

Investigating the durability of a direct methanol fuel cell equipped with commercial Platinum Group Metal-free cathodic electro- catalysts

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Abstract

For the first time a long-term (500 h) durability study in direct methanol fuel cells (DMFCs) is carried out on a Platinum Group Metal-free (PGM-free) cathodic electro-catalyst commercially available on market. The electro-catalyst is tested for 500 h at a fixed cell voltage (0.3 V), recording the polarization curves during the operation. A drastic decrease in performance is observed after the first 100 h (from 220 mA cm⁻² to 75 mA cm⁻²); afterwards, the decrease is flatter, passing from 75 to 25 mA cm⁻² (at 500 h). The causes of this performance degradation are investigated by post-mortem physicochemical analyses, such as x-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and scanning electron microscopy (SEM) with x-ray energy dispersive analysis (EDX). Possible reasons of degradation are indicated to be PGM-free catalyst aggregation, carbon and nitrogen species decrease, Ruthenium dissolution and migration from the anode to the cathode, poisoning both membrane and cathode catalyst.

Keywords: PGM-free catalyst; direct methanol fuel cell; durability; oxygen reduction; fuel cell.

1. Introduction

Nowadays, the search for active and stable catalysts for the oxygen reduction reaction (ORR) in polymer electrolyte fuel cells (PEFCs) and direct methanol fuel cells (DMFCs) still represents a challenge to be overcome [1, 2]. Operation at low temperatures (30-90°C) presents great advantages, like quick start-up and lower degradation constraints but requires using highly active catalysts to reduce the ORR activation energy, and thus obtain suitable performances and efficiencies. Furthermore, for DMFC applications, high selectivity towards ORR is demanded since there is the parasitic reaction of alcohol oxidation due to the well-known crossover effect, which causes a mixed potential at the cathode side, reducing DMFC performance [3-5]. At present, the most active and employed catalysts at the cathode of a DMFC are based on highly dispersed Pt nanoparticles [6-8]. However, these catalysts present several drawbacks, such as limited Earth abundance and, thus, high cost, low tolerance to the presence of alcohols or contaminants and instability due to Pt dissolution as well as carbon support electrochemical oxidation [9-12].

To overcome these issues, several strategies have pursued, in particular alloying Pt with cost-effective and readily available transition metals [13-15], or increasing Pt utilization by means of novel high surface area carbonaceous supports [16-19], or using more alcohol tolerant Pd-based catalysts or non-platinum-group metals (Fe-N-C, Co-N-C, sub-stoichiometric Ta-oxides, etc.) [20-28]. Recently, significant attention has been devoted to the development of transition metal – nitrogen – carbon materials (M-N-C where M = Fe, Co, Mn, etc.) derived from abundant and cheap precursors [29-32], due to their high activity towards ORR and their extraordinary tolerance to the electrooxidation of alcohols like methanol or ethanol [33-39]. The demonstration of high activity and alcohol tolerance of M-N-C catalysts resulted in growing interest from industry; accordingly, several years ago Pajarito Powder, a catalyst manufacturing company, introduced into the market a family of

PGM-free catalysts. The catalyst from this family was successfully integrated into a DMFC providing the highest power output up to now obtained with Fe-N-C type of catalysts, in operation with high methanol concentration [40].

Durability is one of the main drawbacks of DMFCs, characterized by a severe performance decay during operation, in particular when PGM-free catalysts are used at the cathode [41-43]. Actually, most of DMFC investigations are related to the initial performance and/or methanol tolerance of PGM-free ORR catalysts without considering the long-term durability, which is usually studied in rotating disk electrode configurations by accelerated stress tests. Thus, it is mandatory to investigate the durability in a complete cell under more practical conditions (high methanol concentration to increase the energy density of the device). In the present paper, we have carried out, for the first time, a long-term (500 h) durability study in direct methanol fuel cells (DMFCs) of a Fe-N-C cathodic electrocatalyst, commercially available on market, and analysed the possible causes of performance degradation.

