Identical Location Transmission Electron Microscopy in Polymer Electrolyte Environment – Application to the degradation of Pt/C and Pt_3Co/C electrocatalysts under accelerated aging tests

Flávio R. Nikkuni [a,b], Edson A. Ticianelli [a], Laetitia Dubau [b], Marian Chatenet [b]

[a] Instituto de Química de São Carlos, U. de São Paulo, Avenida Trabalhador Sãocarlense, 400 Parque Arnold Schmidt, CP 780, 13560-970 São Carlos, SP, Brazil
[b] Laboratoire d'Electrochimie et de Physico-chimie des Matériaux et des Interfaces LEPMI-Phelma, UMR 5279 CNRS/Grenoble-INP/U. de Savoie/ U. Joseph Fourier, BP 75, 38402 Saint Martin d'Hères Cedex, France

The oxygen reduction reaction (ORR) activity of Pt and Pt_3Co nanoparticles deposited on high surface area carbon (Vulcan XC72) was correlated to their structural, morphological and compositional changes prior/after accelerated electrochemical ageing tests. These tests consisted of stepping the potential during 1 min successively between potentials of 0.9 and 0.1 V vs. RHE or between 0.9 and 0.6 V vs. RHE for 15 h in Nafion® interface, using a "dry cell" [1] and an ultra-microelectrode with cavity [2]. Identical-location transmission electron microscopy (ILTEM) [3] coupled with X-ray energy dispersive spectroscopy (X-EDS) analyses were used to characterize the changes in the morphology and composition of the electrocatalysts before and after the electrochemical ageing tests (Fig. 1). For the first time ever, ILTEM was attempted in Nafion® interface, i.e. in conditions truly mimicking PEMFC operation.

The Pt/C and Pt_3Co/C electrocatalysts are modified upon ageing, following changes in particle size, geometry, and composition (Table 1 and Fig. 2), in a way that differs to that witnessed upon aging in H_2SO_4 electrolyte [4].

After the 0.9 - 0.1 V ageing procedure, the ORR activity of the Pt/C particles is improved, while that of Pt_3Co/C particles only slightly changes (Table 1 and Fig. 2). In the case of Pt/C these effects are related to the favorable increase of the particle sizes [5, 6], favored because the Pt^{z+} ions released by the corrosion of the Pt/C nanoparticles at 0.9 V vs. RHE remains trapped in the Nafion®, thereby favoring its redeposition in the subsequent step at 0.1 V vs. RHE. On the contrary, on Pt_3Co/C these positive effects are counterbalanced by a detrimental (and large) effect of Co dissolution.

After the 0.9 - 0.6 V ageing procedure, the ORR activity always decreases, because the redeposition of Pt is not likely, therefore suppressing the positive effect of particle size increase monitored in the 0.9 - 0.1 V ageing procedure.

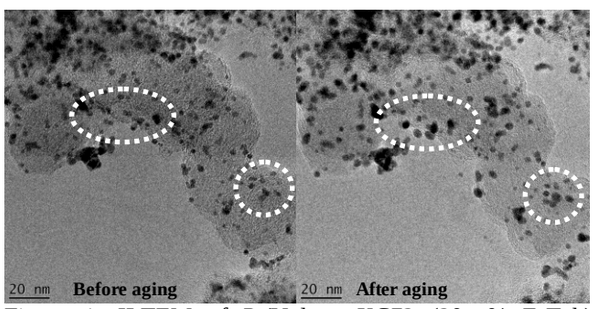

Figure 1: ILTEM of Pt/Vulcan XC72 (20wt% E-Tek) before/after 15 h of potential stepping from 0.1 to 0.9 V vs. RHE (1 min – 1 min) in Nafion® interface. Severe coarsening of the Pt nanoparticles is witnessed after aging due to corrosion/redeposition of Pt (Ostwald ripening).

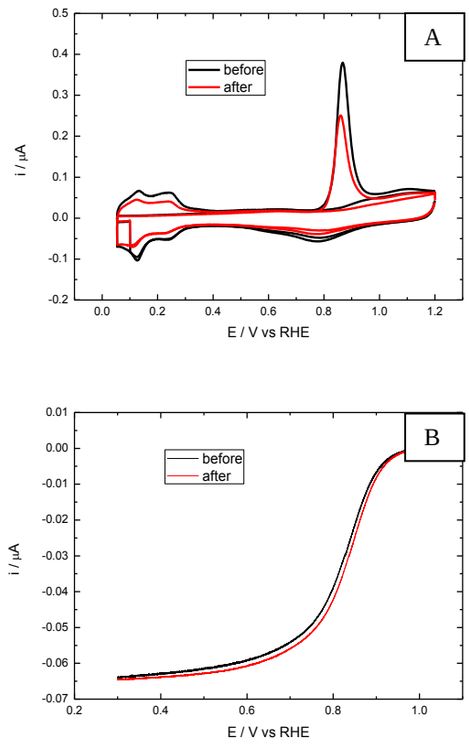

Figure 2: CO-stripping (A) and quasi-stationary ORR voltammograms (B) obtained in the dry cell on a Pt/Vulcan XC72 (20wt% E-Tek) UMEC before/after 15 h of potential stepping from 0.1 to 0.9 V vs. RHE (1 min – 1 min) in Nafion® interface. The coarsening of the Pt nanoparticles is confirmed after aging on the CO-stripping CV (negative shift of the main peak, decrease of the active area) and results in mild increase of the ORR activity due to a favorable particle size effect [5, 6].

Table 1: Specific ORR activity of the electrocatalysts before/after 15 h of potential stepping from 0.1 to 0.9 V vs. RHE or from 0.1 to 0.6 V vs. RHE (1 min – 1 min) in Nafion® interface.

	SA@0.90 V	
	before	after
Pt/C 0.9 – 0.1 V	2.9	5.1
Pt/C 0.9 – 0.6 V	6.0	4.12
Pt_3Co/C 0.9 – 0.1 V	14.7	9.5
Pt_3Co/C 0.9 – 0.6 V	9.2	7.4

References

[1] B. Vion-Dury, M. Chatenet, V. Vivier, 220th ECS Meeting of the Electrochemical Society, The electrochemical society, Boston, 2011.
[2] E. Guilminot, A. Corcella, M. Chatenet, F. Maillard, J. Electroanal. Chem. 599 (2007) 111-120.
[3] K.J.J. Mayrhofer, S.J. Ashton, J.C. Meier, G.K.H. Wiberg, M. Hanzlik, M. Arenz, J. Power Sources. 185 (2008) 734-739.
[4] F. Nikkuni, E. Ticianelli, L. Dubau, M. Chatenet, Electrocatalysis. 4 (2013) 104-116.
[5] Y. Takasu, N. Ohashi, X.G. Zhang, Y. Murakami, H. Minagawa, S. Sato, K. Yahikozawa, Electrochim. Acta. 41 (1996) 2595-2600.
[6] O. Antoine, Y. Bultel, R. Durand, P. Ozil, Electrochim. Acta. 43 (1998) 3681-3691.