



Utilization of graphitized and fluorinated carbon as platinum nanoparticles supports for application in proton exchange membrane fuel cell cathodes



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HIGHLIGHTS

- Pt nanoparticles on fluorinated (or not) graphitic carbon black were synthesized.
- The materials were upscaled for unit PEMFC testing in accelerated stress tests.
- Fluorination is neither positive nor negative in base-load cycle.
- Pt/fluorinated carbon experiences lower ECSA loss in start-stop operation.

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ABSTRACT

In this study, Pt nanoparticles are synthesized on partially graphitic carbons, fluorinated or not. They are characterized for their physicochemical properties and oxygen reduction reaction activity, and tested in membrane electrode assemblies in unit proton exchange membrane fuel cell (PEMFC) cathodes; the results are compared with those of a benchmark TEC10EA40E[®] commercial electrocatalyst based on a low surface area highly-graphitized carbon. The home-made membrane electrode assemblies (MEAs) show performances approaching those of the commercial standard. The effect of the surfacic fluorination of the carbon is neither positive nor negative for the “load-cycling” protocol (benchmark MEAs optimized with the commercial electrocatalyst are more durable than non-optimized MEAs prepared with the two home-made electrocatalysts). In opposition, the fluorinated carbon-based electrocatalyst is the more durable in the AST mimicking repeated “start/stop” operation, at least in terms of electrochemical area losses. This demonstrates that carbon corrosion can be (at least partially) mitigated/slowed-down for a partially-fluorinated carbon versus the non-fluorinated substrate, leaving hope to enhance the durability of PEMFC cathodes for automotive applications. This study further demonstrates that the fate of (fluorinated) carbon-supported Pt nanoparticles may differ when the materials are operated in polymer versus liquid electrolyte.

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1. Introduction

Fuel cells and in particular proton exchange membrane fuel cells (PEMFC) are now seriously envisaged as a means to power mobile or portable electric devices [1]; some good examples are the success of the family of Plug Power PEMFC forklifts (more than 10,000 are currently in practical use in warehouses throughout the world) [2,3] and the recent commercialization of PEMFC-powered personal vehicles [4], like the Toyota Mirai, firstly in Japan and California, then in the rest of North America and Europe [5], the Hyundai Nexu in Korea and United Kingdom [6], or fleet vehicles like the battery-based Kangoo zero-emission equipped with a PEMFC range-extender (built by Symbio in France [7]), and others by competitors. In all these automotive systems, the resistance to highly-degrading environmental/operating conditions is a key to longer durability/reliability on the field [8,9]. Reaching this goal implies that more durable core materials (proton exchange membrane, PEM [10–12]; Pt-based electrocatalysts and supports [13–16]; bipolar plates [17–20], etc.) are used in the PEMFC stack. In particular, the dynamic load cycling and frequent start/stop events encountered in automotive applications endanger the stability of the carbon support used to immobilize the Pt-based nanoparticles in a PEMFC, especially at the cathode [21–29]. The toughness of the carbon-based substrate can be enhanced by using more graphitic carbons [13,29], covering them with more robust metal oxides [30] or even replacing them by metal oxides [31–34] (a strategy that has some drawbacks – see e.g. Refs. [34–37] for details). Recently, another strategy has been put forth, *i.e.* replacing the oxygen dangling groups naturally present in most carbons by fluorinated ones [38,39]. Carbon fluorination has already been (scarcely) mentioned in the literature; however, when such fluorination is usually performed in liquid phase, which is not a selective synthesis protocol (it does not only generate fluorine grafting), as detailed in Refs. [40–44]. Besides, the materials in these studies have not been up-scaled, and ORR kinetics measurements on the so-obtained electrocatalysts and PEMFC tests were only performed in Ref. [44], but not in automotive conditions and not using the standardized FCCJ or DOE ASTs.

In an earlier study of the authors [39], three types of carbon substrates (a highly-defective/non-graphitized carbon aerogel, a high-surface area carbon with combination of defective and graphitized carbon regions, and a low surface area highly-graphitized carbon) have been tested for Pt nanoparticles immobilization using a polyol method (a colloidal method ensuring that no major differences exist in terms of Pt nanoparticles morphology/texture upon deposition on different carbon surfaces). It was demonstrated that “decent” (fluorinated or not) carbon-supported Pt nanoparticles can be obtained regardless of the nature of the support. The initial oxygen reduction reaction (ORR) performances of the three materials in rotating disk electrode (RDE) set-up were comparable to similar state-of-the-art materials (the fluorinated samples being more active than their bare counterparts, owing to a non-negligible ORR activity of fluorinated carbons). They all proved rather durable in RDE characterizations, using two classical accelerated stress tests (AST) derived from the protocols of the Fuel Cell Commercialization Conference of Japan (FCCJ).