2. Methodology and materials

2.1. Catalyst

The Fe-N-C catalyst was provided by Pajarito Powder from their commercial family of Precious Metal Free (PMF) ORR catalysts. It was synthesized by a previously described method [44], which was reoptimized at Pajarito Powder by using proprietary VariPore™ manufacturing platform for DMFC application. In general, VariPore™ is based on making PGM-free materials by high temperature decomposition of organic compounds, transition metal salts in the presence of pore/particle formers. The catalysts morphology and chemical composition can be precisely tuned by combination of different templates and organics. The material used in this work has a surface area of 550 m² g⁻¹. This commercial catalyst is

marketed under the product number PMF-011904 and available to purchase from Pajarito Powder, LLC.

2.2. Physicochemical characterization

Transmission electron microscopy (TEM) images were acquired on the three samples: commercial Fe-N-C in powder, Fe-N-C (with Nafion ionomer) at the beginning of the chrono-amperometry test (BoT) and Fe-N-C (with Nafion ionomer) at the end of the chrono-amperometry test (EoT). The last two samples were scraped from the electrode in which catalysts were deposited on a commercial gas-diffusion layer-coated carbon cloth. The catalysts were first dispersed in isopropyl alcohol and then a few drops of these solutions were deposited on carbon film-coated Cu grids and analyzed with a CM12 microscope (Philips, Eindhoven, The Netherlands).

The morphology of the above-described catalysts was investigated by scanning electron microscopy (SEM) by employing a FEI-XL 30 SEM microscope. The elemental composition and the weight percentage of the samples were determined by energy dispersive X-ray (EDX) spectroscopy at 25 kV with an XL30 SFEG scanning electron microscope (FEI, Eindhoven, The Netherlands).

X-ray photoelectron spectroscopy (XPS) measurements were carried out by using a Physical Electronics (PHI) 5800-01 spectrometer and the data were interpreted by using the online library implemented in the PHI MULTIPAK 6.1 software and the PHI Handbook of X-ray photoelectron spectroscopy.

2.3. Fuel cell tests

Membrane-electrode assembly (MEA) was constructed, as described in our previous paper [40], with unsupported PtRu catalyst (HiSPEC®6000, Alfa Aesar) at the anode ($1.0 \text{ mg cm}^{-2} \text{ Pt + Ru}$) and commercial Fe-N-C at the cathode (6.0 mg cm^{-2}), electrically separated by a Nafion 115 membrane ($\sim 130 \text{ }\mu\text{m}$ thickness). In particular, PtRu-based catalytic ink was prepared by dispersing

the powder in isopropanol/water 3/1 (v/v) solution and 15 wt.% Nafion ionomer. After treatment in an ultrasonic bath at 60°C for 1 h, the ink was deposited by a doctor blade technique onto a gas diffusion layer (GDL-HT, E-TEK). Similarly, Fe–N–C was dispersed in isopropanol/water 3/1 (v/v) solvents with 45 wt% Nafion ionomer and the catalytic ink was sprayed onto a GDL-LT (E-TEK) by an airbrush (Iwata) connected to an air compressor. MEAs were hot pressed, at 130 °C and 30 kgf cm⁻² for 90 s, and mounted in a 5 cm² fuel cell test fixture (Fuel Cell Tech., Inc.). The MEA was subjected to 500 h chronoamperometric analysis at 0.3 V at 90 °C and feeding a 5 M methanol solution at the anode and 100 ml/min oxygen flow at the cathode. Polarization curves were recorded at the beginning, at the end and during stability test.

