Effect of nitrogen doping method on the activity of Fe-N-C catalysts based on carbon xerogels for fuel cells

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The development of active and inexpensive non-precious metal catalysts is a necessary and essential requirement to replace currently used Pt-based catalysts, in order to reduce the cost of polymer electrolyte fuel cells(PEFC). [1] Catalysts based on the Fe-N-C structure develop high electroactivity towards the oxygen reduction reaction (ORR), the limiting reactionin fuel cells. To increase the catalysts activity, Fe must be dispersedin acarbon material with a high surfacearea.In this context, carbon xerogels are excellent candidates, as their main properties can be easily tailored: porosity, electrical conductivity and surface chemistry. [2] The meso/macroporosity of carbon xerogels can be designed by modifying the conditions of the synthesis process, while microporosity can be generated by subsequent carbonization/activation treatments [3].In the present work, on the basis of carbon xerogels with an optimal ratio of micro/meso/macroporosity, we investigate the effect of two different methods of nitrogen-doping in the catalytic activity of Fe-N-C catalysts. Catalysts are evaluated both in half-cell and single-cell configurations and their activity is correlated to their physical-chemical features.

Organic xerogels (OXG) were synthesized by a sol-gel synthesis method from resorcinol and formaldehyde. The first doping method consisted of mixing the OXG with urea followed by pyrolysis at 800ºC (N-CXG-1). The second doping method, consisted of a first pyrolysis of OXG into carbon xerogel (CXG) at 800ºC, and then mixing CXG with urea followed by a second thermal treatment at 800ºC (N-CXG-2). All thermal treatments were carried out in inert atmosphere for 1h duration.The Fe doping was made by mixing either the N-CXG-1 or the N-CXG-2 in a planetary ball mill with iron acetate. The obtained powder was pyrolyzed in N_2 atmosphere at 1050 °C for 1h, obtaining Fe-N-CXG-1 and Fe-N-CXG-2. [5] Subsequently, these materials were treated by a series of acid treatments in $HClO_4$ in order to eliminate inactive iron particles, followed by a thermal treatment at 950 °C in N_2 flow.The textural features of the carbon xerogels were determined by means of N_2 and CO_2physisorption. The physical-chemical characteristics of the catalysts were determined by X-ray photoelectron spectroscopy (XPS), optical emission spectroscopy with inductive coupled plasma (ICP-OES), and elemental analysis (EA). The activity of the catalysts towards the ORR was determined in a three electrode cell with a rotating disk electrode (RDE) and O_2-saturated 0.5 M H_2SO_4 electrolyte.Membrane-electrode assemblies (MEAs) were prepared by hot-pressing of cathode (Fe-N-C catalyst, 4 mg cm^{-2}) and anode (commercial Pt/C, 0.2 mg_{Pt} cm^{-2}) with Nafion®212R membrane. The electrodes were prepared by spraying the catalyst on GDL-39BC (Sigracet) gas diffusion layer. A Fuel Cell Technologies Inc. test station was used to evaluate the MEA performance at a cell temperature of 80ºC and 100%RH.

Table 1 shows the N/C atomic ratio determined by EA and XPS. Figure 1 presents the high-resolution N1s spectra with the N speciation. The Fe-N-CXG-2 catalystpresents a higher N/C and a higher contribution of N-Fe bond compared to Fe-N-CXG-1.

	EA	XPS
	N/C	N/C
N-CXG-1	0.07	0.12
N-CXG-2	0.07	0.09
Fe-N-CXG-1	0.02	0.03
Fe-N-CXG-2	0.05	0.06

Table 1.N/Catomic ratios calculated by EA and XPS.

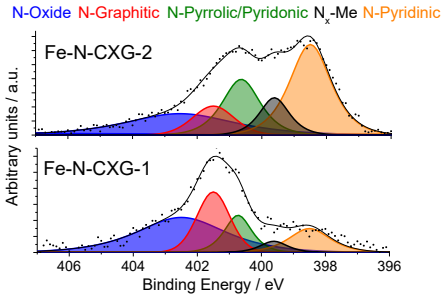

Figure 1. High-resolution N1s spectra fitted with individual peaks.

Figure 2 (a) shows the catalysts activity towards the ORR measured in a three-electrode cell system. Fe-N-CXG-2 presents a significantly higher activity compared to Fe-N-CXG-1, what correlates with its higher N/C and N-Fe content. The half-wave potential for Fe-N-CXG-2 is 110 mV lower that the one for the commercial benchmark catalyst, Pt/C (40wt% Pt, Johnson Matthey). RDE measurementsat different rotation speeds (400 to 2500 rpm) were adjusted to the Koutecky–Levich (KL) equation in order to determine the number of electrons transferred during the ORR (Figure 2 (b)).As expected, the ORR on Pt/C goes through 4e-. Both Fe-N-C catalysts present similar slopesthan Pt/C, meaning that ORR in these catalysts also goes througha four-electron pathway[6].

