of their electronic and geometric structure. With such multi-phase materials, for instance, the analysis of X-ray absorption spectra recorded at the Fe K-edge is quickly overcomplicated since the signal is averaged over all iron centres in the sample.  $^{57}\text{Fe}$  Mössbauer spectroscopy *a priori* leads to a simpler separation of the signals arising from the unwanted Fe-containing bulk phases on the one hand, which are mostly represented by sextets or singlets, and from the  $\text{FeN}_x\text{C}_y$  moieties on the other hand, which are represented by quadrupole doublets with a relatively large quadrupole splitting. While an overlap of the various spectral components occurs at sample velocities in the range of  $\pm 2\text{ mm s}^{-1}$ , linear combination fittings of complex Mössbauer spectra of Fe-N-C catalysts have

been performed in order to (i) obtain information on the Mössbauer parameters of the  $\text{FeN}_x\text{C}_y$  moieties, (ii) estimate the content of the different iron coordinations in Fe-N-C catalysts and (iii) draw correlations between the content of specific  $\text{FeN}_x\text{C}_y$  moieties and the overall ORR activity of Fe-N-C catalysts [34,43,47,53,54]. Thus far, the quantification with  $^{57}\text{Fe}$  Mössbauer spectroscopy of the distinct iron structures and  $\text{FeN}_x\text{C}_y$  moieties in heterogeneous Fe-N-C catalysts has involved (i) the knowledge of the overall bulk Fe content in the catalyst, (ii) the fitting of its complex Mössbauer spectrum with appropriate singlet, doublet and sextet components and (iii) the hypothesis of identical Lamb-Mössbauer factors ( $f_{\text{LM}}$ ) for all Fe species [34,43,47,53,54]. This hypothesis was forced by the fact that the  $f_{\text{LM}}$  factors for  $\text{FeN}_x\text{C}_y$  moieties integrated in, or at the edge of, graphene sheets are hitherto unknown. Generally speaking, the knowledge of the  $f_{\text{LM}}$  factor of the different species contained in a sample is necessary to mathematically relate the relative absorption area below a given spectral component to the relative content of the corresponding iron species. The general relation between the content of any iron species,  $\text{Fe}_i$ , and the relative areas of the various spectral components found in a multiphase Fe-N-C material is given by the following equation:

$$\%(\text{Fe}_i) = \%(\text{Fe}_{\text{tot}}) \frac{\%(A_i)}{f_{\text{LM}i} \cdot \sum_j \% (A_j) / f_{\text{LM}j}} \quad (1)$$

where  $\%(\text{Fe}_i)$  is the weight percentage of the iron species “i” in the catalyst,  $\%(\text{Fe}_{\text{tot}})$  is the total Fe weight content in the catalyst,  $\%(A_i)$  is the relative resonance area % of the iron species “i” and  $f_{\text{LM}i}$  is the Lamb-Mössbauer factor for the iron species “i”. It can be seen from Eq. (1) that the value  $\%(\text{Fe}_i)$  may be directly deduced from the  $\%(A_i)$  measured by Mössbauer spectroscopy and from the knowledge of  $\%(\text{Fe}_{\text{tot}})$  measured with another technique if, and only if, the  $f_{\text{LM}}$  values of all Fe-based species present in a given sample are assumed to be equal. While this assumption is acceptable for a sample containing bulk Fe-containing crystalline phases (similar  $f_{\text{LM}}$  values are commonly measured for  $\alpha$ -Fe,  $\gamma$ -Fe,  $\text{Fe}_3\text{C}$ , etc.), the assumption can lead to a significant errors for Fe-based samples containing both crystalline phases and Fe-containing molecular compounds or complexes. For any iron coordination, the  $f_{\text{LM}}$  value is intimately related to the strength of the binding of the Mössbauer-absorbing  $^{57}\text{Fe}$  nucleus in a solid lattice, and it can be related, in a solid described by the Debye model, to the Debye temperature [52]. For example, at room temperature, the  $f_{\text{LM}}$  values for metallic iron, iron oxides and hydroxides are in the range of 0.65–0.90 [55,56], whereas it can be as low as 0.15 in the case of iron-based organometallics [57,58]. Intuitively, it is thus expected that this parameter is larger for inorganic particles ( $\alpha$ -Fe,  $\gamma$ -Fe and iron carbides) where the atoms are strongly bound in a 3D-lattice than for the  $\text{FeN}_x\text{C}_y$  moieties, where the iron atom is simply coordinated at the centre of a porphyrin-like coordination ring. As a consequence, for Fe-N-C materials comprising both  $\text{FeN}_x\text{C}_y$  moieties and inorganic crystalline phases, the hypothesis of identical  $f_{\text{LM}}$  values leads to an overestimation of the content of Fe-based crystalline phases. Indeed, we recently reported on a *post mortem* Mössbauer investigation of two Fe-N-C catalysts, among which one was nearly free of Fe-containing crystalline species while the other contained significant amounts of them [59]. The large difference observed between the absolute resonance areas in spite of similar iron contents in both samples suggested that  $\text{FeN}_x\text{C}_y$  moieties and Fe-containing crystalline phases have significantly different  $f_{\text{LM}}$  values.

In the present work, we have systematically investigated the temperature dependence of  $^{57}\text{Fe}$  Mössbauer spectra of two Fe-N-C catalysts. The first one comprises quasi-exclusively  $\text{FeN}_x\text{C}_y$  moieties covalently integrated in graphene sheets while the second one comprises  $\text{FeN}_x\text{C}_y$  moieties as well as  $\alpha$ -Fe,  $\gamma$ -Fe and  $\text{Fe}_3\text{C}$  particles. The synthesis, electrochemical characterization and detailed X-ray

Download English Version:

<https://daneshyari.com/en/article/6505142>

Download Persian Version:

<https://daneshyari.com/article/6505142>

[Daneshyari.com](https://daneshyari.com)