Identical-location transmission electron microscopy, a tool to understand PEMFC electrocatalysts degradations

Flávio R. Nikkuni a,b,c, Julien Durst a,b, Luis Castanheira a,b, Edson A. Ticianelli 2, Laetitia Dubau a,b, Frédéric Maillard a,b, Marian Chatenet a,b,c

a U. Grenoble Alpes, LEPML, F-38000 Grenoble, France
b CNRS, LEPML, F-38000 Grenoble, France
c Instituto de Química de São Carlos, U. de São Paulo, São Carlos, SP, Brazil

* Member of the French University Institute (IUF)

It is no secret that PEMFC performances decay upon operation, owing to the degradation of their core materials [1]. As the activity of the PtM/C electrocatalysts of the cathode active layer is strongly related to their size, shape and composition, and that these features can be severely modified upon aging, transmission electron microscopy (TEM) analyzes are often used to complement oxygen reduction reaction (ORR) activity (and PEMFC performance) measurements prior/after PEMFC operation. Refining the data obtained from the field, it soon appeared that the materials degradation were not homogeneous within a PEMFC. If one limits to the cathode active layer, there are three distinct levels of degradation heterogeneities: (i) at the scale of the MEA, the degradations are neither homogeneous along the gas channels of the bipolar plates (BP, from the inlet to the outlet) [2], nor along the active layer thickness (from the membrane interface to the diffusion layer interface) [2, 3]; (ii) the BP geometry also matters, since in the particular case of repeated start/stop and associated fuel-starvation events, harsher degradation was observed for the cathode regions facing the anode regions located under the land of the BP [4]; (iii) finally, not all the cells operate and age in the same manner at the stack level [5]. From these observations, one concludes that TEM analyzes of the PtM/C electrocatalysts from regions randomly scrapped from used MEA can be misleading, explaining why the identical location TEM (IL-TEM) technique emerged [6]. Unfortunately, this technique is usually performed in liquid electrolyte, i.e. in conditions that strongly differ to real PEMFC environment, which brings another bias.

In the present study, we performed IL-TEM analyzes to characterize morphological and composition changes of Pt/C and PtCo/C nanoparticles before and after accelerated stress tests (AST) performed in polymer electrolyte environment, using a “dry cell”. Upon electrochemical ageing, changes in nanoparticle size, geometry and composition are observed, but in a lesser extent than in H2SO4 electrolyte, owing to the lack of liquid water, a reactant in both carbon corrosion and Pt (PtCo) corrosion/dissolution reactions. Also, the low negative vertex potential modifies the fate of Pt+ cations towards redespersion, but also somewhat governs carbon corrosion. Besides, the presence of cobalt in PtCo alloys slows-down the Pt corrosion and carbon corrosion, since cobalt acts as a sacrificial anode.

These changes were linked to the ORR intrinsic activity of the electrocatalysts, also measured at the interface with a polymer electrolyte using an ultramicroelectrode with cavity. It only improved for Pt/C nanoparticles when the AST contained the lower vertex potential (0.1 V vs. RHE), thanks to the favorable increase of the particle sizes, favoring the Pt+ ions released by the corrosion of the Pt/C nanoparticles at 0.9 V vs. RHE remaining trapped in the Nafion® membrane, thereby easing their redeposition in the subsequent step at 0.1 V vs. RHE. In all the other cases, the ORR activity decreased upon the AST. For PtCo/C, the positive effect of Pt redeposition in the 0.1-0.9 V vs. RHE ageing procedure is counterbalanced by the detrimental Co dissolution into Co++, which adversely affects the ORR and pollutes the polymer electrolyte membrane (the Co++ cations hinder O2 and H+ in the electrolyte membrane). After the 0.6-0.9 V vs. RHE 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 at 0.1 V vs. RHE low-vertex, and because Co dissolution and adverse effect is maintained.

Figure 1: (a) IL-TEM images of PtCo/C nanoparticles before and after ageing in dry cell (Nafon® 115 electrolyte) in the 0.1-0.9 V vs. RHE protocol under Ar atmosphere and (b) corresponding particle size distribution histograms. The (non-comprehensive) markers on the figure highlight representative examples of ageing phenomena that occurred during the AST. Micrographs reproduced from Ref. [7] with permission from Elsevier.

References