

Structural durability of Fe local neighbourhood in nitrogen-modified Fe/C composite used as fuel cell electrocatalyst: XAFS and XPS study

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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. In this context, non-precious metal catalysts are actively searched for. Among various materials, nitrogen-modified carbons containing non-precious transition metals (such as e.g. Fe, Co, Cu) are considered interesting because of their optimized morphology (in terms of porosity and specific surface area), activity closely approaching those of commercial Pt catalysts and reliability [1, 2].

Present contribution is dedicated to nitrogen-modified Fe/C composite used as Pt-free electrocatalyst for oxygen reduction reaction in DHFCs. Innovation of considered catalyst involves the use of organic compound, glucose, as a precursor of carbon (hereafter catalyst is shortly called Fe-GAG). Catalyst was prepared by high-temperature pyrolysis in N₂ atmosphere [2]. Catalytic ink and electrodes for FC tests were prepared in a standard way. Resulting Fe loading in the catalytic layer was about 0.1-0.2 mg/cm². For the structural study pristine powder, conditioned and degraded in real FC electrodes were used. Three types of aging procedure were applied to test the catalyst durability. Cathode electrocatalyst was subjected to operation under: i) steady state condition at 0.8 V (SS08), ii) steady state condition at 0.4 V (SS04) and iii) accelerate stress condition by load cycling from 0.4 V to 0.6 V (square wave potential cycling, SW04-06). All durability procedures were performed by 50 hours. Every 15 minutes of operation fast polarization curve collection was performed to check the pathway of the degradation process, data necessary to determine whether and to what extent changes in the iron local environment

affect the catalyst electrochemical stability and fuel cell performance. Then, the electrodes were recovered for ex situ X-ray Absorption Fine Structure (XAFS) and X-ray Photoelectron Spectroscopy (XPS) experiments. XAFS and XPS measurements and analysis were performed to define the location and local structure of metal centres and their chemical states. Fe K-edge XAFS spectra in both near-edge (XANES) and extended (EXAFS) range were recorded at ELETTRA 11.1XAFS station. XANES data were analyzed on the base of the theoretical calculation realized by means of the MXAN code [3], whereas EXAFS data-analysis were performed using the GNXAS method [4]. The XPS spectra were collected using a laboratory non-monochromatic source (Mg K α). Then, standard peak-fitting analysis was carried out using a non-linear Shirley background and taking into account various chemical components.

In all studied samples Fe-Fe configurations (up to 4th 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. Only in the case of Fe-GAG pristine powder the Fe-C/O/N distribution is well defined, giving in EXAFS signal comparable contribution with the Fe metallic phase. This observation confirms XANES estimated Fe metallic phase contents which equals only of about 20% in Fe-GAG pristine powder and over 60% in all studied electrodes. Additionally, it should be underlined that the main working conditions induced changes are correlated with Fe metallic phase and precisely follow the changes in relative current density loss: metallic phase is more degraded (smaller coordination number, higher disorder) larger loss in relative current density is observed. Thus, differences noted between electrodes subjected to various degradation protocols clearly indicate that the highest electrochemical and simultaneously structural stability Fe-GAG catalyst exhibits at SS08 working condition. On the other hand, it is least suitable for operation under SW04-06 condition.

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- [1] M. Lefevre, E. Proietti, F. Jaouen, J-P. Dodelet, *Science* **324** (2009) 71.
 - [2] I. Galbiati, C. L. Bianchi, M. Longhi, A. Carra, L. Formaro, *Fuel Cells* **10** (2010) 251.
 - [3] M. Benfatto, A. Congiu-Castellano, A. Daniele, S. DellaLunga, *J. Synchr. Rad.* **8** (2001) 267.
 - [4] A. Filipponi, A. Di Cicco, C. R. Natoli, *Phys. Rev. B* **52** (1995) 15122.