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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, Rod W. Boswell

Abstract – A Transformer Coupled Plasma (TCP) sputtering reactor is used for depositing porous carbon platinum proton exchange membrane fuel cell electrodes. Carbon nanocolumns decorated by platinum nanoclusters are thus obtained.

The needs for clean energy production have strongly reactivated the interest for fuel cells. Especially, the low temperature fuel cells such as PEMFC (Proton Exchange Membrane Fuel Cell) 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 (M.E.A.) formed by two electrodes 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 of 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 three-fold 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].

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 formed of metal nanoclusters with a decreasing density from the surface exposed to the plasma to the substrate [11]. In this article, 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 transformed coupled plasma device (AprimVide; height=260 mm, diameter=210 mm). An argon plasma is created in the chamber by a Radio Frequency external antenna (13.56 MHz - 300 W) with a planar spiral shape (3 rotations) cooled by a water flow. The base pressure is about 5.10^{-5} Pa and the working pressure is between 0.5 and 5 Pa. Two planar targets (50x50 mm) are used: one of graphite carbon (99.9999 %) and the other one of platinum (99.999 %), 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° 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 (10x10 mm²) 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 Figure 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 5nm. However, the nanoclusters density and size (observed by a dark contrast in fig1) vary with the depth. Close to the surface, a 20nm layer composed of nanoclusters in the 4-5nm diameter range with a high density is observed leading to a quasi-continuous layer. After this 20nm depth layer, the nanoclusters density decreases with a homogeneous distribution along all the columns. The nanoclusters size decreases to 2-3nm.

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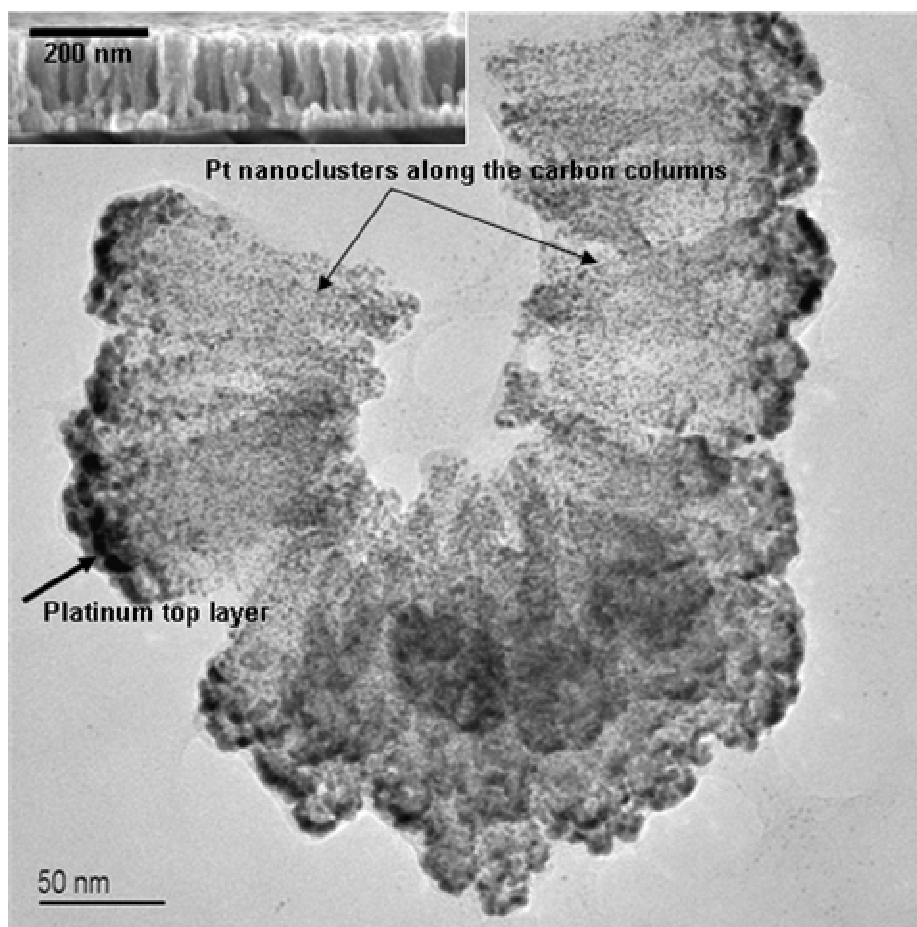


Fig. 1. TEM view of scratched carbon platinum nanocolumns deposited by TCP sputtering. The Pt nanoclusters are seen as the darker region. The left arrow is pointing out the Pt covered top carbon columns, while the other arrows are pointing out the Pt nanoclusters along the length of the carbon columns.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

The carbon – platinum columns are thus capped with platinum at the surface and decorated by nanoclusters along the columns. Such carbon platinum layer are now suitable as fuel cells electrodes.

REFERENCES

- [1] G. Hoogers, *Fuel Cell Technology Handbook* (CRC Press London, 2002)
- [2] S. J. Shina, J. K. Leeb, H. Y. Haa, S. A. Hong, H. S. Chunb, I. H. Oh, *J. Power Sources* 106, 146-152 (2002)
- [3] J. Lobato, M. Rodrigo, J. Linares, K. Scott, *J. Power Sources* 157, 284-292 (2006)
- [4] P. Brault, A. Caillard, A.-L. Thomann, J. Mathias, C. Charles, R. W. Boswell, S. Escibano, J. Durand, T. Sauvage, *J. Phys. D* 37, 3419-3423 (2004)
- [5] C. H. Wan, M. T. Lin, Q. H. Zhuang, C. H. Lin, *Surf. Coat. Technol.* 201, 214-222 (2006)
- [6] S. Escibano, J. F. Blachot, J. Ethève, A. Morin, R. Mosdale, *J. Power Sources*, 156, 8-13 (2006)
- [7] S. Litster, G. McLean, *J. Power Sources* 130, 61-76 (2004)
- [8] F. Yuan, H. Ryu, *Nanotechnology* 15, 596-602 (2004)
- [9] Z. R. Ismagilov, M. A. Kerzhentsev, N. V. Shikina, A. S. Lisitsyn, L. B. Okhlopova, C. N. Barnakov, M. Sakashita, T. Iijima, K. Tadokoro, *Catal. Today* 102-103, 58-66 (2005)
- [10] O. Antoine, Y. Bultel, P. Ozil, R. Durand, *Electrochim. Acta* 45, 4493-4500 (2000)
- [11] A. Caillard, P. Brault, J. Mathias, C. Charles, R. W. Boswell, T. Sauvage, *Surf. Coat. Technol.* 200, 391-394 (2005)
- [12] A. Caillard, C. Charles, R. Boswell, P. Brault, Ch. Coutanceau, *Appl. Phys. Lett.* 90, 223119 (2007)
- [13] A. Caillard, C. Coutanceau, P. Brault, J. Mathias, J.-M. Léger, *J. Power Sources* 162, 66-73 (2006)
- [14] A.-L. Thomann, J.-P. Rozenbaum, P. Brault, C. Andreazza-Vignolle, P. Andreazza, *Appl. Surf. Sci.* 158, 172-183 (2000)
- [15] P. Brault, A.-L. Thomann, C. Andreazza-Vignolle, *Surf. Sci.* 406, L597-L602 (1998)