

Comparison of two atmospheric plasma routes for the synthesis of Pt nanoparticles for fuel cell applications

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Abstract: Pt nanoparticles were synthesized by reduction of Pt acetylacetonate in the post-discharge of a RF atmospheric torch, on one hand, and by reduction of a Pt precursor in liquid using a microplasma, on the other hand. Both approaches lead to particles in the range of 2-5 nm diameter that present a catalytic activity similar to conventional electrocatalysts.

Keywords: Pt nanoparticles, RF torch, microplasma, fuel cells.

1. Introduction

Fuel cells represent an interesting green route for energy use. They offer a greater energy efficiency than combustion engines for transport, and static installation can run on the long term without emission of greenhouse gases. Although the concept of fuel cells is not new, many researches are still going on in that domain, regarding : the behaviour of the bipolar plates, the proton exchange membrane, the electrodes support, the catalyst nanoparticles and the triple interface (membrane, catalyst, support). Although many attempts have been done to replace platinum, it remains still the metal of choice for the hydrogen fuel cells. In that respect, achieving nanoparticles of the right size, well grafted, with good electrocatalytic activity remains a challenge. In this paper we present two routes for synthesizing and grafting Pt nanoparticles on carbon-based substrates. The first approach is to reduce a mix of a Pt precursor directly on the substrate using the post-discharge of an atmospheric RF plasma torch. The second route consists in synthesizing Pt NPs in solution using a microplasma needle, and to spray the resulting colloid in the post-discharge of the RF plasma torch to favour grafting on the substrate.

2. Experimental

Pt(II) acetylacetonate ($\text{Pt}(\text{acac})_2$) was used as precursor for the two routes.

In the first route, the precursor is mixed with carbon black, carbon xerogel, or carbon nanotubes, dispersed in methanol and treated by a RF argon plasma (SurfX Technologies).

In the second route, the Pt precursor is dissolved in methanol, and the resulting solution is exposed to a microplasma. The experimental setup has been described elsewhere [1]

The efficiency of the reduction process is determined by X-ray photoelectron spectroscopy (XPS). The average size of the nanoparticles, and their dispersion on the substrates is studied by transmission electron microscopy (TEM). The catalytic efficiency is analysed by cyclic voltammetry (CV).

3. Results

3.1. synthesis of Pt NPs using the RF torch

Reduction of $\text{Pt}(\text{acac})_2$ was achieved by exposing the substrate/precursor mixture to variable plasma power and treatment times. **Figure 1** shows the evolution of the spectral envelope of the Pt 4f peak as a function of the treatment time.

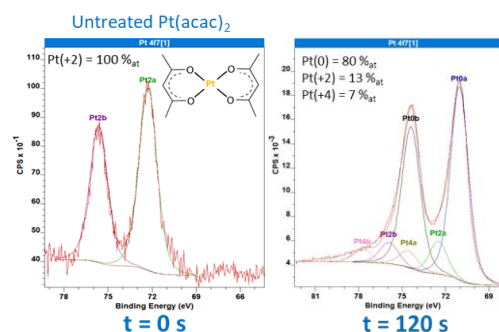


Figure 1: Reduction of $\text{Pt}(\text{acac})_2$ exposed to the post-discharge of a RF argon plasma.

After 120 sec of treatment time, the Pt 4f peak evidence a vast majority of Pt(0) component, signature for metallic platinum. TEM data evidence that Pt nanoparticles of an average diameter of 2.7 nm were formed, as shown in **Figure 2**.

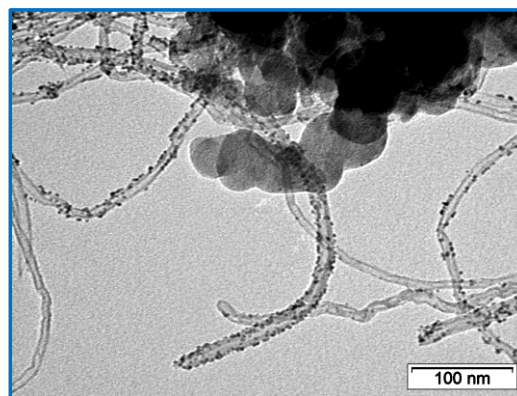


Figure 2 : Pt nanoparticles grafted on carbon nanotubes from reduction of $\text{Pt}(\text{acac})_2$ with a RF plasma torch

Electrochemical data reveal an average electrochemical active surface area of 58 m²/g platinum.

