

## Plasma co-sputtering methods for the one-step synthesis of Pt-C nanowires composites with enhanced electrocatalytic properties

C. Coutanceau<sup>1,\*</sup>, A. Caillard<sup>2</sup>, M. Mougenot<sup>2</sup>, P. Andreatza<sup>3</sup>, C. Andreatza-Vignolle<sup>3</sup>, S. Cuyenet<sup>2</sup>, S. Baranton<sup>1</sup>, P. Brault<sup>2</sup>

<sup>1</sup> Université de Poitiers, IC2MP, UMR CNRS 7285, Laboratoire de Catalyse et Milieux Non-Conventionnels, 4 rue Michel Brunet, B 27, 86022 Poitiers Cedex, France.

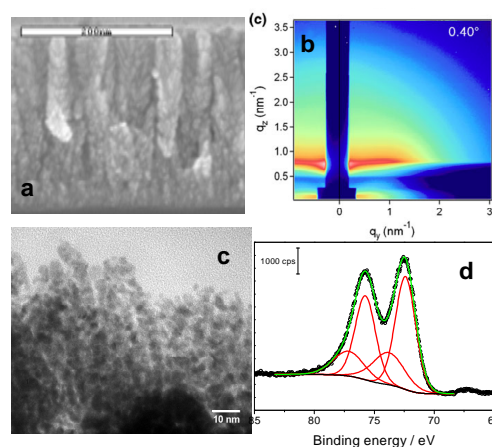
<sup>2</sup> Université d'Orléans, GREMI, UMR CNRS 7344, 14, rue d'Issoudun, 45067, Orléans cedex 2, France.

<sup>3</sup> Université d'Orléans, 1b rue de la Férellerie, CRMD, 45071 Orleans Cedex 2, France

Because the small size of nanoparticles (NPs) induces specific properties,<sup>[1,2]</sup> nanomaterials have found numerous applications in chemistry, electronics, optics, information storage, medical, biotechnology and catalysis.<sup>[3]</sup> Many processes of heterogeneous catalysis (vehicle exhaust and industrial effluent treatments, petrochemistry, sensors, energy storage and conversion...) use costly and strategic metals from the platinum group.<sup>[4]</sup> Here, a high surface-to-volume ratio leading to a large fraction of accessible atoms is required for increasing the activity of the catalyst.<sup>[5]</sup> There is thus a real interest in obtaining the highest catalytic surface area from a low metal weight, particularly in the case of electrochemical reactors (fuel cells, electrolysis cells) and sensors. Indeed, commercial fuel cells currently available have a specific power of 1 or 2 kW g<sub>Pt</sub>. The high amount of platinum makes commercial fuel cells reliable but the noble metal efficiency is far too low to allow a scalable industrial implementation. Several solutions can be provided, such as developing new Pt-based active layers architecture/structure leading to high metal utilization. 3-D nanostructures of active layers are proposed as enhanced architectures.

On one hand, carbon nanofibers or carbon nanotubes have been proposed as electrocatalytic metal supports<sup>[6-8]</sup> in place of carbon powders because of their high electrical conductivity, unique surface structure, large surface area and chemical inertia. Moreover, metal NPs deposited on carbon nanotubes or carbon nanofibers display higher electrocatalytic activity and stability. Therefore, numerous multistep syntheses of carbon nanowire arrays were developed, such as template methods<sup>[9]</sup> and catalytic growths<sup>[10]</sup>. On the other hand, plasma deposition techniques are very convenient for the preparation of metals clusters supported on a substrate<sup>[11]</sup>. Plasma sputtering deposition allows a very good control of the metal nanoparticles content and morphology/structure. Such technique allows depositing very small amounts of material, changing the nanostructure (clusters, thin films, alloys, multilayers, etc.)<sup>[11,12]</sup> and optimizing the composition of the catalysts only by varying deposition parameters (co-sputtering, alternated sputtering, applied power, target voltage, etc.). Hence and also because it is an environmental-friendly process (time, energy and atom savings, no harmful chemicals, organic solvent or precursor), physical deposition methods based on plasma sputtering are now widely used in the industry for numerous applications, and in research for the fabrication of fuel cell catalytic layers<sup>[13]</sup> as an example.

The co-sputtering technique can be particularly interesting for preparing unique structure. It is indeed possible to simultaneously sputter a metal and carbon on a substrate, by using two appropriate targets in the plasma reactor. Such synthesis method is convenient for controlling the metal spreading on a porous support, its localization in depth of the substrate and the metal NPs size distribution. In the present communication, we describe a one-step plasma-assisted synthesis of Pt-C nanowires (Pt-CNW) composite by co-sputtering of Pt and carbon. The co-sputtering of Pt and C atoms is achieved either on a silicon substrate or on an E-Tek® carbon porous layer (CPL). The structure and composition of the nanocomposite are established by GISAXS, SEM, TEM, RBS, XPS, TOF SIMS and electrochemical characterizations (Fig. 1 with example of TEM, GISAXS and XPS characterizations). Then, the electrocatalytic activity will be presented and the relation structure/activity/stability discussed. In particular, knowing that the oxygen reduction reaction is the sluggish fuel cell reaction and that it implies harsh conditions for the catalyst, the enhanced behavior of Pt/C nanowires (Pt-CNW) composite will be exemplified under proton exchange membrane fuel cell conditions. Very high platinum utilization rate of ca. 20 kW g<sub>Pt</sub><sup>-1</sup> was obtained under H<sub>2</sub>/O<sub>2</sub> fuel cell conditions at 80°C.



**Figure 1.** Top: Pt-C co-deposition on a silicon wafer; (a) TEM image, (b) 2D GISAXS intensity patterns recorded at incidence angles  $\alpha = 0.40^\circ$  (low intensities in blue, high intensities in white). Bottom: Pt-C co-deposition on a commercial carbon porous layer; (c) TEM image, (d) XPS spectra for Pt 4f orbital of 0.010 mg<sub>Pt</sub> cm<sup>-2</sup> Pt-CNW.

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\* Corresponding author : [christophe.coutanceau@univ-poitiers.fr](mailto:christophe.coutanceau@univ-poitiers.fr)

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