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PdPt nanocatalyst synthesis via liquid medium sputtering

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Abstract: PdPt nano-catalysts were synthesized via magnetron sputtering method in vacuum on vegetal glycerin as liquid substrate. The nanoparticles formation and their dispersion in the liquid phase have been studied by varying deposition parameters as the argon pressure, the magnetron power and glycerin temperature. Pt-based nano-catalysts are incorporated into electrochemical cells and their catalytic activities towards oxygen reduction reaction (ORR) are evaluated.

Keywords: Magnetron Sputtering, liquid substrate, Nanoparticles, Catalysts

1. Introduction

Pt-based nanoparticles (NPs) are widely used as catalysts for oxygen reduction reactions (ORR) in electrochemical systems such as proton exchange membrane fuel cell (PEMFC). Further enhancements of the Pt catalytic activity while reducing its amount inside the fuel cell is one of the main issues for practical application of these systems due to the limited abundance of Pt on Earth. Since ORR is a surface phenomenon, a high fraction of surface atoms is desirable to achieve efficient Pt utilization and so small NPs with size ranging from 2 to 4 nm must be preferred [1].

Depending on the size range and the future applications, several techniques exists to prepare metallic NPs. These are mainly categorized into "bottom up" and "top down" methods, which utilize solution-phase colloidal chemistry and conventional physical methods on solid substrates [2]. The chemical methods are very versatile in terms of controlling NPs shape and size by varying the reaction conditions. However, NPs chemical synthesis require additives, which generate by-products difficult to remove and NPs with limited purity. On the other hand, physical methods on solid substrates avoid to use additives allowing to produce pure metallic NPs with the same starting material composition [3].

Among physical techniques to prepare Pt-based nano-catalyst, magnetron sputtering has produced active Pt based nano-catalysts on carbon porous electrode [4], but the control of the NPs properties and the production of large quantity of materials is difficult using the sputtering onto such substrate. A solution consists to synthesize Pt nano-catalysts directly in liquid phase using vacuum magnetron sputtering technique [3, 5]. Such substrate is known to form colloidal solution made of NPs dispersed in the liquid substrate but thin film can also appears on the surface of this liquid. This innovative method takes advantages of the extremely low vapor pressure of liquid such as ionic liquid, vegetable oil and silicon oils compatible to vacuum techniques [6].

In this context, the present study aims to synthesize PdPt based NPs in vegetal glycerin using a plasma sputtering process, to obtain stable colloidal NPs solutions compatibles with the preparation of catalytic ink. The NPs properties (dispersion and morphology) as function of the deposition parameters (liquid temperature, magnetron power and gas pressure) were investigated. Finally, these NPs transferred into catalytic inks were tested in a electrochemical cell in order to qualify their activity towards to the ORR.

2. Experimental details

The experimental setup displayed in Fig. 1 consists of a HV cross-shaped sputter chamber equipped with a DC 2 inches in diameter DC magnetron and a $Pd_{0.95}Pt_{0.05}$ target. The vacuum system consists of a primary and turbomolecular pump allowing to achieve a vacuum of 10^{-4} Pa in the deposition chamber without liquid in the chamber deposition. 4 ml of vegetal glycerin contained in a glass vial is placed on a sample holder. The glycerin with a vapor pressure inferior to 1.33 Pa (20 °C) is sufficiently low to a base pressure of 10^{-3} Pa in the deposition chamber without any visible transformation of the liquid. However, the pumping speed was adjusted to obtain a pressure of 10^{-2} Pa by a gate valve placed between the deposition chamber and the turbomolecular pump to limit the glycerin evaporation. The distance between the glycerin surface and the target surface (PdPt or Pt) was fixed at 12 cm.

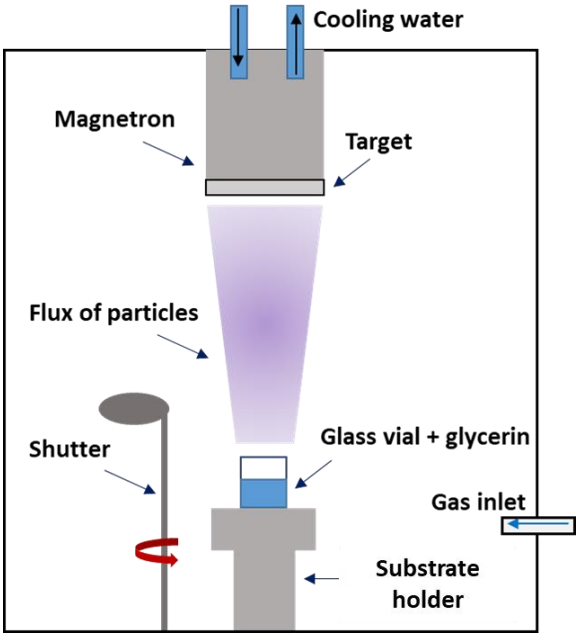

Fig. 1. Schematic of the experimental set-up allowing the growth of NPs inside vegetal glycerine by plasma magnetron sputtering.

