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Fluorination: a new way to enhance the durability of carbon supports for PEMFC application

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Proton exchange membrane fuel cells (PEMFC) are energy converters that can power nomad, automotive or stationary systems without emission of pollutants. This technology is already used for niche markets, but some challenges must be overcome to enable large-scale deployment. In particular, the electrochemical corrosion of the carbon support at the cathode remains a major concern especially under start-stop conditions. This corrosion causes massive detachment of the supported Pt-based nanocrystallites, negatively affects water management and ultimately results into a collapse of the electrode structure.

In this study, we bridged the textural and the structural properties of a set of carbons supports to their resistance to corrosion. The stability of carbon nanotubes (CNT, graphitized but with a low specific surface area), carbon blacks (featuring either large specific surface area but poorly-structured, CBe, or low specific surface area and high degree of graphitization, CBs) and carbon aerogel (controlled texture but low degree of organization, CA) was investigated via accelerated stress tests derived from the FCCJ organization. A trade-off was found in terms of properties: graphitic carbons are more resistant to oxidation, whereas carbon supports featuring high specific surface areas are more favorable to the dispersion of a large amount of catalyst nanoparticles per unit volume.

Controlled fluorination of these model carbon supports was performed so as to improve their resistance to electrochemical corrosion [1]. The fluorination was carried out by an easily scalable solid gas process using pure molecular fluorine [2]. The parameters were set in order to limit the fluorination below 0.2 fluorine atom per carbon atom and to avoid any carbon decomposition into gaseous fluorinated compounds such as CF_4 and C_2F_6 [3]. Platinum nanoparticles were also deposited (40 wt.%) by a colloid (polyol) method on the bare and fluorinated carbons. The samples were physically and chemically characterized by XRD, TEM (Figure 1), nitrogen sorption, FTIR and TGA. The catalytic activity of these electrocatalysts towards the oxygen reduction reaction was determined by linear sweep voltammetry (rotating disk electrode technique). Accelerated stress tests, load cycle (0.6-1.0 V) and start-up/shutdown (1.0-1.5 V) protocols, conducted at $T = 80^{\circ}$ C in a four-electrode cell [4], were performed to investigate the robustness of the bare and fluorinated Pt electrocatalysts. The results and the impact of the fluorination are discussed and compared to those of a commercial 40 wt.% electrocatalysts.

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[2] N. Batisse, P. Bonnet, M. Dubois, K. Guérin, Fluorination of 0D, 1D and 2D nanocarbons" In: Carbon Nanomaterials Sourcebook (Eds. Taylor & Francis Publisher), 2016

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[4] L. Dubau, F. Maillard, "Unveiling the crucial role of temperature on the stability of oxygen reduction reaction electrocatalysts", Electrochem. Commun., 63 (2016) 65-69.

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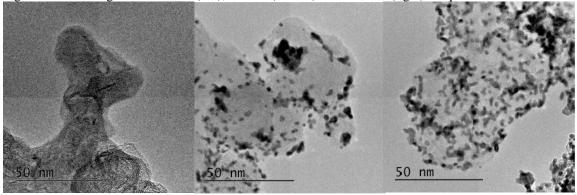


Figure 1: TEM images of bare CBe (left), Pt/CBe (middle) and Pt/F-CB (right) samples.