

Pt-based nanoparticles and carbon to the test of PEMFC operation

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Fundamental and technological aspects of low temperature proton-exchange membrane fuel cells (PEMFC) have amazingly progressed during the last ten years (1, 2). They now possess sufficient electrical performance for widespread commercialization but their catalytic materials (bimetallic Pt-M nanoparticles supported on a high surface area carbon, with M a transition metal) feature insufficient durability (3-6).

In this study, we firstly combined conventional and advanced electron and X-ray based techniques to provide new insights into the structural changes of Pt₃Co/C nanocrystallites in PEMFC conditions. X-ray absorption measurements suggest that oxygen can penetrate inside the bulk of the Pt-Co/C nanocrystallites ("place exchange" process). Scanning transmission electron microscopy (STEM) coupled with electron energy loss spectroscopy (EELS) indicate the formation of three different types of Pt-Co nanostructures over time: (i) Pt-Co/C core-shell particles characterized by an alloyed (but depleted, compared to the fresh material) core surrounded by a 3-5 monolayer thick Pt-rich shell, (ii) Pt-Co/C "hollow" particles and (iii) pure Pt/C "hollow" particles, from which Co dissolution has been completed (7). The formation of the "hollow" nanoparticles is attributed to the tendency of cobalt atoms to segregate to the surface under large coverage of oxygen originating from water splitting (high electrochemical potential) or oxygen reduction reaction (ORR) (8, 9). Therefore, their presence in some regions of the catalytic layer is believed to sign full effectiveness of these zones (10). These particles, once formed, remain structurally stable over more than 2000 hours in PEMFC conditions (Figure 1), and display 2-3 fold enhancement of the ORR specific activity with respect to the mother Pt-alloy.

The second part of the talk will be devoted to the investigation of the influence of oxygen-containing carbon surface groups (CO_{surf}) in the degradation of carbon-supported metal nanocrystallites. The nature and the content of the CO_{surf} groups depend on the structural properties of the fresh carbon support and on the applied electrochemical potential. Combined electrochemical and physicochemical techniques reveal that the carbon surface chemistry plays a key role in the crystallite migration/aggregation process, (11) and in the kinetics of the carbon oxidation reaction. A correlation with the

observations derived from aged PEMFC electrodes is made.

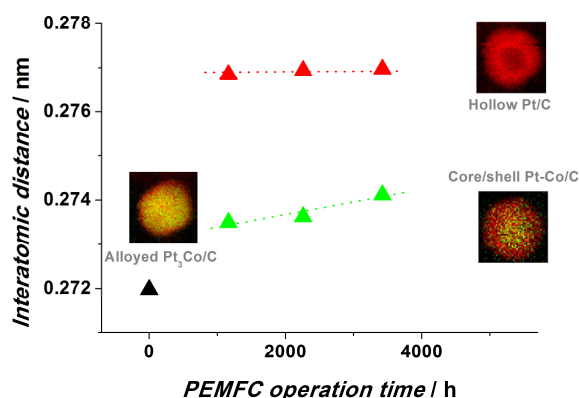


Figure 1. Evolution of the interatomic distance of Pt₃Co/C nanocrystallites during a 3422 h PEMFC aging test ($j = 0.6 \text{ A cm}^{-2}$, $T = 70^\circ\text{C}$, humidified air at the cathode (65 % relative humidity (RH), 1.1 bar abs., gas stoichiometry of 2.5), and dry pure dihydrogen at the anode (0 % RH, 1.3 bar abs., dead-end mode, corresponding to an average H₂ stoichiometry of ca. 1).

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