Prior to sputtering experiments, the target surface was sputter cleaned in argon plasma during 5 min with the presence of a shutter. The sputtering of the metallic target was performed in pure Ar (40 sccm) and three series of PdPt NPs depositions were performed. For the first series, magnetron power and Ar pressure was fixed at 100 W and 1 Pa respectively, while the surface temperature of vegetal glycerin was modulated (from 27°C to -6°C) using a circulation chiller. The temperature at the glycerin surface was measured by using a thermocouple immersed in the liquid. In the second series, a constant 100W DC power was delivered to the cathode and the Ar pressure was adjusted to 1, 4 and 9 Pa. At last, for the third series, the Ar pressure was fixed at 1 Pa and the magnetron power was adjusted to 13, 50 and 100 W. In all cases, the sputtering deposition was carried out for 20 min.

During sputtering, atoms that are ejected from the target material condense on the glycerin surface, form NPs (which could be assembled in a network) and then diffuse within the glycerin and form a colloidal solution. This mechanism is still under investigations and discussions [3]. The NPs were then transferred to carbon NPs to form NPs-supported carbon. For that, Vulcan XC-72 previously treated under N_2 at 400°C for 4 hours, was directly added to the colloidal solution in order to obtain a mass metal/carbon ratio of 0.1. After, this mixture was successively filtered and washed several times with ultrapure water and acetone. Finally, a process dry was carried out at 70°C in an oven. The obtained PdPt/C catalytic powders were used for the catalytic ink preparation.

The catalytic powder was investigated by a Transmission Electron Microscope (TEM - Philips CM20) operating at 200 kV and equipped with a Lab6 filament. The powder was previously dissolved in ethanol and a droplet was deposited onto a TEM grid (Cu with a holey carbon foil).

The electrochemical measurements have been performed in a conventional three-electrode electrochemical cell at room temperature. The working electrode was prepared by deposition of the catalytic ink onto a glassy carbon disc (0.71 cm^{-2} geometric surface area). Cyclic voltammograms of PdPt/C were recorded in a N_2- saturated 0.1 M NaOH and 0.5M H_2SO_4.

3. Results

As shown on pictures of Fig. 2, a homogeneous black solution is obtained at 27°C (a) which seems to indicate that the metal is dispersed in the liquid phase while thin films on the liquid are observed at -6°C (d). This film is not continuous and has been broken in at least 5 parts (during the deposition or during the air venting). For intermediate temperature, 19°C and 5°C, the presence of a film on the surface and materials in the liquid are observed. In most cases, the film on the surface tends to disappear/diffuse on the liquid phase after few hours. Such observation could be related to the glycerin viscosity which tends to increase with the temperature decrease. More investigation are required to clearly explain this phenomenon, but in any case, it seems that the glycerin surface temperature drive the NPs formation and one parameter which can control the NPs growth.

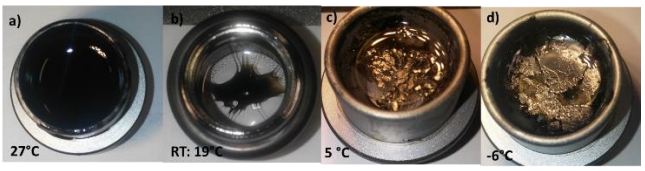

Fig. 2. Sample pictures immediately after the PdPt sputter deposition onto vegetal glycerine at a) 27°C, b) RT: 19°C, c) 5°C and d)-6°C

Fig. 3 shows the TEM images corresponding to PdPt NPs-supported carbon of the second deposition run synthesized at 100 W and different Ar pressure (1, 4 et 9 Pa). We do not show TEM results on the two other run/series due to the limited number of page. The influence of the liquid temperature and the power will presented later during the ISPC24 conference.