3. Results and discussion

The performance of the PGM-free catalyst at the cathode of a DMFC was analyzed in a previous paper [40]. In the latter work, the effect of different PGM-free loadings (2, 4 and 6 mg cm⁻²) and methanol concentrations (1, 2, 5 and 10 M) was evaluated at two temperatures (60°C and 90°C). It was demonstrated that a high PGM-free catalyst loading (6 mg cm⁻²) at the cathode helps to counteract the increased cross-over rate caused by the use of a high methanol concentration at the anode. High methanol concentration leads to high energy density and more prolonged operation in DMFC, but also to an increase in methanol cross-over through the polymeric membrane, resulting in a mixed potential at the cathode. This phenomenon can be mitigated by the presence of high loading and tolerant Fe-N-C catalyst, as previously demonstrated [40]. In the present work, a chronoamperometric study has been carried out on the DMFC equipped with the highest and optimal Fe-N-C loading (6 mg cm⁻²) and fed with 5 M methanol solution at the anode. The investigated temperature has been fixed at 90°C in order to accelerate the degradation phenomena (i.e., methanol permeability [45], carbon corrosion [46], etc.), but also improve the kinetics for methanol oxidation and oxygen reduction.

Fig. 1 shows the durability test of 500 h for the MEA based on this catalyst with 6 mg cm⁻² loading (45 wt.% Nafion) at 0.3 V, 90°C and 5 M methanol feed. A significant decrease in performance is observed after the first 100 h (from 220 mA cm⁻² to 75 mA cm⁻²). This behavior is similar to that one previously reported by our group for the lab-synthesized catalysts of the same nature [33, 47-49].

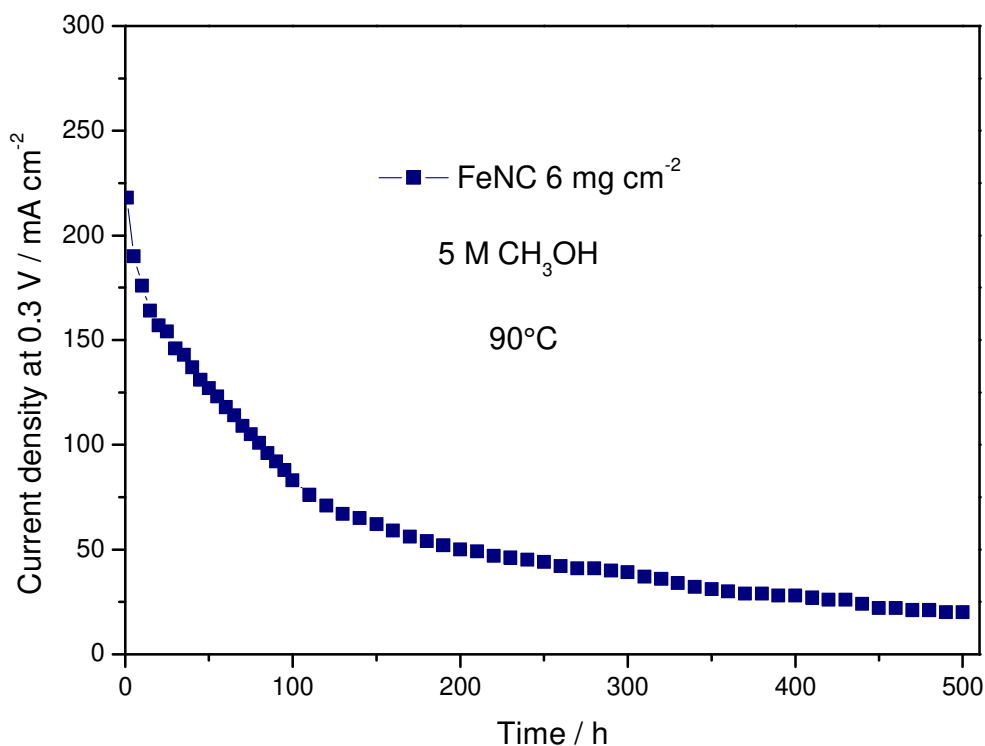


Fig. 1. Durability tests carried out at 0.3 V and 90 °C on the MEA based on the commercial Fe-N-C catalyst at the cathode.

