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Fe local structure in Pt-free nitrogen-modified carbon based electrocatalysts: XAFS study

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Abstract. The paper presents a new results on the bonding environment (coordination number and geometry) and on oxidation states of Fe in nitrogen-modified Fe/C composites used as Pt-free catalysts for oxygen reduction in Direct Hydrogen Fuel Cells. Starting from glucose or fructose, two catalysts displaying different electrochemical performance were prepared and studied in the form of pristine powder and thin catalytic layer of electrode by Fe K-edge XAFS spectroscopy. The results show how the Fe local structure varies as a function of different synthesis conditions and how changes in the structural properties of the catalysts are related to fuel cell electrochemical performance increase during a cell activation period.

1. Introduction

Nowadays, Direct Hydrogen Fuel Cells (DHFCs) represent one of the most promising alternatives for the development of low temperature power devices. However, one of the most severe limitations to a large-scale application of this technology is the high cost of both polymeric membranes and of catalytic electrode materials, commonly requiring noble metals as Pt due to the intrinsic difficulty of the cathodic Oxygen Reduction Reaction (ORR). In this context, non-precious metal catalysts are actively searched for, such as to meet already established operational benchmarks for conventional platinum low temperature FC vehicular requirements, with the additional benefit of significant cost reduction and stability increase.

Among various materials, nitrogen-modified carbons containing non-precious transition metals are considered interesting because of their optimized morphology (in terms of porosity and specific surface area), ORR activity (closely approaching those of commercial Pt catalysts) and reliability as confirmed by results from independent groups [1, 2, 3]. This work is dedicated to nitrogen-modified carbons containing Fe centres. Innovation of considered catalysts involves the use of organic compounds, fructose and glucose, as a precursor of carbon. Very promising electrochemical performance (clearly revealed by rotating disk electrode measurements), electrochemical stability (depending on the synthesis procedure and working conditions in real FC) and a very scarce data about the nano and atomic-level structure of these catalysts became the motivation of the present study. Scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray Absorption Fine Structure (XAFS) measurements and analysis



were performed to define the location and local structure of metal centres and their chemical states in the catalyst at various stages of the electrode preparation and to determine if and how changes in the iron local environment affect the catalyst stability.

2. Materials

Among several preparation approaches, thermal treatment of mixed precursors from a carbon and nitrogen source added with transition metal salts [4] seems promising due to the ease and flexibility of the synthetic route. Thus, nitrogen-modified carbons containing Fe centres (about 1-2 wt.%) were prepared by high-temperature pyrolysis in N_2 atmosphere of a gel formed by organic precursors of C (fructose or glucose), N (guanidine acetate) and Fe (Fe(II) acetate) [3]. For the structural study pristine powders and conditioned in real FC electrodes prepared on the base of these powders were used. Catalytic inks and electrodes for FC test were prepared in a standard way. Resulting Fe loading in the catalytic layer was about $0.1\text{-}0.2\text{ mg/cm}^2$. Electrode conditioning was realized passing fully humidified oxygen and hydrogen at cathode and anode side, respectively, at $T_{O_2}/T_{H_2}/T_{cell} = 70/70/70^\circ\text{C}$. Activation process was conducted at 0.6 V by about 3 h, until stable polarization curve was obtained. The obtained samples are hereafter called Fe-FAG and Fe-GAG when fructose and glucose, respectively, was used as a C source.

3. Results and discussion

X-ray diffraction data of Fe-FAG and Fe-GAG pristine powders are shown in Figure 1. Obtained patterns exhibit apparent differences between Fe-FAG and Fe-GAG samples. In Fe-FAG pristine powder, it can be easily observed the presence of ordered carbon or carbon-iron phases (peaks indicated by full circles in Figure 1). The broad nature of these reflections in Fe-GAG pristine powder pattern indicate poor ordering of the carbon structure. Moreover, it should be underlined that additional diffraction peaks (indicated by crosses in Figure 1), related to the presence of small amount of metallic Fe, can also be noticed, but only in the pattern of Fe-FAG pristine powder. At the same time, SEM images show the presence of small (nanometric) spherules in both cases (see Figure 2). However, the spherules are more numerous in Fe-FAG powder than in Fe-GAG one, thus explaining the absence of metallic iron diffraction peaks in Fe-GAG pattern.

