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3D carbon-based nanostructured thin films by means of vertical spray casting: a disruptive method to design high performance electrodes for fuel cell

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ABSTRACT: *In this study, graphene oxides (GO) and multi-walled carbon nanotubes (MWNTs) have been selected as alternative catalytic supports for the fabrication of high performance and light-platinum proton exchange membrane fuel cells (PEMFCs) electrodes. This paper aims to assess the behaviour of two original electrodes made of MWCNTs and GO decorated with platinum (Pt) nanoparticles produced by means of a "fast prepared" spray casting technique. Grown films present nanostructured 3D porous networks for both systems. Polarization measurements show that the use of vertical spray casting is a powerful tool allowing the design of high performance electrodes. These results highlight that new carbon based films like GO and MWCNTs obtained by spray casting could be suitable alternatives to classical electrodes, with high Pt utilization.*

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Highlights

- A "fast prepared" casting spraying deposition technique for PEMFCs electrode.
- The balance between electrical and proton conductivity need to be built.
- The performance of hydrogen fuel cell increases by using MWNTs and GO as catalytic support.

I. INTRODUCTION

The climate change has prompted the need for renewable power sources to replace fossil fuels. Polymer electrolyte membrane fuel cells (PEMFCs) are considered as the next generation of clean energy systems due to their high efficiencies and zero emissions, making this technology interesting for portable, stationary and automotive applications [1]. PEMFCs are able to replace partly the conventional internal combustion engine by converting the fuels (H_2 and O_2) directly into electricity in a membrane electrode assembly (MEA) [1-2]. Some of the major challenges to overcome for the commercialization of PEMFCs are the high cost of electrocatalyst Platinum (Pt) for the cathodic oxygen reduction reaction (ORR) [3], and the kinetic of this electrochemical reaction that is much slower than the anodic hydrogen oxidation reaction (HOR). Consequently, performances of current hydrogen fuel cells should be improved by decreasing Pt loading while maintaining or even increasing Pt utilization [4].

It is now well known that continuous pathway of protons to the electrolyte and electrons to the electrode are responsible of high proton and electron conductivity [5]. A good balance between electronic and ionic conducting media on a nanoscale is therefore crucial to find in order to reduce the amount of platinum catalyst and ultimately enhance the performance of fuel cells [5]. Previous research efforts on optimizing the nanostructured electrocatalysts can be categorized to: (i) Pt alloy catalyst (with Pd, Ni, Co, etc.) [6], (ii) Pt decorated on carbonaceous materials (carbon black, carbon nanotubes, etc.) [7], (iii) Pt free electrodes [8]. Recently we have shown that it was possible to maintain a high energy conversion efficiency with a reduction of Pt loading. However, our approach, based on dipped layer-by-layer [9] assembly, remains difficult for being transferred to in-line manufacturing because it is a time consuming method. Recently, we showed an easy technique, based on alternate deposition of nanomaterials by adsorption, allowing to design high performance nanostructured electrodes for PEMFCs [10-12]. We have demonstrated the possibility to design high performance fuel cells electrodes by alternately spraying the dispersed nanoparticles onto both sides of commercial Nafion membrane [10-12]. In addition, a very small amount of dispersion solvent was sprayed out which allowed us to optimize the thickness of each coating to the nanoscale level. Consequently, highly homogeneous 3D nanostructured electrodes were obtained. Nevertheless, this technique remains difficult to transfer to in-line manufacturing due to the fact that a large amount of solution is lost by drainage during the process.

Another challenge concerns the long-term stability of fuel cells system [13-15]. As a matter of fact, catalytic supports made of carbon materials corrode in electrochemical environments such as acidic pH, elevated potential, and high oxygen concentrations. This contributes to the degradation of the catalyst support and eventually impairs the efficiency of the cell as the 3D electrode structure collapses. Graphene oxides and MWNTs are interesting materials for hydrogen-based technologies as they exhibit a better corrosion resistance than conventional carbon black [13] and exceptional physical properties. Hu *et al.* [16] demonstrated that two-dimensional (2D) graphene decorated with catalytic metal nanoparticles possess an extraordinary proton conductivity. Therefore, we are convinced that carbon nanoparticles (such as graphene oxide (GO) and MWNTs) decorated with Pt nanoparticles could be interesting nanostructured electrodes and improve the performance of PEMFCs. In this work, multilayered nanocomposites of Pt/MWNTs and Pt/GO were made by a spray casting deposition technique. The size and the distribution of Pt nanoparticles were studied by transmission electron microscopy (TEM). Electrode morphology was obtained through scanning electron microscopy (SEM). Polarization measurements were also performed to calculate the power density output of the electrodes.