After the first 100 h of operation, the decrease in current density is less accentuated, passing from 75 to 25 mA cm⁻² (at 500 h). Thus, the overall loss of current density at the end of the test is more than 80%. The electrochemical behaviour during the evolution of the test has been monitored by recording the polarization curves. They are reported in Fig. 2. After 20 h of continuous operation at 0.3 V, the open circuit potential (OCP) starts decreasing (~10 mV), together with the overall performance; in fact, the maximum power density passes

from 72 to 54 mW cm^{-2} , whereas a decrease in current density of 100 mA cm^{-2} is also observed. This performance reduction is more exacerbated after 100 h, being more than 50% in terms of power density (32 vs. 72 mW cm^{-2}) and almost a half in current density (290 vs. 545 A cm^{-2}). A progressive degradation of the performance is also observed from the polarization curves at different times, reaching about 10 mW cm^{-2} after 430 h and 500 h.

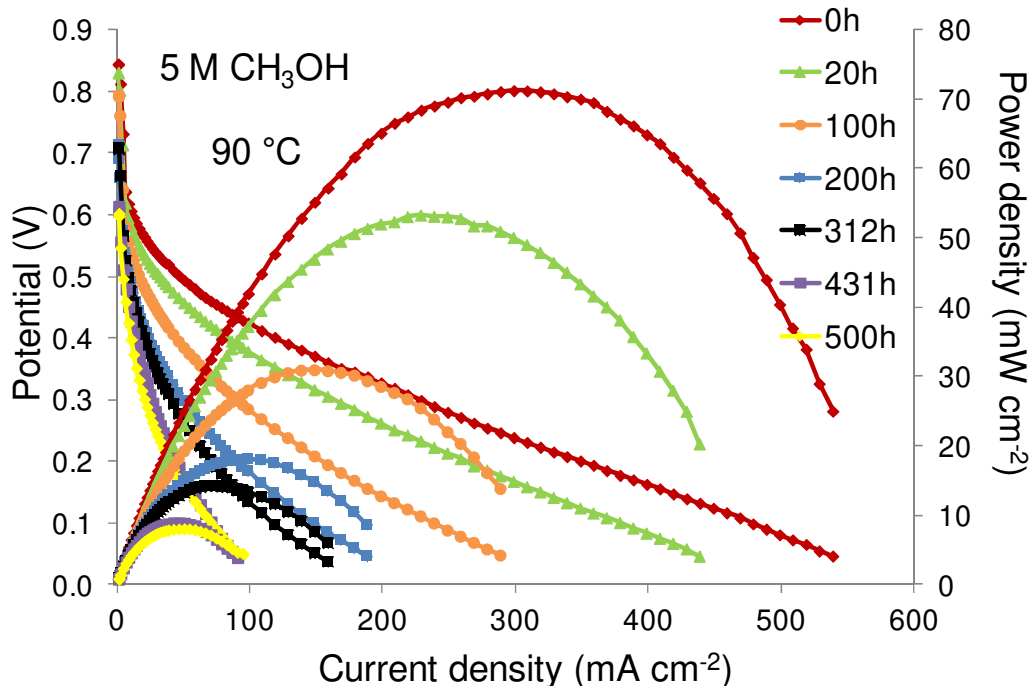


Fig. 2. Polarization and power density curves at 90 °C, recorded at different times during the chronoamperometric analysis.

Several papers in the literature also report this initial rapid decay [26, 33, 50, 51]. Osmieri et al. [26] attributed the performance loss to the high flow rate of methanol used (5.0 ml min^{-1}) and to the flooding of the micropores, which accounted 50% of the total surface area of the Fe-N-C catalyst. Chenitz et al. [50] investigated this initial fast decay which occurred at 25 and 80 °C (also at different potentials from 0.2 to 0.8 V) in PEFCs. They attribute this effect to a specific demetallation mechanism; in particular, when micropores are lower than 0.7 nm, iron ions coordinated out of plane are released and

transferred by the water flux, causing the demetallation of the Fe-N₄ sites in the micropores. Martinaiou et al. [51], using the Mössbauer spectroscopy before and after 12 and 24 h of DMFC operation, attribute the decrease in the catalytic performance to demetallation of FeN₄ sites and subsequent formation of iron / iron oxide clusters.