The “load-cycling” protocol (0.6–1.0 V vs. RHE) caused dissolution/redeposition of the Pt nanocrystallites via Ostwald ripening and led to mild and similar losses of electrochemically active surface area (ECSA) and ORR activity for the Pt nanoparticles deposited on raw or fluorinated carbons (regardless of their initial degree of organization). In essence, the differences of durability between the various carbon substrates were little in these “load-cycling” conditions (which promote mainly Ostwald ripening of the Pt nanoparticles and Pt-assisted corrosion of the carbon support [29,45]), because these essentially are harmful to the Pt nanoparticles and not so much to their support.

The picture changed for the “start/stop” protocol (1.0–1.5 V vs. RHE): in these conditions, the larger the organization (graphitization) of the bare (non-fluorinated) carbons, the larger their resistance to

corrosion/degradation. In any case, the degradations resulted in pronounced detachment of the Pt nanocrystallites but not to any substantial growth in their size (because they are passivated by a layer of Pt-oxides and because redeposition is not favored in this potential domain). In addition, fluorination revealed not beneficial for the structurally-ordered support (graphitic carbon), because fluorination of structurally-ordered (graphitic) carbon supports creates structural disorder (C-C bonds are broken during the process) and depreciates their resistance to electrochemical corrosion, at least in the presence of excess liquid water encountered in RDE tests. As a result, surfacic fluorination of a high surface area carbon (with graphitic and amorphous domains coexisting) seemed to be the optimized way to render the Pt-based electrocatalyst material more durable to an AST mimicking frequent start/stops, at least in liquid electrolyte environment. The interested readers are advised to check [39] for more details about the behavior of (fluorinated or not) carbon-supported Pt nanoparticles for the ORR in liquid electrolyte.

Now, although the interest of RDE studies performed in liquid electrolyte cannot be denied, one must nevertheless admit that such studies are not performed in conditions that truly mimic PEMFC operation. Excess liquid water and presence of free anions are involved, and it has been shown in a recent past that a given AST protocol performed in liquid electrolyte was not necessarily leading to similar results than when the same electrocatalyst material is tested in polymer electrolyte environment. This was asserted using the identical—location transmission electron microscopy (IL-TEM) technique for Pt/Vulcan XC72 (and Pt₃Co/Vulcan XC72) electrocatalysts in both acidic [46–48] and alkaline [49–51] environments. Hence, it is mandatory to test the electrocatalyst materials studied in RDE configuration in Ref. [39] in PEMFC environment, to assert (or not) the relevance of fluorination as a means to render carbon supports tougher against corrosion in PEMFC operation. To that goal, it was firstly necessary to upscale the synthesis of these electrocatalyst materials, and then to implement them in unit-PEMFC for activity assessment and AST. The following sections will detail the methodologies and findings related to that strategy. Because it is evident from on-the-field studies that partially graphitic carbon is very efficient to prolong the durability of PEMFC cathodes, the present paper will focus on carbon substrates that show a non-negligible degree of organization.

2. Experimental

2.1. Materials

The electrocatalyst materials tested herein are similar to the ones previously reported in Ref. [39]. They have been prepared in scaled-up syntheses using the same modified polyol method described in this earlier contribution, and their physicochemical characteristics (fresh samples) correspond to those presented in Ref. [39]. More specifically, the present study focuses on the material prepared with the graphitized carbon black (YS, from SN2A: Société du Noir d'Acétylène de l'Aubette) and its partially-fluorinated counterpart (YS-F-14%) (see Ref. [39] for more details). Unless otherwise stated, the experimental procedures and materials tested herein correspond to those described in Ref. [39]. Specific to this study, are the tests performed in unit PEMFC and the characterizations of PEMFC membrane electrode assemblies (MEAs), as described hereafter.

2.2. Materials characterizations of fresh/aged MEA

The crystalline structure of the fresh/aged electrocatalyst materials were determined by X-ray diffraction (XRD) using a Philips TW 1730 vertical goniometer-diffractometer equipped with a diffracted-beam monochromator using Cu (K α 1) radiation = 1.541 Å. To that goal, disks of 1.0 cm² were perforated in fresh/aged MEA cathodes.

Field-emission gun scanning electron microscopy (FEG-SEM)

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