

# TCP Plasma Sputtering of Nanostructured Fuel Cell Electrodes

Hervé Rabat, Caroline Andreazza, Pascal Brault, Anne-Lise Thomann, Marjorie Cavarroc, Yves Tessier, Amaël Caillard, Christine Charles, and Rod W. Boswell

**Abstract**—A transformer-coupled plasma sputtering reactor is used for depositing porous carbon–platinum proton exchange membrane fuel cell electrodes. Carbon nanocolumns decorated by platinum nanoclusters are thus obtained.

**Index Terms**—Diffusion in porous layer, fuel cell electrodes, plasma sputtering, porous carbon layer.

THE NEED for clean energy production has strongly reactivated the interest for fuel cells. In particular, the low-temperature fuel cells, such as proton exchange membrane fuel cells (PEMFC), are promising power sources due to their high energy conversion efficiency for portable, transport, and stationary applications [1]. The core of a PEMFC consists of a membrane electrode assembly formed by two electrodes that are separated by a proton-conducting polymer often called the membrane. The electrodes are one of the critical components in the cell electrochemical process. They generally consist of a carbon cloth, which behaves like a diffusion layer for the gases, and an active layer of a few tens of micrometers made of carbon powders supporting a catalyst (platinum or Pt-alloys), the ionic conductor, and a solvent [2], [3]. For significant efficiency, the threefold contact between carbon, catalyst, and the ionic conductor must be extended into the active layer. The active layer should be porous for mass transport efficiency. Carbon cloth, carbon paper, or carbon nanotubes are currently used as a direct physical support for the catalyst layer [4]–[8]. New improved supports should provide an increased catalyst activity for a reduced catalyst loading and a decrease in electrode thickness while maintaining good efficiency for a reduced production cost. [9].

The location of the catalyst inside the active layer has a great influence on the fuel cell efficiency. For a porous support, the greatest quantity of catalyst must be close to the membrane with a decreasing concentration gradient in the active layer [10].

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H. Rabat and M. Cavarroc are with the Groupe de Recherches sur l’Énergétique des Milieux Ionisés, CNRS–Université d’Orléans, 45067 Orléans Cedex 2, France and also with MID-CADD, Dreux, France.

C. Andreazza is with the Centre de Recherche sur la Matière Divisée, CNRS–Université d’Orléans, 45067 Orléans Cedex 2, France.

P. Brault, A.-L. Thomann, and Y. Tessier are with the Groupe de Recherches sur l’Énergétique des Milieux Ionisés, CNRS–Université d’Orléans, 45067 Orléans Cedex 2, France (e-mail: Pascal.Brault@univ-orleans.fr).

A. Caillard, C. Charles, and R. W. Boswell are with the SP3 Group, Plasma Research Laboratory, Research School of Physical Sciences and Engineering, Australian National University, Canberra, ACT 0200, Australia.