To understand the causes of the performance degradation in the present study, several physicochemical characterizations have been employed to analyse the cathodic electrode before (BoT) and after the test (EoT). However, they depend not only on the cathode catalyst. The cell set-up used for this investigation did not allow registering both the polarization curves of the complete cell and the anodic and cathodic contributions (the cell did not include any RHE or DHE). The work aims to investigate the durability of a DMFC equipped with a commercial Platinum Group Metal-free cathodic electro-catalyst by monitoring the characteristics change of the Fe-N-C cathode catalyst subjected to 500 h of operation in a complete cell. In any case, since the stability of the PGM-free catalyst is of extreme importance to justify its employment in fuel cells, an ex-situ accelerated degradation test (ADT) in rotating disc electrode (RDE) configuration has been performed. The results are presented in Fig. S1 of the supplementary information; the potential was swept between 0.6 V and 1.0 V vs. RHE at a scan rate of 50 mV s⁻¹ for 5000 cycles in helium-saturated environment. The cyclic voltammetry (CV) curves do not change significantly after 5000 cycles. The linear sweep voltammeteries (LSV) at the beginning (BoT) and end of the cycling test (EoT) show a very slight decrease of performance, with a 20 mV reduction in half-wave potential ($E_{1/2}$), as reported in Fig. S2. This test demonstrates a proper stability of the PGM-free catalyst in ex-situ experiments.

Fig. 3 shows TEM micrographs of the Fe-N-C catalyst at different states/timing: a) bare powder before electrode preparation; b) catalyst scratched from the electrode (with the presence also of the Nafion ionomer) before operation in the DMFC; c) catalyst scratched from the electrode after 500 h operation. The morphology of the catalyst did not change

significantly passing from the bare powder to the electrode. The situation is extremely different after the long-term chronoamperometric test in DMFC at 0.3 V and 90°C. Particles migration and agglomeration were observed, with regions presenting very few particles and other ones with large aggregates.

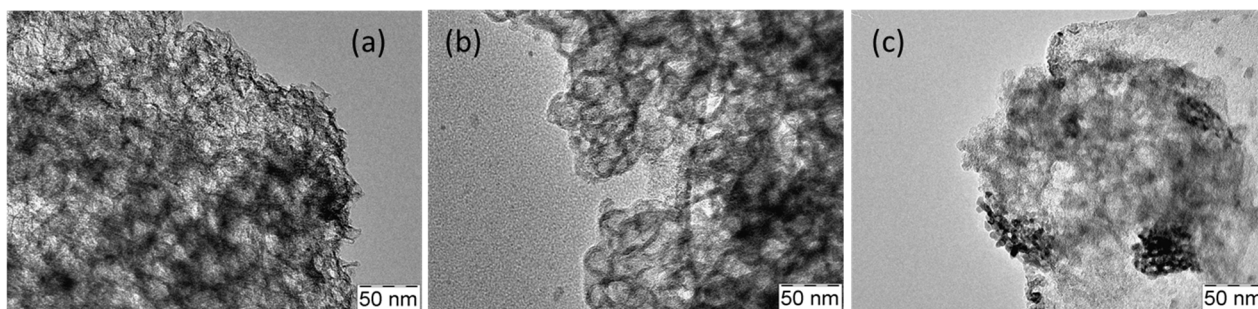


Fig. 3. TEM micrographs of (a) the bare catalyst powder, (b) catalyst scratched from the electrode at the BoT, (c) catalyst scratched from the electrode at the EoT.

