Platinum nanoparticles produced by EG/PVP method: The effect of cleaning on the electro-oxidation of glycerol

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The authors dedicate this article to their dear friend and colleague Dra. Élida Beatriz Castro (In memoriam).

ABSTRACT

Carbon supported Pt nanoparticles (NPs) have been prepared through polyols method using PVP. As observed with a large number of surfactants employed in NPs synthesis, it is very difficult to attain an efficient NPs cleaning, which is a fundamental requirement in catalysis researches. The aim of this paper was to obtain clean NPs, beginning by using "soft" methods, in order to keep unaltered both the NPs size and shape; however, an important surfactant remnant was observed. Consequently, it was performed an electrochemical cleaning through PVP and glycolate electro-oxidation, being accompanied with important perturbations of NPs atoms and dissolution and re-deposition of Pt. Finally, the performance of the catalyst towards the glycerol electro-oxidation reaction (GER), before and after the cleaning process was studied. In addition, we demonstrate how the impurities bring about poor reproducibility in this kind of experiments due to the fact that the cleaning process is occurring at the same time that the GER and because cleaning extent along cycles varies for each independent experiment.

1. Introduction

Since it was published for the first time in 2005 [1], the use of polyvinylpyrrolidone (PVP) combined with ethylene glycol method for the synthesis of platinum nanoparticles (NPs) has been widely used. This large applicability is due to a combination of simplicity of the method, reproducibility and to the facility in obtaining highly dispersed NPs over different kinds of carbons with a narrow size distribution, a feature which is especially interesting in catalysis [2,3]. However, NPs obtained by this method, even after being carefully cleaned, still present important amounts of surfactant that block Pt catalytic sites and compromise the catalytic activity of the material. In order to minimize such problem we used several methods to obtain clean NPs. In this sense, we carried out a thorough cleaning of the catalyst by using different solvents or solutions: (i) several cycles of cleaning with water; (ii) with acetone; (iii) with a combination of both substances and (iv) by using a mixture of H_2O_2 and H_2SO_4 [4]. After obtaining negative results, we performed electrochemical cleaning [5] using CV within different potential domains.

Glycerol is a good candidate to be utilized in direct alcohol fuel cells (DAFC) and the GER is being intensely studied during the last years [6]. Complete electro-oxidation of glycerol yielding CO_2 produces 14 F per mol of glycerol, whereas that of ethanol produces 12 F and methanol only 6 F. Besides, C—C breaking is one of the main barriers to obtain better performances with alcohols with more than one carbon atoms. On this subject, glycerol is better candidate than ethanol, since the cleavage of C—C bonds is easier with glycerol than with ethanol [7]. Another positive aspect of glycerol is related to its low-cost, as it is produced in huge amounts as by-product (10%p/p) of biodiesel synthesis [8]. Hence, we decided to study the catalytic activity of the catalyst towards the GER before and after the cleaning process which produce completely clean NPs.

In this work we applied several methods of cleaning of NPs present in the literature, having not succeeded in obtaining completely clean NPs, as it was mentioned by other authors [9]. Also, we present a method which generates thoroughly cleaned platinum NPs (100 voltammetric cycles in the $0.05 < E < 1.45$ V range). Nevertheless, this method produces physical changes on the catalyst, as showed by high-resolution transmission electron microscopy, performed before and after the cleaning process. Besides, we examine

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some of the main processes occurring during the electrochemical cleaning of Pt NPs and demonstrate that the presence of impurities generates continuous variations in the electrochemical response, which are not reproducible along cycles, a fact that could explain the contradictory results usually found in the literature for similar systems [10].

2. Experimental

The synthesis of Pt NPs dispersed over carbon Vulcan XC72® was made as described elsewhere [1], but with slight differences: (i) the PVP monomer/Pt atom molar ratio was adjusted at 0.3 and (ii) the Pt/C ratio (w/w) was 40%.

Electrochemical experiments were carried out employing a three-electrode cell in aqueous acid medium. Carbon supported NPs were used as a working electrode, a high area Pt electrode was used as counter electrode (CE) and the electric potentials were measured against a reversible hydrogen reference electrode (RHE) in the same electrolyte and are presented in the same scale. The working electrode was prepared as follows. A polycrystalline gold disk of 0.98 cm^2 of geometric area was used as support. Cleaning procedure of gold disk involved a first treatment with an aqueous alkaline KMnO$_4$ solution followed by an aqueous acid H$_2$O$_2$ solution, being the disk finally thoroughly washed with Milli-Q® water. The disk was polished to a mirror finish and heated on a plate at 50 ± 2 °C. 1 mg of the Pt/C powder was dispersed in 2-propanol and 50 μl Nafion® 5% by ultrasonic bath for 30 min in order to obtain a highly homogeneous dispersion. Then, an aliquot of 50 μl from the dispersion and 50 μl of diluted Nafion® solution (1 mL of Nafion® 5%: 20 mL of 2-propanol) was applied over the gold disk. Before each experiment, the electrode was washed with water in order to pull out some particles not well adhered. All electrochemical runs were performed at 25 °C under oxygen-free conditions. In order to perform the electrochemical cleaning or to characterize the electrode surface an aqueous solution containing 0.1 M H$_2$SO$_4$ was used whereas the electrochemical activity of Pt NPs towards GER was examined using 0.1 M H$_2$SO$_4$ + 0.255 M glycerol solutions.

