

Pt Nanoparticles Supported on Porous Antimony-Doped Tin Dioxide Aerogel as Cathode Material for Proton-Exchange Membrane Fuel Cells: Electrocatalytic Activity and Degradation Mechanism

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Proton Exchange Membrane Fuel Cells (PEMFC) are high-efficiency energy converters that can be deployed for mobile, transport and stationary applications in an eco-friendly manner. Nevertheless, their large-scale development requires further improvements, specifically regarding their lifetime in operation¹. In abnormal PEMFC operating conditions, *e.g.* start-up/shutdown events² or localized fuel starvation³, the positive electrode may reach potentials of 1.5 V vs the reversible hydrogen electrode (RHE), which triggers extensive carbon support corrosion at the cathode side.

To tackle this problem, one of the solution studied in the literature is to use (more robust) carbon-free catalyst supports based on metal oxides⁴⁻⁶. To represent viable alternatives to conventional carbon blacks, metal-oxide substrates must fulfill three criteria: be electron-conducting, resist corrosion and possess an opened porous structure compatible with facile ionomer insertion and efficient mass-transport properties.

This study focuses on aerogel structures obtained using a sol-gel route, based on antimony-doped tin dioxide (ATO) with different doping levels (0, 5, 10 and 15 at.%). A Pt nanoparticles colloidal solution, obtained *via* a modified polyol route, was deposited on the ATO (Pt/ATO) featuring the best properties (10 at.% Sb-doped SnO₂), and, for comparison, on a Vulcan XC72 carbon (Pt/C) and on an undoped tin dioxide aerogel (Pt/SnO₂). This strategy allowed the straightforward comparison of the Pt/ATO, Pt/C and Pt/SnO₂ electrocatalysts in terms of catalytic activity for the oxygen reduction reaction (ORR) and durability.

A 2-fold enhancement in specific activity for the ORR was measured on Pt/ATO over the reference Pt/C, suggesting strong metal support interactions between the Pt nanoparticles and the ATO support. An accelerated stress test (AST) protocol (5,000 or 10,000 potential cycles

between 1.0 and 1.5 V *vs* RHE) enabled to determine the robustness of the Pt/ATO and the Pt/C electrocatalysts during model start-up/shut-down events. Figure 1 illustrates that Pt/C did not withstand operation in these conditions, as observed from the massive detachment of Pt nanoparticles from the carbon support following its corrosion. On the contrary, the Pt nanoparticles did not detach from the ATO support during ageing. However, evidences were provided that a core@shell structure with a Sb-poor surface covering a core with a Sb content close to the nominal forms during the AST. This core@shell structure restricts the capacity of the Pt nanoparticles to exchange electrons, as evidenced by the attenuated Pt surface oxide formation/reduction features, and the decreased catalytic activity for the ORR.

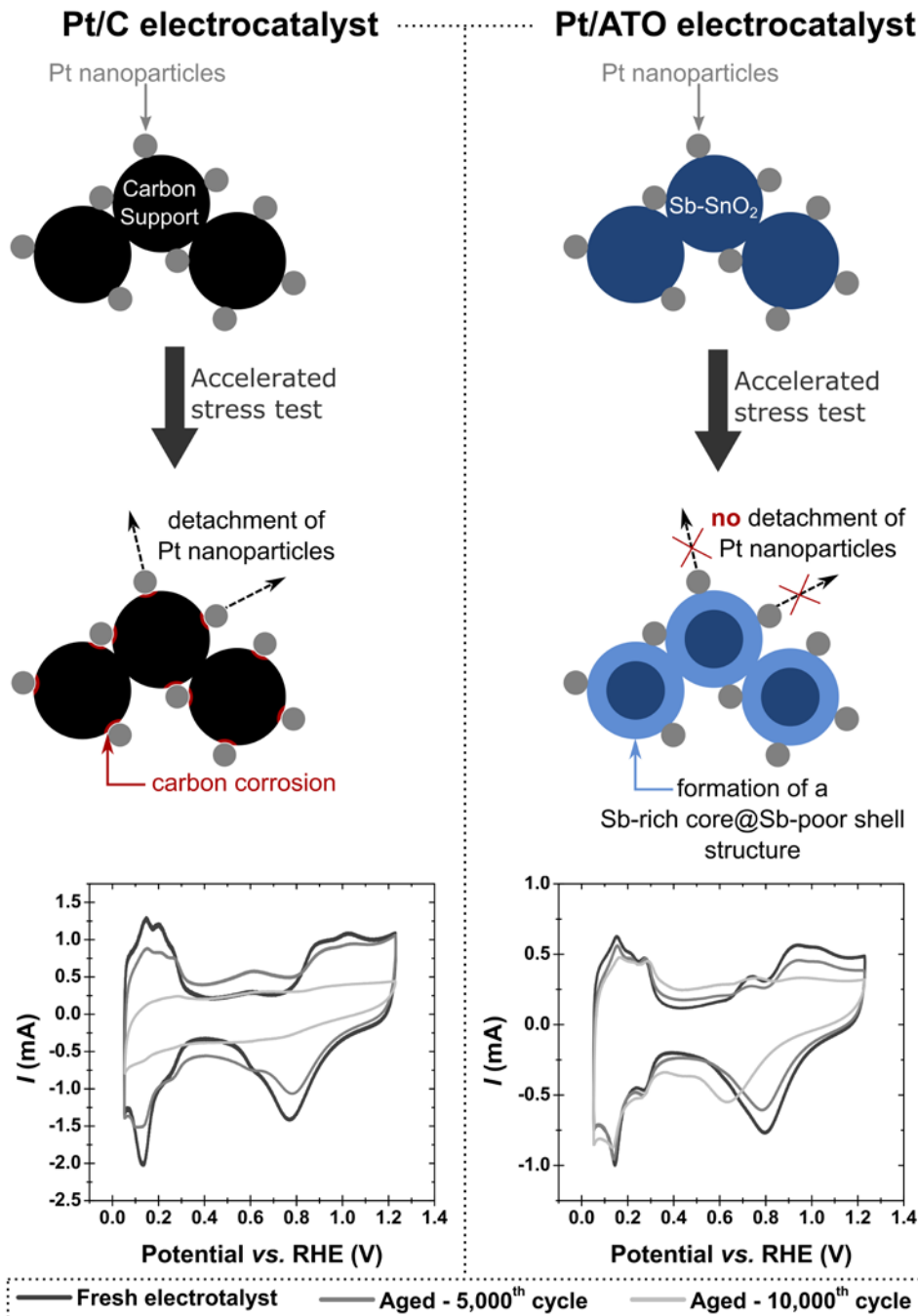


Figure 1. Degradation of Pt nanoparticles supported on a carbon support and on ATO support during an accelerated stress test mimicking start-up/shut-down operating conditions.

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