An analysis of the composition has been carried out by EDX during the SEM characterization (see Fig. S3). The bare powder showed mainly the presence of C (98.84 wt.%), with about 1% attributable to Fe. When the catalyst is derived from the electrode before testing, the presence of F and S from Nafion was also observed. After the 500h test, the composition of the electrode changed significantly, showing not only a reduction of the presence of Fe and F (about the half for both elements), but the appearance of Ru coming from the anode (Table 1). As previously reported in the literature [52-54], Ru is not stable at a potential higher than 0.8 V vs. RHE. The cell operating condition of 0.3 V can cause Ru dissolution and migration to the cathode leading to a decrease of membrane proton conductivity and loss of cathode catalyst activity due to the Ru deposition [52-55]. Furthermore, the anode performance could be negatively affected due to a change in the Pt:Ru atomic ratio. Of other possible degradation mechanisms reported in the literature, demetallation and carbon oxidation are found to be the most likely reasons for M-N-C catalysts degradation [41, 56, 57]. Moreover, during the operation of the DMFC, methanol

permeating the membrane, although it does not oxidize on the PGM-free catalyst, could have a significant impact on the hydrophilicity/hydrophobicity of the cathode, affecting the oxygen transfer. The same drawback can be caused by high humidity. These aspects were not considered here, but they have also a significant contribution on the durability of the DMFC. In a previous work [58], using a 3D multiphysics model, a relationship between water saturation and oxygen consumption was shown. The model allowed evaluating a non-homogeneous distribution of oxygen in the cathodic catalytic layer. Accordingly, the current density was not homogeneously distributed due to oxygen starvation caused by water saturation. The effect of water saturation was demonstrated to be more pronounced at low cell potentials and at high inlet methanol concentration at the anode side (more crossovered methanol through the membrane, which remains unreacted at the cathode), with consequent more pronounced flooding effect, which affects negatively the DMFC performance, especially when using a non-PGM catalyst at the cathode side [58].

To investigate more in depth the causes of degradation and, in particular, the changes occurred at the surface of the cathode catalyst, an XPS analysis was carried out on the bare catalyst powder and after the electrochemical test (Fig. 4).