X-ray diffraction patterns (XRD) of the samples were obtained with a Miniflex II model Rigaku diffractometer using CuKα radiation (λ = 0.15406 nm). The diffractograms were recorded at 2θ in the range 20–90°.

Before and after electrochemical treatment of the catalyst, TEM and HRTEM experiments were performed in a CM 200 Philips transmission electron microscope. The microscope operates with a LaB6 emission gun. TEM is equipped with an ultratwin objective lens and it was operated at 200 keV. An EDS detector (Energy-Dispersive X-ray Spectroscopy) is attached to the TEM which allows to determine the elemental chemical composition of small regions.

3. Results and discussion

3.1. Non-electrochemical cleaning

In 2007, Brimaud et al. [11] published a work dealing with the "Influence of surfactant removal by chemical or thermal methods on structure and electroactivity of Pt/C catalysts prepared by water-in-oil microemulsion". Authors claimed that they succeeded in NPs cleaning through applying soft methods, but in the same article they state "Before electrochemical measurements, the Pt/C electrodes undergo thirty voltammetric cycles between 0.05 and 1.3 V vs. RHE, until stable voltammograms are recorded". The fact that the voltammograms were changing along cycling indicates that this procedure is participating in the NPs cleaning which is not mentioned in the article [11].
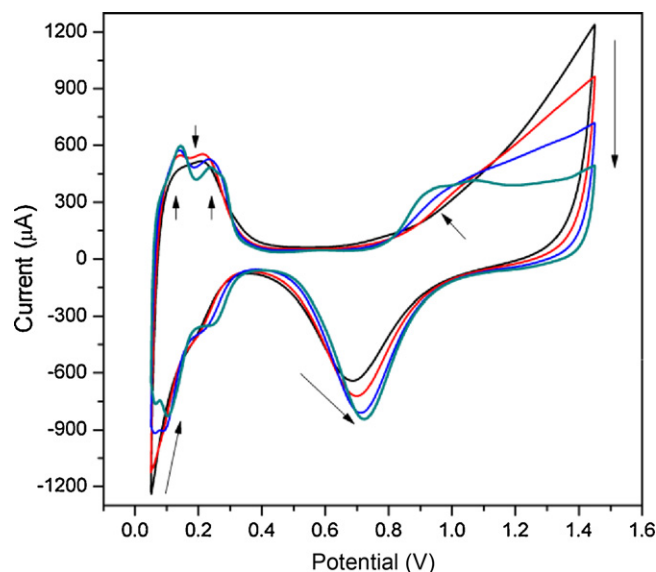

Fig. 1. Voltammograms obtained during the electrochemical cleaning for cycles 2 (black), 20 (red), 50 (blue) and 100 (green). v = 0.1 V s^{-1}. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Recently, Li et al. [12] published an interesting paper focusing on the same topic. Nevertheless, a different approach was used, that gives, in our opinion, totally complementary information to this area. They succeed in the NPs cleaning using relatively low-temperature thermal annealing producing negligible changes in their size and shape. However, the voltammogram obtained in acidic media does not exhibit well-developed H peaks, indicating that some surfactant remains on the NPs surface. This fact was confirmed by the authors in the supporting information of their work [12], where a voltammogram of a cleaner Pt surface was obtained after 20 CVs in 0.1 M HClO$_4$. The relation between the voltammetric response of Pt NPs in acidic media and the cleanliness of the surface will be explained in detail in the next section.

The Pt NPs washed only with water will be named as unclean from now on. In order to carry out a basic study of the electrocatalytic activity of any material it is necessary that its surface be free of impurities, so we started to search for the proper way to obtain a clean catalyst. Based in a previous work [5] we first treated the unclean NPs with acetone but the results were similar to that presented in Fig. 1, cycle 2, showing that the procedure is not able to eliminate the surfactants residues. After that, we applied the protocol proposed in a recent paper [4] in which faceted Pt NPs are cleaned by placing them in contact with a H$_2$O$_2$/H$_2$SO$_4$ mixture. The authors assert that bubbles of O$_2$ generated on Pt surface are able to displace the PVP. Nevertheless, we did not observe any important change in the voltammetric profile of the unclean NPs.

The fact that we obtained results different from those reported in the mentioned articles [4,5] is not unexpected by several factors. In none of these articles ethylene glycol is used neither as reducing nor as solvent. The ethylene glycol method produces glycolate, which act as a surfactant, being one of the impurities present on the Pt surface [9]. In [4] the authors used polyethyleneglycol-dodecylether as surfactant while we used PVP. Another very important difference is that in our case the NPs were dispersed over a porous carbon substrate, differently from the conditions used in both articles just cited [4,5], where the NPs were directly attached to an Au electrode. In the last case, the rough electrode is more similar to a planar electrode than that to a very porous one as that we used. To achieve a clean material in our catalyst, a PVP chain (or

any impurity) needs to diffuse through the porous structure of the catalyst until getting the solution bulk.

