

# Synthesis of Pt/Carbon Xerogel Electrocatalysts for PEM Fuel Cells by the Multiple SEA Method

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## 1 Introduction

Proton exchange membrane fuel cell (PEMFC) catalysts are generally made of carbon black-supported Pt-based nanoparticles. However, carbon blacks do not display optimal properties for electrocatalysis: they may contain high amount of chemical impurities, are essentially microporous, and the final structure of the electrodes is hardly tunable, which may cause diffusional limitations within the catalytic layer [1]. A possible solution to these drawbacks is the use of synthetic nanostructured materials with a controllable and reproducible texture and with a pure, known and constant chemical composition; carbon xerogels (CX) exhibit such properties [2]. In addition, high Pt weight percentages are necessary to achieve high electrical performance with thin electrodes.

Highly dispersed CX-supported Pt nanoparticles catalysts (Pt/CX) can be prepared by the strong electrostatic adsorption (SEA) method [3,4]. This method consists in impregnating the CX support by a solution of metal precursor at an optimum pH measured beforehand (2.4-2.5 for the impregnation of CX with  $\text{H}_2\text{PtCl}_6$  [5]). If the conditions of synthesis are well controlled, the coulombic interactions between the support and the metal precursor are maximized. Metal nanoparticles are obtained after filtration, drying and reduction under hydrogen.

However, achieving high Pt weight percentages requires multiple “impregnation-drying-reduction” cycles [4]. The use of large volumes of fresh  $1 \text{ g}_{\text{Pt}} \text{ L}^{-1}$  solution for each impregnation step induces unacceptable Pt losses. In order to improve the synthesis efficiency, efforts were targeted so as to re-use the same, highly loaded Pt solution for several impregnation steps. The present study is focused on the synthesis and the characterization of Pt/CX nanoparticles by the “multiple SEA method” in view of testing and using them as PEMFC electrocatalysts.

## 2 Experimental

The support used in this work was a CX prepared by drying and pyrolysis of a resorcinol-formaldehyde aqueous gel [6]. The pore size distribution of this CX was centred at 80 nm. After pyrolysis, the CX was crushed and sieved between 75 and 250  $\mu\text{m}$ . To synthesize Pt/CX catalysts, 1 g of CX powder was first mixed with 567 mL of an  $\text{H}_2\text{PtCl}_6$  solution at  $8.97 \text{ mmol L}^{-1}$  (*i.e.*  $1.75 \text{ g}_{\text{Pt}} \text{ L}^{-1}$ ) with an initial pH of 2.5. The surface loading (SL), *i.e.* the total area of CX surface in solution, was equal to  $1000 \text{ m}^2 \text{ L}^{-1}$  and the concentration of  $\text{H}_2\text{PtCl}_6$  was chosen high enough to re-use the solution five times. After 1 h of stirring, the mixture was filtered and the filtrate was kept for re-use in another impregnation step. The solid was dried in an oven at 333 K during 12 h. Then, the dried material was reduced at 473 K under  $\text{H}_2$  flow ( $0.04 \text{ mmol s}^{-1}$ ) during 1 h to obtain carbon-supported Pt nanoparticles. In order to synthesize several catalysts with various Pt weight percentages, the complete procedure was repeated one to five times on the same support. After the last impregnation, each catalyst was reduced at 723 K under  $\text{H}_2$  ( $0.04 \text{ mmol s}^{-1}$ ) during 5 h to clean the surface of the Pt particles from chlorine residues [4]. The five catalysts are labelled according to the number of “impregnation-drying-reduction” cycles (*e.g.* Pt-2 for the catalyst obtained after two cycles).

The Pt weight percentage of the catalysts was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The Pt particles were observed by transmission electron microscopy (TEM) and analysed by X-ray diffraction (XRD). The electro-active surface area of the Pt nanoparticles was measured by CO stripping voltammetry performed in 1 M sulphuric acid aqueous solution [7-9]. The specific activity of Pt particles for the Oxygen Reduction Reaction (ORR) was measured on a rotating disk electrode (RDE) in the same liquid electrolyte.

## 3 Results and discussion

Table 1 summarizes some characteristics of the synthesized catalysts. The multiple SEA method leads to the synthesis of well dispersed Pt/CX catalysts with high Pt weight percentage,  $Pt_{\text{ICP}}$ , which can be adjusted *via* the number of “impregnation-drying-reduction” cycles, and reaches 25 wt.% after five cycles. It is worth noting that the quantity of Pt deposited on the CX in one cycle,  $m_{\text{Pt}}$ , decreases after the first two cycles. This might be due to the successive impregnations in the acidic solution, the pH of which equals 2.4 - 2.5, and to the successive reduction steps: both procedures probably modify the surface chemistry of the CX, and leads to a shift of the optimal adsorption pH. This pH shift would induce a decrease in the amount of Pt deposited during the next cycles. This hypothesis remains under investigation.