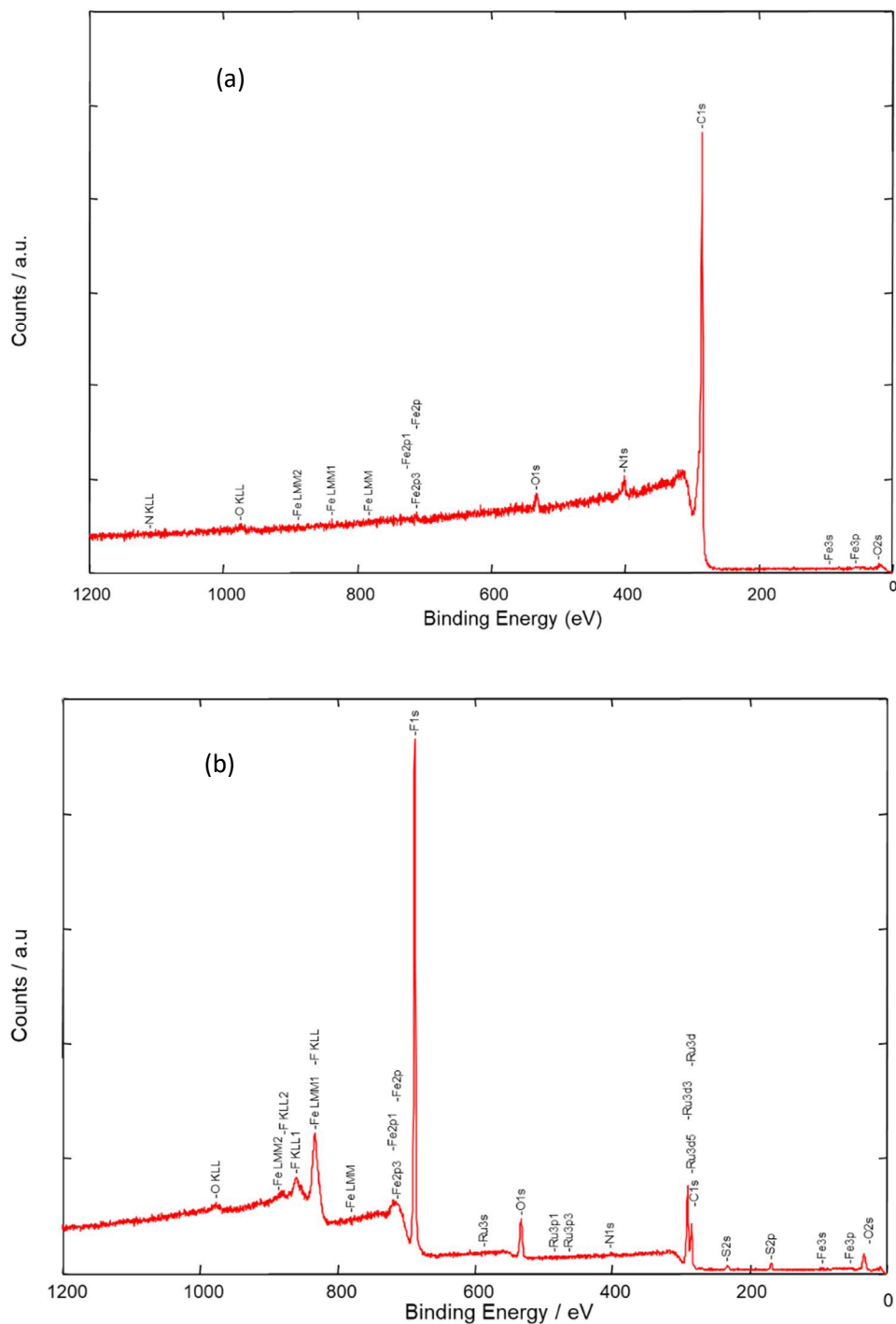


Fig. 4. XPS survey of (a) the bare catalyst powder, (b) catalyst scratched from the electrode at the EoT.

After the chronoamperometric test, Ru appears on the cathode catalyst, although it is quite difficult to quantify its amount, since the C signal interferes with the Ru3d line, which is clearly observed in the survey spectrum of the sample after the electrochemical test (Fig. 4b). The bare powder presents only the presence of C1s (95.4 at.%), N1s (2.7 at.%), O1s (1.7 at.%) and Fe2p (0.2

at.%) lines; whereas, after the test, also Ru coming from the anode, F and S belonging to Nafion ionomer loaded into the electrode are observed. It is pointed out that N species decrease from 2.7 to 0.9 at.% which could also explain the loss of performance, together with the presence of Ru, indicating a restructuring of the catalyst structure, less favorable to the catalysis of oxygen reduction.

4. Conclusions

Here, for the first time the long-term (500 h) durability of a DMFC equipped at the cathode with an Fe-N-C catalyst, commercially available on the market, has been investigated, feeding a highly concentrated (5 M) methanol solution. A significant decrease of current density (~ 80%) during the chronoamperometric analysis at 0.3 V and 90°C after 500 h, being more accentuated after the first 100 h (62%). This fast decay of performance has been analysed by TEM, SEM-EDX and XPS characterization of the cathodic catalyst before and after the test, to find possible causes. From these analyses it is derived that, beside the degradation mechanisms already reported in the literature, such as demetallation of the Fe-N₄ sites, flooding of the micropores and carbon oxidation, a significant contribution to the performance loss with time is given by Ru dissolution from the anode and migration to the cathode, which leads to a decrease of membrane proton conductivity and loss of cathode catalyst activity due to the Ru deposition and a restructuring of the catalyst structure, less favorable to the catalysis of oxygen reduction.

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Table 1. EDX weight composition (%) of the bare catalyst powder, the BoT and EoT catalyst scratched from the electrodes.

Element	Bare powder (wt.%)	BoT electrode (wt.%)	EoT electrode (wt.%)
C	98.84	78.65	86.66
Fe	1.16	0.99	0.50
S	-	1.18	0.86
F	-	19.18	10.37
Ru	-	-	1.16