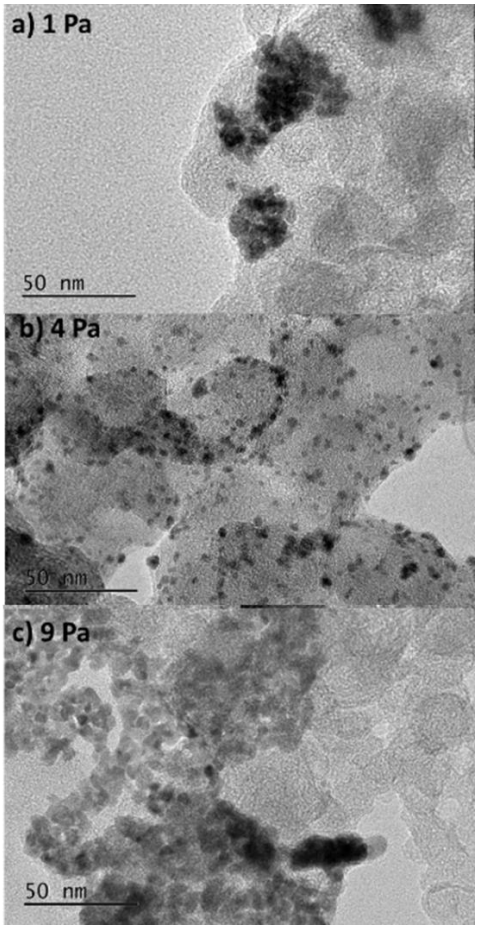

Fig. 3. TEM images corresponding to PdPt NPs supported on carbon NPs synthesized at 100 W and different Ar pressure: a) 1Pa, b) 4Pa and c) 9 Pa.

On TEM images of Fig 3a corresponding to 1 Pa, the NPs seems to be assembly in agglomerates with a size of few 10's of nanometres, whereas on TEM images of Fig. 3b (4 Pa) and 3c (9 Pa), PdPt NPs are clearly visible. For 4 Pa, the NPs are well-dispersed but for 9 Pa the NPs seems to form a ramified network. Due to the low resolution of this TEM, the precise measurement (regarding the structure/morphology/size) is rather difficult. However, the mean NPs size could be estimated to about 5 nm for 4 Pa and 10 nm for 9 Pa. Such increased of the NPs size is typical for magnetron sputtering when a solid substrate is used [7]. Consequently, the argon pressure is another parameter (after the liquid temperature) affecting the NPs properties and this parameter could be one of the parameters used to control the NPs size. The influence of the sputtering pressure on the NPs formation could be related to the energy of the sputtered atoms when arriving on the liquid surface. A low pressure, the atoms have a long mean free path in the gas phase and consequently a high kinetic energy at the liquid surface which lead to the formation of dense agglomerate. In contrast, for high pressure, the atoms have a low kinetic energy which lead to porous NPs based thin film which can be easily dispersed in liquid. This could explain the formation of agglomerates at low pressure and dispersed NPs at high pressure.

In addition, there are several sputtering parameters (discharge voltage, sputtering time, inert gas pressure, target temperature and liquid target-distance) and liquid environment properties (surface or bulk) that can control the grow mechanisms of sputtered NPs [4]. To date the NPs grow kinetic in a liquid environment is not defined and it is still a topic of discussion as already mentioned.

Fig. 4 displays the cyclic voltammogram of PdPt/C synthesized at 50 W and 1 Pa in 0.1 M NaOH (red) and 0.5M H_2SO_4 (black). A single reduction peak corresponding to the Pt- oxide reduction peak at potentials ranging from 0.6 to 0.8V (vs.RHE) is observed in both medium. The presence of this peak clearly shows that the PdPt catalyt is active for the ORR. The comparison of all catalysts is under investigation and the calculation of the electrochemical active surface area (EASA) will be obtained by the integration of the reduction peak.

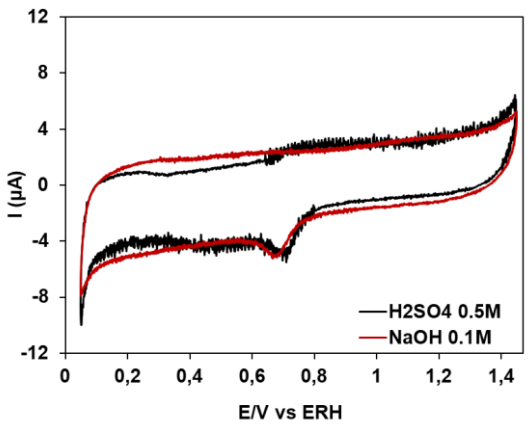

Fig. 4. Cyclic voltamograms recorded on a PdPt/C catalyst (scan rate: 10mV s^{-1}, N_2 saturated 0.5M H_2SO_4 and 0.1M NaOH)

4. Conclusions

PdPt based NPs were synthesized by a plasma sputtering process on vegetal glycerin. We have shown that the glycerin surface temperature and the argon pressure strongly affect the NPs formation. At high temperature, a colloidal solution is obtained whereas a thin films on liquid are obtained at low temperature. A argon pressure of 4 Pa induces the formation of well-dispersed NPs on carbon whereas at lower and higher pressure, large agglomerates and ramified networks of NPs are observed.

We have shown that the PdPt catalysts is active for the ORR, but a full investigation of all catalysts is necessary and will be presented in the ISPC24 conference. We planned to measure the efficiency of the catalyst in PEMFC

conditions, after the incorporation of the catalysts at the PEM/electrode interface.

5. Acknowledgements

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