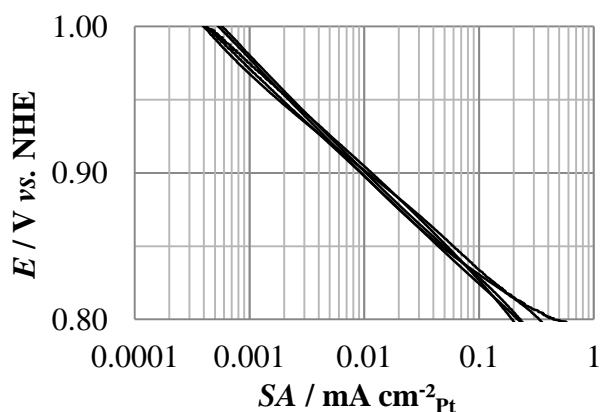
The analysis of TEM micrographs indicates that the five catalysts display the same mean Pt particle size,  $d_{\text{TEM}}$ . This is corroborated by the comparison between the surface-averaged mean particle size,  $d_{\text{S}}$ , and the CO equivalent diameter,  $d_{\text{CO}}$ , or between the volume-averaged mean particle size,  $d_{\text{V}}$ , and the average crystallite size calculated

from XRD,  $d_{\text{XRD}}$ . The values of the electroactive specific surface area of the Pt particles calculated from CO stripping,  $S_{\text{CO}}$ , are the same for all the catalysts (*ca.* 95 m<sup>2</sup> g<sub>Pt</sub><sup>-1</sup>). The specific activity,  $SA$ , of the catalysts for the ORR is derived from the value of the Tafel plots and intercept. Fig. 1 shows that the Tafel plots are superimposed; as a result, the values of the specific activity at a given electrode potential are nearly identical for the five catalysts, and the Tafel slope, which is characteristic of the reaction mechanism, is almost constant as well (*ca.* -74 mV dec<sup>-1</sup>). Since the specific activity depends on the average size of the Pt nanoparticles (the ORR is a structure-sensitive reaction), this result indicates that the number of impregnation sequences has no impact on the Pt nanoparticle size, and degree of agglomeration.

**Table 1.** Physico-chemical characteristics of the synthesized Pt/CX electrocatalysts.

Catalyst	$Pt_{\text{ICP}}/\text{wt.}\%$ $\pm 0.1$	$m_{\text{Pt}}/\text{g}_{\text{Pt}}\text{ g}_{\text{C}}^{-1}$ $\pm 0.0010$	$d_{\text{TEM}}/\text{nm}$ $\pm 0.7$	$d_{\text{S}}/\text{nm}$	$d_{\text{V}}/\text{nm}$	$d_{\text{XRD}}/\text{nm}$ $\pm 0.5$	$S_{\text{CO}}/\text{m}^2\text{ g}_{\text{Pt}}^{-1}$ $\pm 10\%$	$d_{\text{CO}}/\text{nm}$ $\pm 10\%$
Pt-1	8.4	0.0870	2.3	2.7	2.9	2.6	109	2.5
Pt-2	14.7	0.0895	2.2	2.7	3.0	2.3	93	3.0
Pt-3	19.0	0.0581	2.1	2.5	2.7	2.5	94	2.9
Pt-4	22.2	0.0475	2.2	2.6	2.8	2.4	96	2.9
Pt-5	25.3	0.0512	2.1	2.6	2.8	2.6	96	2.9

$Pt_{\text{ICP}}$ : Pt weight percentage of the catalyst measured by ICP-AES;  $m_{\text{Pt}}$ : mass of Pt deposited at each step divided by the mass of CX support in the catalyst;  $d_{\text{TEM}}$ : number-averaged mean Pt particle size estimated from TEM;  $d_{\text{S}}$ : surface-averaged mean Pt particle size estimated from TEM;  $d_{\text{V}}$ : volume-averaged mean Pt particle size estimated from TEM;  $d_{\text{XRD}}$ : average size of the Pt crystallites calculated from X-ray diffraction peaks *via* the Scherrer equation;  $S_{\text{CO}}$ : electroactive specific surface area of Pt particles calculated from CO stripping measurements;  $d_{\text{CO}}$ : CO equivalent diameter of the Pt particles obtained by  $d_{\text{CO}}=6000/(\rho_{\text{Pt}} S_{\text{CO}})$  where  $\rho_{\text{Pt}}$  is the density of Pt (21.4 g cm<sup>-3</sup>).



**Fig. 1.** Tafel plots of the five catalysts: specific activity,  $SA$ , as a function of the electrode potential,  $E$ . The plots are not labelled because of their superposition.

#### 4 Conclusions

The multiple SEA method allows obtaining well dispersed Pt/CX catalysts with high weight percentage up to 25 wt.%, and particle size close to *ca.* 2.5 nm. Studies are in progress to determine the maximum weight percentage that can be achieved without alteration of the metal dispersion. The multiple SEA method requires the use of less Pt than the SEA method from which it is inspired. Considering the synthesis of a 25 wt.% Pt/CX, the two methods require five “impregnation-drying-reduction” cycles but, for the SEA method, five solutions of 1 g<sub>Pt</sub> L<sup>-1</sup> are used instead of only one solution of 1.75 g<sub>Pt</sub> L<sup>-1</sup>, the latter being re-used in the case of multiple SEA. This difference leads to a nearly threefold decrease in the consumption of Pt. Further analyses will be performed so as to determine the optimal Pt weight percentage and the optimal thickness of the catalytic layer by modifying these two variables in a series of membrane-electrodes assemblies.

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