II. EXPERIMENTAL

All materials as received from Sigma-Aldrich were used in this study. Nano graphene platelets (N006-010-N) and Nafion 117 solution (5% Nafion®) were respectively purchased from Angstron Materials and Sigma-Aldrich.

2.1 Functionalization of GO and MWNTs with Pt

200 mg of GO in 40 ml of ethylene glycol (EG) were stirred for 10 min under sonication, 200 mg of chloroplatinic acid hexahydrate ($H_2PtCl_6.6H_2O$) was agitated in 60 ml of EG, and the solution was then heated to 140°C for 1.5 h under reflux. Pt/GO was collected through filtration, and cleaned with water. Pt/MWNTs were prepared using the same method.

2.2 MEA preparation

Two different types of electrodes were investigated in this work:

i) Cathodes and Anodes made of 50 layers of Graphene oxides (GO) decorated with Pt nanoparticles : $(Pt/GO)_{50}$,

ii) Cathodes and anodes made of 50 layers of MWNTs decorated with Pt nanoparticles : $(Pt/MWNTs)_{50}$
50 corresponding to the number of deposited layers. The Electrodes were prepared by alternating vertical spraying of Pt/carbon nanoparticles onto previously cleaned and protonated Nafion® 117 membrane (Fig. 1) placed on a heating plate (80°C). Pt/carbon nanoparticles were dispersed for 30 min in isopropanol under sonication. 1 mL of Nafion® solution (5%wt) was added to the suspension to obtain a stable dispersed solution.

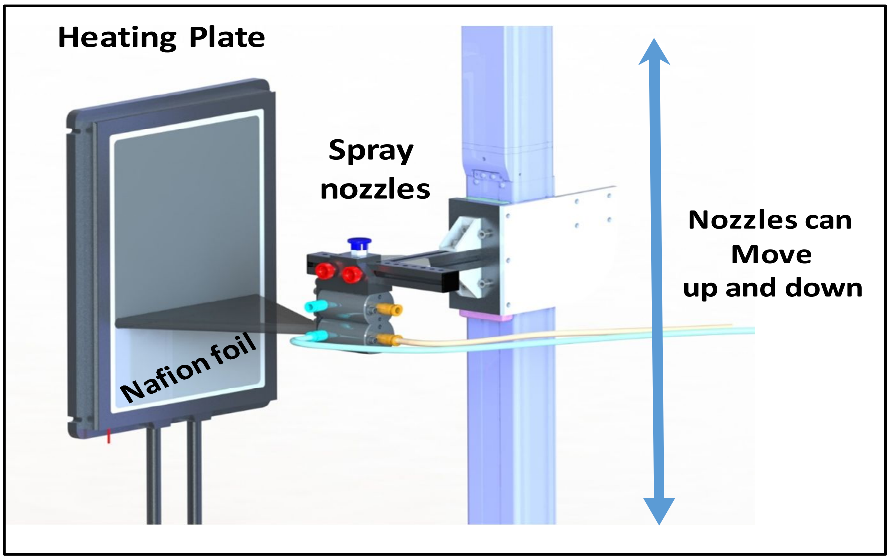

Figure 1. Schematic representation of the vertical spray prototype used for the deposition of Pt/Carbon nanomaterials. The nozzle was placed at a distance of 15 cm from the Nafion. The up and down speed rate was 10 cm.s^{-1}.

2.3 Physical characterizations

X-ray photoelectron spectroscopy (XPS) was used to determine the compositions of the nanocomposites. Measurements were conducted on a Kratos AXIS Ultra DLD system fitted with a hemispheric energy analyser and a 225 W monochromatic Al Kα X-ray source (hυ=1486.6 eV). The pass energy was set for survey scans at 160 eV and for core level spectra at 40 eV, with a spot diameter of 110 µm. Pt/carbon nanoparticles catalysts were dispersed in isopropanol (without Nafion®) before being deposited onto a 1 cm^2 silicon wafer.