3.2. synthesis of Pt NPs by microplasma

The reduction of metallic salts in water-based solution by microplasma has already been demonstrated [2]. Ag and Au NPs can be easily synthesized, although the reduction pathway is different, the latter involving most probably H₂O₂, where the first one is probably closer to a direct reduction by electrons. However, for other metals, due to the redox potential of water, the reduction of to the metal form is sometimes not feasible. An alternative is to operate in non-aqueous solution, such as methanol. Figure 3 shows a STEM image of Pt nanoparticles formed from reduction in methanol.

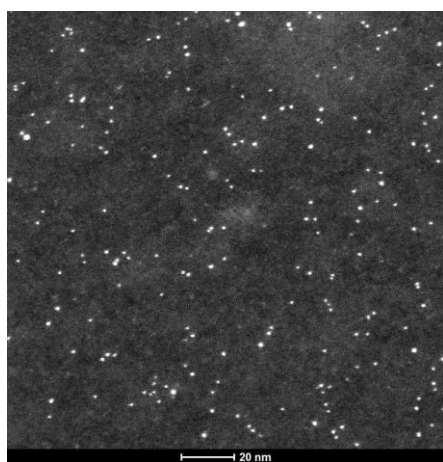


Figure 3: STEM picture of Pt nanoparticles formed by microplasma in methanol solution.

In this case also, the XPS analysis of the formed particles reveal that they are mostly in metallic form, (**Figure 4**)

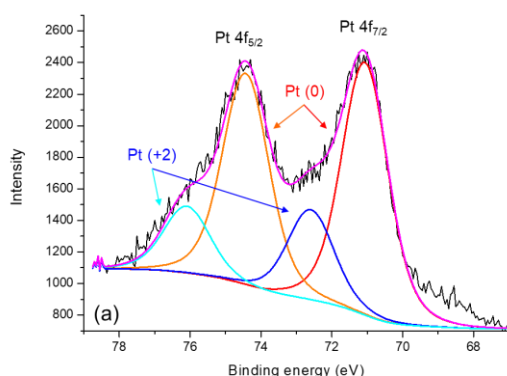


Figure 4: XPS Pt 4f spectrum of NPs synthesized by microplasma in methanol.

The catalytic activity of the formed particles was probed by cyclic voltammetry. **Figure 5** shows an excellent stability of the particles with the number of cycles,

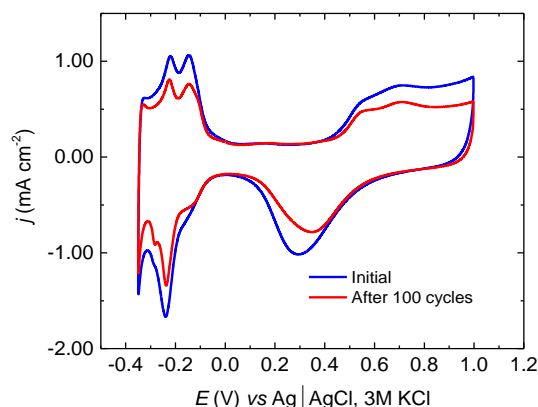


Figure 5: cyclic voltammetry on Pt nanoparticles (after being prepared on a glassy carbon electrode).

3.3. Comparison of the two synthesis methods

Both approaches lead to the easy formation of Pt nanoparticles in the metal state. The average size of the formed particles is similar (around 3 nm diameter), and can be tuned by the operational parameters (concentration in the methanol solution, treatment time, current, plasma power). The electrochemical activities of the particles, once grafted on the appropriate electrode are similar, and give results comparable to commercially available catalysts.

4. Acknowledgements

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5. References

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