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Pt and hollow PtCo nanoparticles supported on carbon xerogels for PEM fuel cell catalyst layers

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Carbon black remains the most widespread support to prepare catalytic layers of Proton Exchange Membrane Fuel Cells (PEMFCs). The composition and the pore texture of these carbons are key variables to the device performance, through (i) the ability of the support to disperse metals, (ii) the electrolyte/carbon contact and (iii) the reactant/product mass transport within the porosity [1]. However, in the case of carbon black, the pore texture of the final electrode is not controllable since it largely depends on its processing, and not on the material itself.

Replacing these conventional carbons by nanostructured materials, such as carbon xerogels (CXs), allows for improving their performance and understanding the impact of the pore texture on the catalytic layer performance [2]. CXs are very pure carbons with tunable meso-macropore sizes ranging from a few nm to a few μm , with pore volumes as high as $3 \text{ cm}^3/\text{g}$ and large specific surface area ($\sim 600 \text{ m}^2/\text{g}$). Those texture-tailored supports were used to synthesize Pt catalysts with excellent dispersion (particle size $\sim 3\text{-}4 \text{ nm}$, Fig. 1a) and high mass fractions (min. 40% wt.) [3], which is mandatory to manufacture thin electrodes.

Although the final electrodes display excellent intrinsic catalytic activities with interesting mass transport properties compared to those elaborated from supported catalysts on carbon black, Pt nanoparticles are not stable under operating conditions. This is why the same type of nanostructured carbon were used to synthesize supported hollow PtCo nanoparticles (Fig. 1b) [4]. The addition of Co leads to the Pt lattice contraction, and thus to much higher catalytic activity while the hollow structure allows for relatively good metal utilization ratio despite the large particle size. PtCo/CX catalysts with 10 wt.% Pt were prepared; residual Co content ranged from 0.3 to 4.6 wt.%.

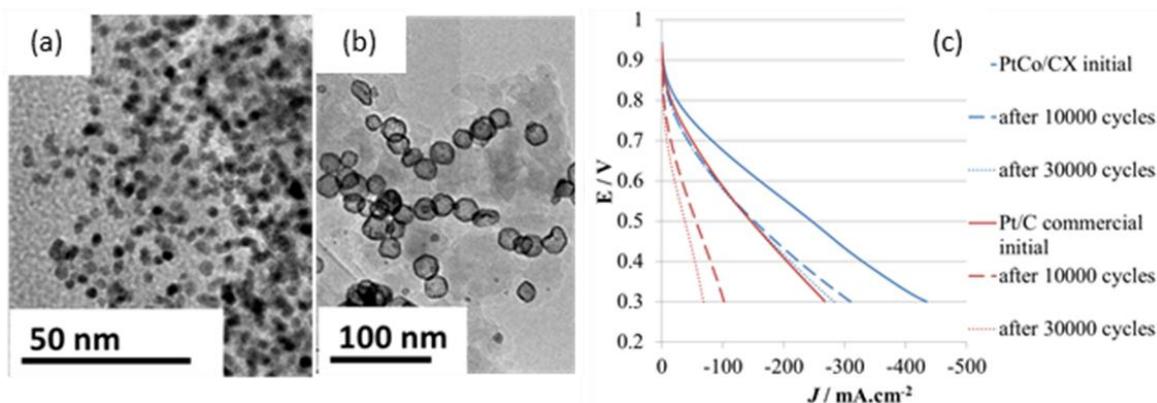


Figure 1. (a) TEM picture of a Pt/CX catalyst (40% wt.) prepared by impregnation-reduction process [3]. (b) TEM picture of hollow PtCo/C nanoparticles [4]. (c) Comparison between commercial Pt/carbon black and hollow PtCo/CX catalysts in MEA (H_2/O_2); the Pt content is constant ($0.033 \text{ mg}_{Pt}/\text{cm}^2_{\text{electrode}}$), and cells were cycled up to 30,000 times between 0.6 and 1.0 V to accelerate ageing [4].

These catalysts were thoroughly characterized using physico-chemical and electrochemical techniques, including Accelerated Stress Tests (ASTs) in Membrane-Electrode Assembly configuration, *i.e.* in complete fuel cell using a classical Pt/carbon black at the anode, and PtCo/CX at the cathode. ASTs consists in sharp voltage increase and decrease between 0.6 and 1.0 V to accelerate the catalyst ageing. Results show that the hollow PtCo/CX catalysts display much better stability than pure Pt/CX and Pt/carbon black samples. Indeed, while the performances of Pt nanoparticles continually decrease with ageing time, the current-voltage curves obtained with PtCo/CX hollow particles fully stabilize: no difference is observed between 10,000 and 30,000 ageing cycles. The reasons for enhanced stability probably lies in the large size and regular shape of the hollow nanoparticles. Current research goes towards the increase of the PtCo/CX metal loading so as to reach higher current densities.

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