The electrode morphologies were observed with scanning electron microscopy (SEM) using a field-emission gun scanning electron microscope (Quanta FEG 200 FEI Nova, Netherlands). The sample was cut to a 1 cm * 0.2 cm piece and placed on a SEM holder to determine the thickness of the electrodes.

TEM analyzes were performed on a ZEISS LEO922 running at a speed voltage of 200 kV. Images were acquired in Bright-Field (BF) mode and captured directly on a camera with a TRS CCD. TEM samples were prepared from the Pt/carbon nanoparticles-containing suspensions. One droplet of each suspension was deposited on typical Cu TEM grid.

Pt loadings on carbon nanoparticles were obtained using thermogravimetric analysis (TGA; Netzsch STA 409) under air atmosphere from 20°C to 120°C at $10°C.min^{-1}$. In order to remove the solvent, the temperature was stabilised for 30 min, then the composite was always heated to 1200°C with a heating rate of $10° C.min^{-1}$.

Cyclic voltammograms (CVs) were measured using a Gamry Potentiostat Reference 600 (USA) in a typical three-compartment glass electrochemical cell with a glassy carbon working electrode (Ø = 3 mm), a counter-electrode Pt wire and a reference electrode SCE. The measurements were carried out in 0.5 M H_2SO_4 and the potential between the working electrode (WE) and the reference electrode was measured with a sweep rate of 50 $mV.s^{-1}$ between -0.2 and 1 V. The electrolyte solution was purged with Ar for 10 min before processing to remove oxygen. The WE was polished before each experiment with 1 µm diamond paste and cleaned to extract residual surface oxides using 2000 CVs restructuring cycles between 0–1,6 V with a sweep rate of 10 $cm.s^{-1}$ in 0,5 MH_2SO_4 solution.

2.4 Fuel cell measurements

The electrodes were placed between two gas diffusion layers (GDL; H2315-13 carbon paper), and then sandwiched between two bipolar plates. Electrodes were fed at atmospheric pressure with 150 $mL.min^{-1}$ of H_2 and 75 $mL.min^{-1}$ of high-purity O_2 under a humid atmosphere (100 %). Polarization curves were collected using a FuelCon Evaluator C50 (FuelCon AG, Germany), in galvanostatic mode.

III. RESULTS AND DISCUSSION

MWNTs and GO were first slightly oxidized by nitric acid in order to create nucleation centers on their surfaces for the Pt nanoparticles growth occurring when H_2PtCl_6 is reduced. The design of nanostructured Pt/MWNTs and Pt/GO electrodes assembly requires a control of size and spatial distribution of the Pt nanoparticles as well as their strong connection to the carbon-based materials. Transmission electron microscopy (TEM) investigations, (Fig.2) show the spatial distribution of Pt nanoparticles is fairly uniform over the surface of MWNTs (Fig.2a) and GO (Fig.2b). Nevertheless, it seems that the Pt nanoparticles coverage is higher for GO than for MWNTs.

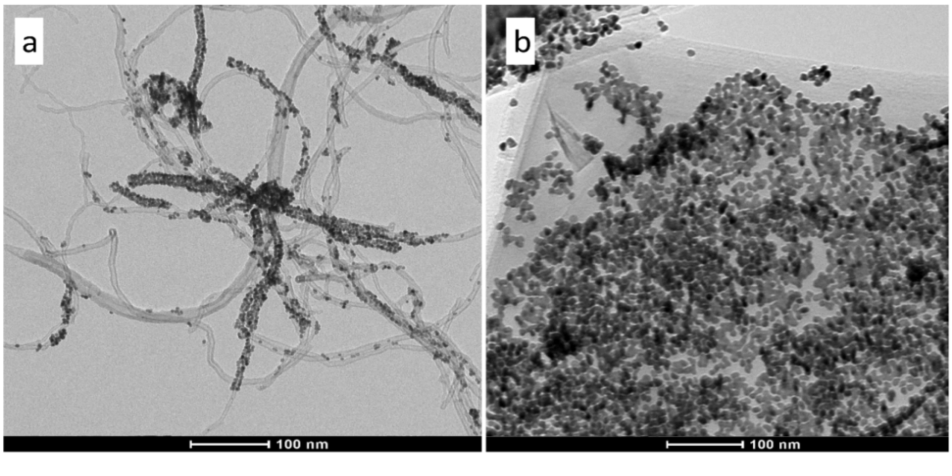

Figure 2. TEM micrographs of Pt/MWNTs (a) and Pt/GO (b) systems.