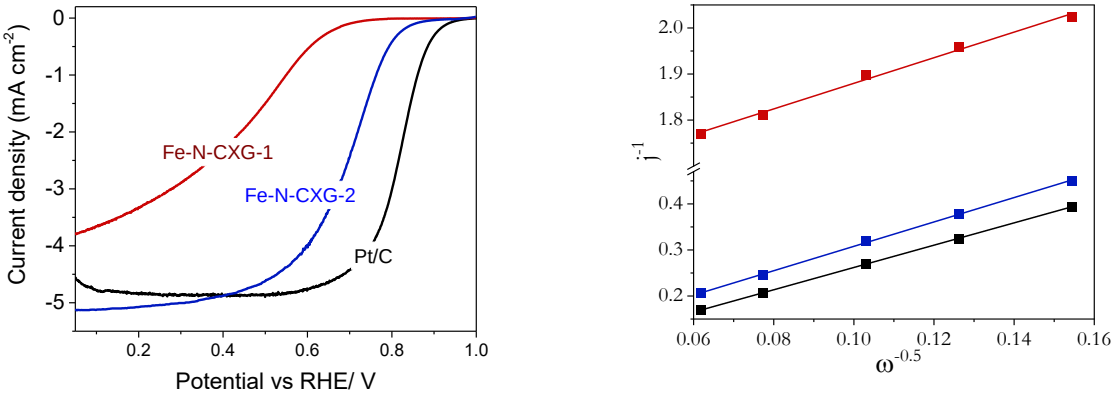

Figure 2. (a) Polarization curves for the ORR, in RDE at 1600 rpm in O_2-saturated 0.5M H_2SO_4. (b) Koutecky-Levich plot j^{-1} vs. $\omega^{-0.5}$ at 0.6V vs. RHE.

The Fe-N-C catalysts activity and durability was also studied in a PEFC single cell. Fig. 3 (a) shows the polarization curves at the beginning (0h) and after 20h operation at 0.5 V while Fig. 3 (b) shows the power density curves. The Fe-N-CXG-2 catalyst exhibits a polarization curve about 100 mV better than Fe-N-CXG-1, in line with 3-electrode cell results. Therefore, the maximum power density is about 80% higher for Fe-N-CXG-2. After 20h operation, the Fe-N-CXG-2 also shows a lower loss in performance compared to its counterpart Fe-N-CXG-1. From these results, the two step nitrogen-doping method appears more effective for the preparation of Fe-N-C catalysts based on carbon xerogel substrate since a larger amount of Fe-N species is favoured according to XPS results.

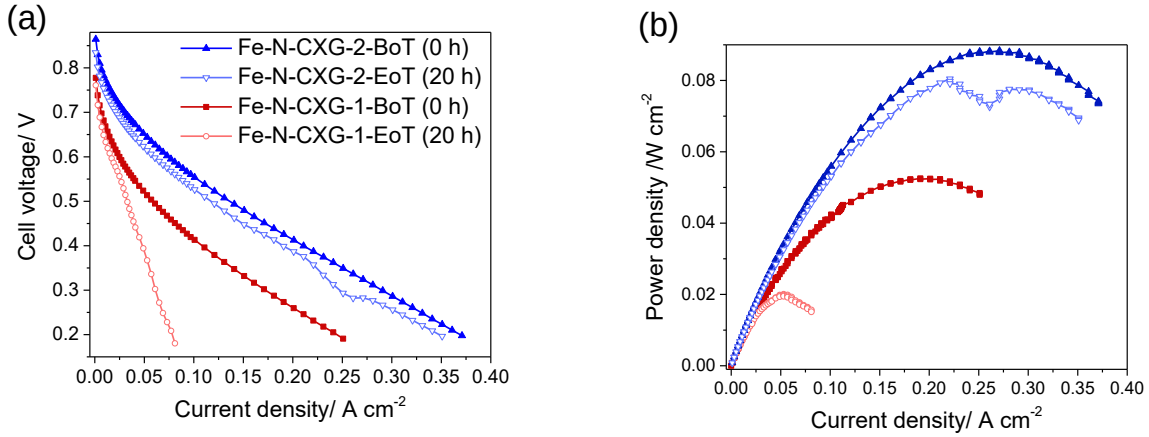

Figure 3. (a) Polarization curves for MEAs comprising a cathode made with Fe-N-CXG after and before of 20 h operation test. (b) Power density curves. Cell temperature 80ºC, 100% RH, hydrogen/oxygen (150/130 kPa-g backpressure).

Acknowledgements

The authors wish to thank the Ministry of Science and Innovation and the AEI(MCIN/AEI/10.13039/501100011033)for the funding received with the reference project PID2020-115848RB-C21 and the Government of Aragon for funding the T06-20R group. L. Álvarez-Manuel wish to thank the Government of Aragon for her pre-doctoral contract.

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