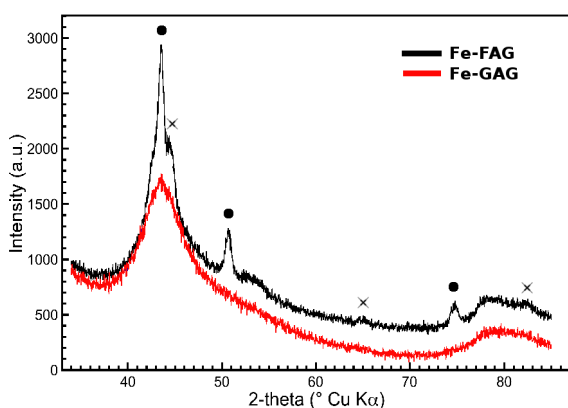


Figure 1. X-ray diffraction patterns of Fe-FAG and Fe-GAG pristine powders. Full circles – poorly ordered carbon or carbon-iron phases, crosses – metallic Fe.

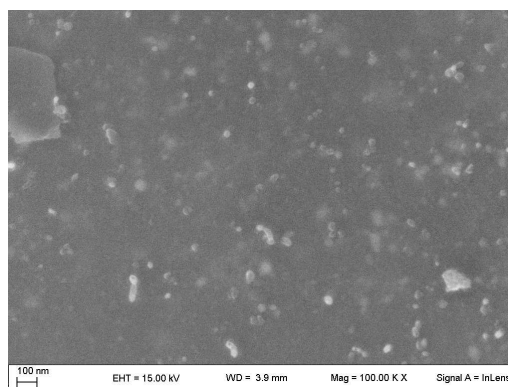


Figure 2. SEM image of the Fe-FAG powder displaying nanometric spherules (possibly agglomerates of metallic Fe or carbon-iron compounds).

Fe K-edge XAFS measurements in both near-edge (XANES) and extended (EXAFS) range were also performed. Spectra of pristine powders, conditioned electrodes and a series of reference

samples were recorded at ELETTRA 11.1 XAFS station. All XAFS measurements were realized ex situ at RT using transmission geometry. Coarse comparison of the XANES spectra (Figure 3) and Fourier transforms (FTs) of the total EXAFS spectra (Figure 4) reveals a strong difference in the Fe local structure for catalysts prepared in the various synthesis conditions (compare pristine powders of Fe-FAG and Fe-GAG). Then, it should be noted that in both catalysts electrode preparation and activation process realized in a real FC changed Fe local structure. However, the most pronounced structural modification occurred in the case of Fe-GAG. Thus, resulted XAFS spectra of both conditioned electrocatalysts are rather similar (differences are observed especially in the near-edge region, see inset in Figure 3).

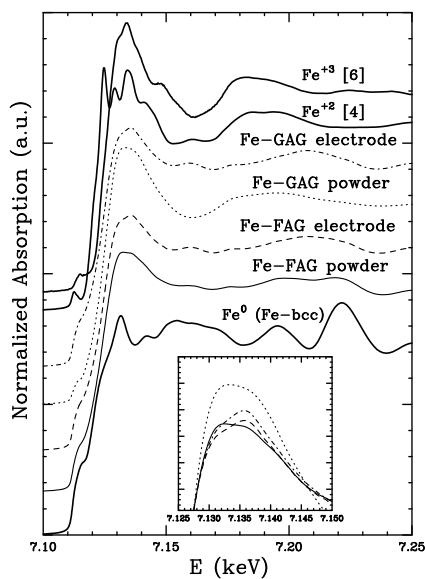


Figure 3. Fe K-edge normalized XANES spectra of Fe-FAG, Fe-GAG samples and of some reference bulk samples (thick solid lines). Inset: Fe-FAG and Fe-GAG white line intensity and shape comparison.

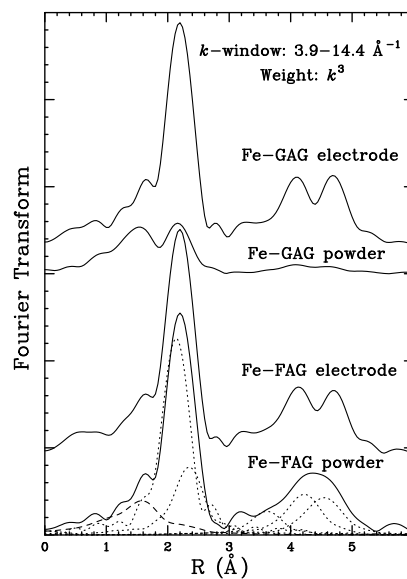


Figure 4. Fourier transforms of the EXAFS experimental signals of Fe-FAG and Fe-GAG samples. Theoretical partial $\gamma^{(n)}$ signals used in GNXAS analysis are also shown: dashed line – Fe-C; dotted lines – nano Fe-bcc.