The method used to build the electrodes was based on spray casting deposition. To this aim, a vertical configuration instead of horizontal was envisaged in order to take advantage of the drainage effect that can be controlled by applying the appropriate heating plate temperature. In this case 80°C was found to be the optimized temperature.

The multilayered films surface morphologies were investigated with scanning electron microscopy (SEM). Fig.3a and 3b show the surface topology of Pt/MWNTs and Pt/GO electrodes, respectively. The different morphologies of MWNTs (nanotubes) and GO (sheets) are clearly visible. Moreover, Pt/MWNTs and Pt/GO nanostructured films are well packed and homogeneous (Fig.3c and 3d). This strongly highlights the fact that our spraying approach based on vertical spray leads to homogeneous 3D nanostructured thin films. It was expected to have highly porous nanostructured electrodes allowing the reactants and products to pass trough. The average film thicknesses are 5.61 µm and 3.13 µm, respectively, which correspond to an average thickness of each layer of 0.11 µm and 0.062 µm. As a matter of fact, catalytic films were controlled at the nanoscale level, and the nanostructured 3D network might increase the probability of contact between reactant and electrocatalytic sites for MWNTs as well as GO sheets. Ultimately it should decrease the mass transport induced voltage loss.

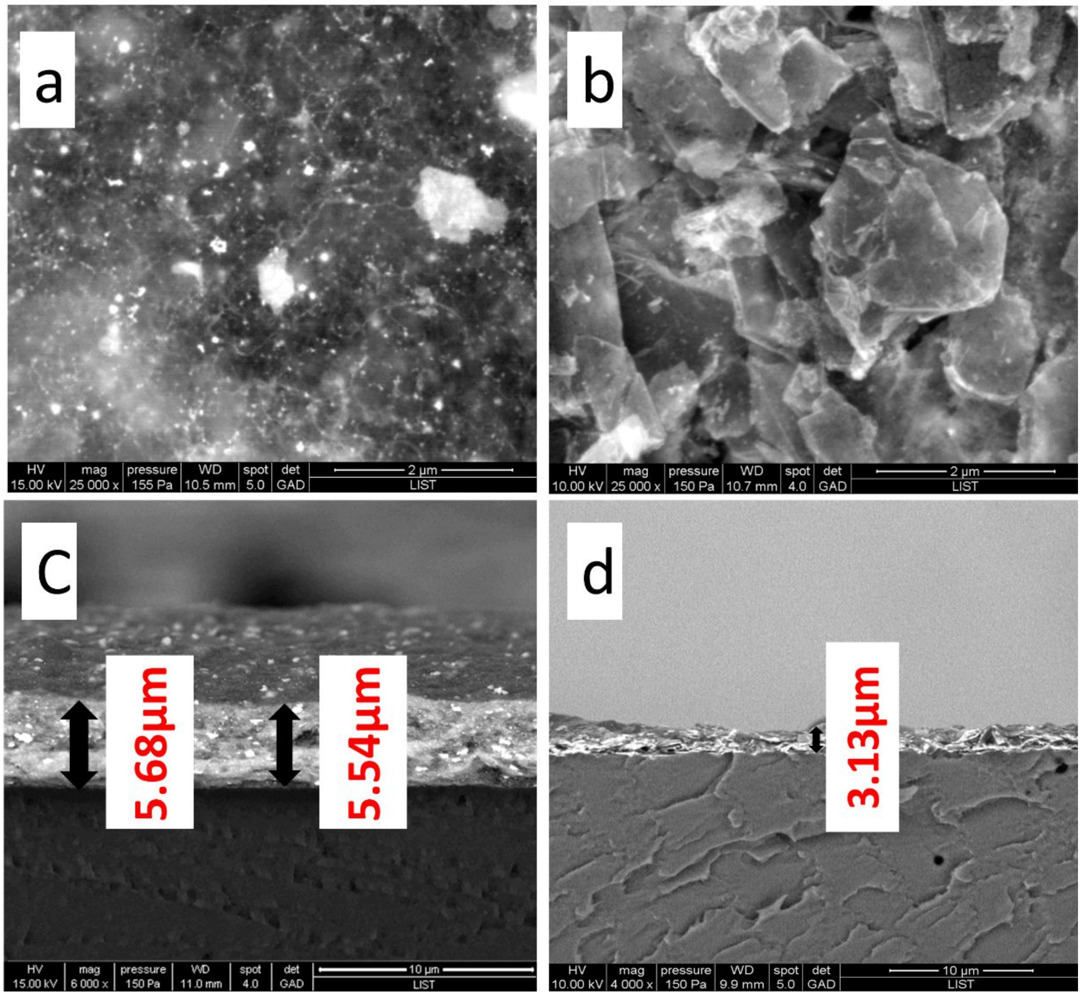

Figure 3. SEM micrograph top-views of (a) Pt/MWNTs and (b) Pt/GO electrodes and the cross-section of (c) Pt/MWNTs and (d) Pt/GO electrodes.

XPS analyses were carried out at different stages of the synthesis: with pure GO, Pt/MWNTs, and Pt/GO (Table 1). The absence of chlorine in those measurements proves the complete reduction of H_2PtCl_6 salt into metallic Pt^0 at the surface of the MWNTs and GO. Added to TEM results, it highlights the fact that Pt nanoparticles are strongly attached onto catalytic supports. In addition, it can be observed that the percentage of Pt is significantly higher for GO than for MWNTs due to the larger specific surface area of GO.

Sample		**O 1s %**	**Si 1s %**	**C 1s %**	**Pt 4f %**
1-	GO	3.1	0.0	96.9	0.0
2-	Pt/MWNTs	21.7	0.2	67.2	10.9
3-	Pt/GO	2.5	0.0	80.2	17.3

Table1. Surface elemental composition measured by XPS for GO, Pt/MWNTs and Pt/GO electrodes.

The electrochemical performances of Pt/GO and Pt/MWNTs electrodes were investigated by Cyclic Voltammetry (CV). The catalyst composites were mixed with 1% wt. of Nafion ® ionomer which improve significantly the dispersion.

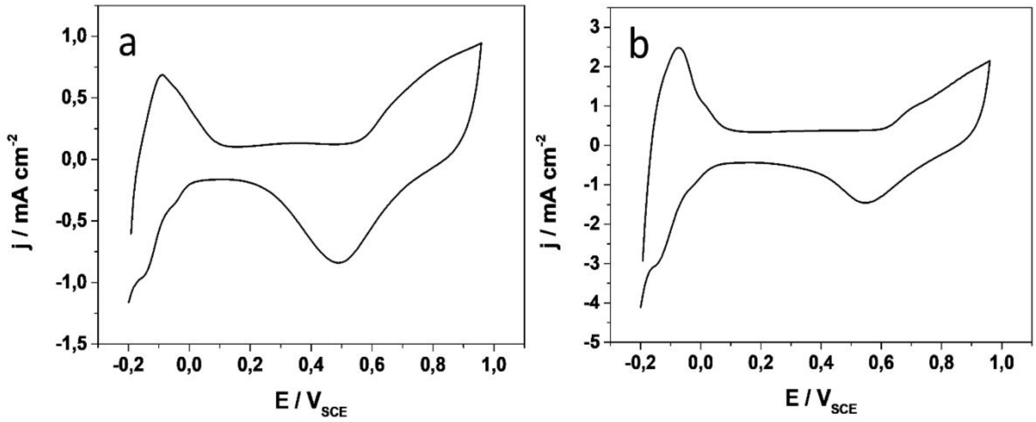

Figure 4. Voltammograms cycles (1800 cycles) of Pt/MWNTs (a), Pt/GO (b). Data were recorded in 0.5 M H_2SO_4 at 25°C and a sweep rate of 50 mV.s^{-1}.