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Many methods are commonly employed to form active catalyst layers either by chemical routes such as colloidal, carbonyl, or chemical impregnation from salts. Another way is physical deposition like plasma sputtering [11]–[13]. Even if less often used, plasma sputter deposition of Pt or Pt-alloys catalyst onto porous films of carbon has shown promising results [11]–[13]. This technique allows the control of the deposited quantities, concentration depth profiles, and morphologies of the thin films [14], [15]. The deposit is composed of metal nanoclusters with a decreasing density from the surface exposed to the plasma to the substrate [11]. In this paper, we present a new way for building the whole active layer directly by plasma sputtering of carbon and platinum. The depositions are performed in a low-pressure transformer-coupled plasma device (AprimVide: height = 260 mm and diameter = 210 mm). An argon plasma is created in the chamber by a radio-frequency external antenna (13.56 MHz and 300 W) with a planar spiral shape (three rotations) cooled by a water flow. The base pressure is about  $5 \times 10^{-5}$  Pa, and the working pressure is between 0.5 and 5 Pa. Two planar targets ( $50 \times 50$  mm) are used: one of graphite carbon (99.9999%) and the other one of platinum (99.999%), which are placed at the middle height in the chamber. The dc target bias voltages are fixed to  $-300$  V. The samples are set on a rotating grounded substrate holder. The distance between the substrate and the target is 80 mm for an angle of  $45^\circ$  with the substrate holder axis. The carbon/platinum layers are deposited in two steps. First, a carbon layer is grown at room temperature on a Si wafer ( $10 \times 10$  mm<sup>2</sup>) during 60 min with 2-Pa argon pressure. The second step consists in depositing the platinum onto the porous carbon layer during 1 min at 1-Pa argon pressure. The scanning electron microscopy (SEM) micrograph in the inset of Fig. 1 shows a typical cross section of the platinum-coated carbon layer. Some columns are observed with 100–150-nm height and 20–50-nm width. Transmission electron microscopy (TEM) micrographs confirmed that platinum diffused along all the carbon column depth and formed nanoclusters with a diameter varying from 2 to 5 nm. However, the nanoclusters’ density and size (observed by a dark contrast in Fig. 1) vary with the depth. Close to the surface, a 20-nm layer composed of nanoclusters in the 4–5-nm-diameter range with a high density is observed leading to a quasi-continuous layer. After this 20-nm-depth layer, the nanocluster density decreases with a homogeneous distribution along all the columns. The nanocluster size decreases to 2–3 nm.

The carbon–platinum columns are thus capped with platinum at the surface and decorated by nanoclusters along the columns.

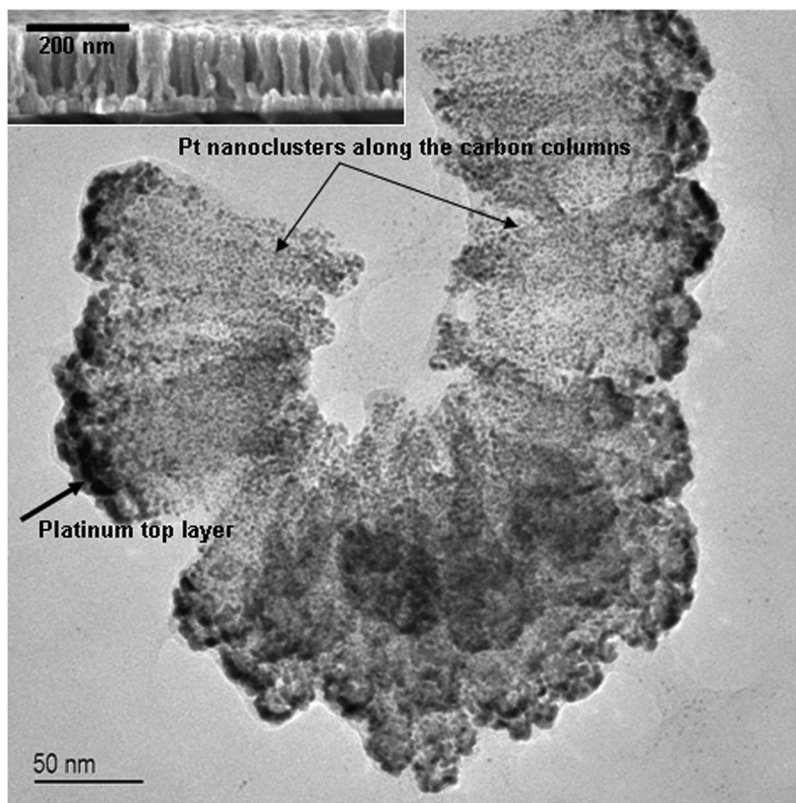


Fig. 1. TEM view of scratched carbon–platinum nanocolumns deposited by TCP sputtering. The Pt nanoclusters are seen as the darker region. The left arrow is pointing out the Pt-covered top carbon columns, whereas the other arrows are pointing out the Pt nanoclusters along the length of the carbon columns. The inset displays a SEM cross-sectional view exhibiting the deposited carbon columns.

Such carbon–platinum layers are now suitable as fuel cell electrodes.

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