Qualitative structural analysis of studied samples was started by performing reference spectra linear combination fitting in the XANES region. However, it should be underlined that fit result for any spectra combination was not satisfactory. Thus, only Fe metallic phase contents was properly estimated. Obtained values (over 50% for Fe-FAG powder, about 20% for Fe-GAG powder and over 60% for both activated electrodes) fully confirm XRD and SEM observations.

Then, structural models for detailed EXAFS data-analysis performed using the GNXAS method [5] were constructed taking into account the above mentioned results. Thus, the calculated signals were modeled based on the Fe_3C structure (only first shell Fe-C two-body contribution) and Fe-bcc structure (two- and three-body contributions, up to 5th coordination shell) – see FT of Fe-FAG pristine powder spectra in Figure 4. Best fit results for the first-shell structural parameters are shown in Table 1. First of all, it should be mentioned that in all studied samples Fe-Fe configurations (up to 5th coordination shell) precisely reconstruct metallic Fe-bcc structure. However, reduction of coordination numbers and higher value of disorder parameters in respect to bulk metallic iron, indicate the presence of nanostructured Fe. Moreover, it is interesting to note that obtained Fe local structure parameters are different for Fe-FAG and Fe-GAG conditioned electrodes, especially these which describe metallic phase structure. In Fe-FAG electrode, larger Fe nanoparticles with more disordered Fe-Fe distributions can be detected.

Table 1. The best GNXAS fit results for the first shell Fe-C and Fe-Fe configurations obtained for all considered samples: R [Å] – the average inter-atomic distance, σ^2 [10^{-3}Å^2] – the standard deviation of distance, β – asymmetry parameter and N – the coordination number.

Sample	$R_{\text{Fe-C}}$	$\sigma_{\text{Fe-C}}^2$	$\beta_{\text{Fe-C}}$	$N_{\text{Fe-C}}$	$R_{\text{Fe-Fe}}$	$\sigma_{\text{Fe-Fe}}^2$	$N_{\text{Fe-Fe}}$
Fe-FAG powder	1.97(1)	12(1)	0.1	6.1(6)	2.475(5)	6.0(6)	5.1(2)
Fe-FAG electrode	1.96(1)	9(1)	0.05	4.2(4)	2.488(5)	8.0(8)	7.0(3)
Fe-GAG powder	1.94(1)	8(1)	0.0	4.8(5)	2.47(1)	8(1)	1.4(1)
Fe-GAG electrode	1.96(1)	10(1)	0.05	4.4(4)	2.489(5)	6.9(7)	6.3(3)

These differences may cause different catalyst activity and stability observed when durability tests are performed. At the same time, in all samples Fe-C distribution is broad and slightly asymmetric. Only in the case of Fe-GAG powder the distribution is a little better defined, giving in EXAFS signal comparable contribution with the Fe metallic phase. However, there can not be clearly concluded whether Fe-C contribution is related to carbon-iron compounds or Fe nanoparticle attached to carbon support. Therefore, detailed XANES spectra analysis based on the theoretical calculations realized by means of the MXAN code [6] were performed. MXAN preliminary results, obtained using the model structure constructed on the base of Fe-C and Fe-Fe distances and multiplicities determined by EXAFS data analysis (Table 1), show the possible existence of small Fe clusters attached to a grafen-like layer. In particular, model structure with a single Fe atom attached to that layer produces theoretical spectra similar to that of Fe-GAG pristine powder, whereas larger Fe cluster supported on the grafen-like structure gives theoretical spectra more similar to the spectra measured for Fe-FAG powder and conditioned electrodes. However, more advanced and sophisticated calculations are necessary to define precisely the coordination geometry of Fe ions and location of Fe nanoparticles.

4. Conclusions

XANES and EXAFS results combined with XRD and SEM analysis allowed us to construct model of Fe environment in nitrogen-modified carbon based electrocatalysts in which organic compounds, fructose and glucose, were used as a carbon precursor. Detected subtle structural differences and changes occurred on the atomic level during the catalysts preparation and activation in real FC were used as a possible explanation of a different catalysts stability and their electrochemical activity observed during the fuel cell operation. In order to improve our knowledge about Pt-free catalysts degradation mechanisms, detailed structural analysis of considered catalysts subjected to durability tests (various protocols were applied) are in progress.

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