The CVs were performed between -0.2 and 1 V vs. SCE reference electrode (for each measurement, 1.2 mg of the catalysts were deposited on a 1 cm diameter glassy carbon electrode). Results Fig. 4a and 4b show that Pt nanoparticles deposited on both GO or MWNTs substrates are active as electrocatalytic sites. Indeed, the characteristic CV peaks corresponding to the hydrogen adsorption/desorption and the oxygen adsorption/desorption are visible. This result demonstrates that carbon-based catalytic supports decorated by Pt nanoparticles exhibit good electrochemical responses. Nevertheless, the Pt/MWNTs film reaches a higher current density than the Pt/GO one, suggesting a better continuous pathway for both proton and electron due to an improved porous nanostructure.

Single test fuel cell measurements were performed by using a FuelCon Evaluator C50 test bench in order to further understand these two different nanostructured films. H_2 and O_2 were fed in the anode and cathode of the fuel cell respectively. The Pt/GO, Pt/MWNTs and Pt decorated standard carbon black (used as a reference) were tested.

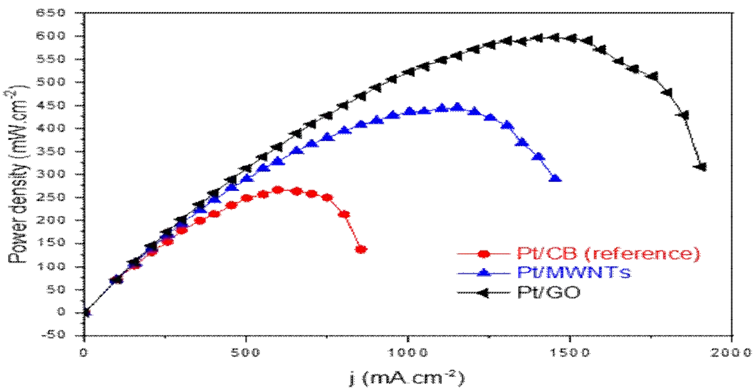

Figure 5. Polarization tests of fuel cell Pt/GO, Pt/MWNTs and Pt/CB (used as a reference).

Maximum power densities for Pt/GO and Pt/MWNTs are 602 mW.cm^{-2} and 450 mW.cm^{-2} respectively (Fig.5). It is much higher than Pt/CB power density with a value of 275 mW.cm^{-2} (used as a reference). The high value of power density obtained with GO might be due to a tile-like structure with a tight contact with the Nafion membrane along with a probable optimization of TPB. Concerning the concentration loss, Pt/MWNTs and Pt/GO electrodes reach this zone at the relatively high current density of 1250 and 1600 mA.cm^{-2} (Fig.4), respectively. However, the Pt/MWNTs electrode has a rather brutal crash. This might be due to the inability to maintain primary concentrations to the anode and the cathode, corresponding to the mass transport induced potential losses.

A thermogravimetric analysis (TGA) (not presented here) has been done to determine the amount of Pt contained in the nanostructured films, by completely oxidizing the composites. Values as high as 17 wt.% and 19 wt.% were measured for Pt/MWNTs and Pt/GO, respectively. It corresponds to a Pt loading per surface area of 0.09 and 0.11 mg$_{Pt.}$.cm^{-2}, respectively. Taking into account the Pt loadings and the power densities, we were able to estimate the Pt utilization of our electrodes. Values as high as 5472 mW.mg$_{Pt}$ and 5000 mW.mg$_{Pt}$ were obtained for Pt/GO and Pt/MWNTs, respectively. These relatively high Pt utilizations indicate that both films are well organized in the composite and allow a good accessibility to electrocatalytic sites.

IV. CONCLUSIONS

This work showed “fast prepared” and high performance nanostructured electrodes using a spraying casting technique that can be transferrable to in-line process. The porous 3D network in between each layer seems to facilitate the path of reactants and reaction products through the membrane. Pt/GO presented high performances thanks to the tight contact with Nafion membrane. Nevertheless, the Pt utilization of Pt/MWNTs is lower than Pt/GO due to a lower accessibility for the reactants and products to the catalytic sites.

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