3.2. Electrochemical cleaning

Due to the lack of success by employing the cleaning procedures mentioned earlier, we tried to oxidize electrochemically the impurities without affecting the arrangement of the atoms at the NP surface [5]. With this purpose, we performed 200 CVs at 0.2 V s^{-1} in the potential domain of 0.05 V < E < 1.00 V. Once more, the voltammogram remained similar to that observed for unclean NPs (only slight changes were perceived), suggesting that the upper potential limit (1.00 V) was too low to achieve a thorough oxidation of impurities, at least in a relatively short time. Hence, to accomplish a more efficient cleaning of the NPs 100 voltammetric cycles at 0.1 V s^{-1} were performed with the upper potential limit being shifted to 1.45 V. Fig. 1 shows some selected cycles obtained during this procedure. Under these conditions a typical voltammetric profile of Pt was obtained after 100 cycles, which suggests a successful oxidation of superficial impurities and the achievement of a clean Pt surface.

Fig. 1 shows a progressive change of the voltammetric profile with the number of cycles. CV is a very useful tool to evaluate the surface state of a huge quantity of materials. In the case of Pt, the fact that the response of this material in several electrolytes is very stable and well known makes that the voltammetric response with number of cycles be a unique in situ evaluation tool in a very simple and sensitive manner. At the beginning of the potential cycling (cycle 2-black curve) both, H- and O-electroadsorption and electrodesorption are hindered as revealed by the ill-defined profiles, suggesting that Pt surface is blocked by PVP. Nevertheless, as the number of cycles increases, a better definition of both potential domains is achieved due to the progressive impurities oxidation; consequently Pt surface acquires free sites allowing O-electrosorption to take place. The later is reflected through a shift of the beginning of O-electrosorption toward lower potentials, a better profile definition and a current increase in the range of 0.8–1.0 V. Conversely, the current associated with impurities oxidation decreases with the number of cycles.

The H-electroadsorption starts at 0.2 V (Fig. 1, cycle 2) and shows a very poor definition of the peaks suggesting that the Pt surface is severely blocked by some adsorbates. Nevertheless, as the electrode is cycled, the corresponding current peaks become better defined and shift toward positive potentials. The same tendency is observed for H-electrodesorption peaks. Both behaviors strongly suggest that the Pt surface becomes increasingly clean with the number of cycles.

Within the H-domain it can be seen a fast increase of the charge density from cycle 2 to cycle 10; after this fast rise, the charge remains growing at long of the whole series but in a slower fashion. The comparison between the H-electrosorption (0.05–0.35 V) and O-electrosorption (0.8–1.45 V) domains indicates that impurities have a more pronounced effect on O- than on H-region. This fact is well illustrated in cycle 20 and can be rationalized as follows: from 0.8 to 1.45 V the OH- and O-electrosorption and adsorbates oxidation are taking place whereas from 0.05 to 0.35 V impurities are electrochemically stable. Once impurities are oxidized they release Pt sites which are able to electroadsorb O- and OH- species. However, the only cathodic process taking place is O-electrodesorption. For this reason, the charge densities ratio corresponding to electro-oxidation and electro-reduction processes should be different from 1 (>1).

In order to quantify the effect of cycling on the reactions occurring on Pt NPs we followed the change of relative H-electrodesorption charge with the number of cycles (Fig. 2, blue dots). The ratio was calculated respect to the first one. Fig. 2 shows
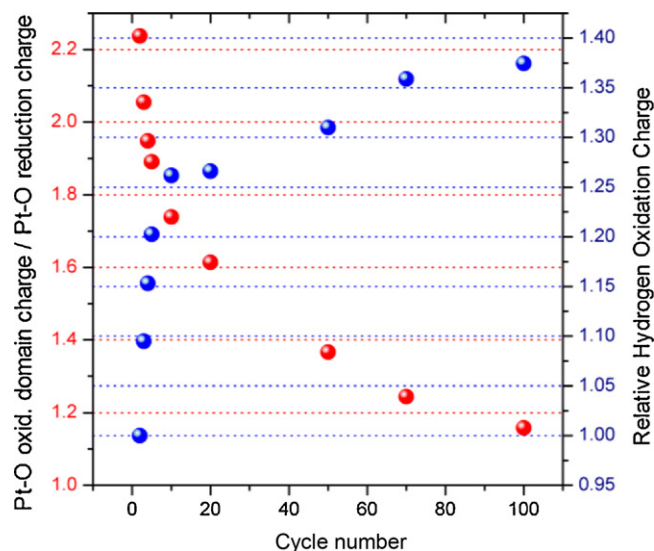

Fig. 2. Pt oxidation domain charge related to Pt—O reduction charge (red spheres) and relative hydrogen oxidation charge (blue spheres) vs. cycle number. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

that the first cycles (1–10) present a sudden increase of the charge (from 1 to ca. 1.25) followed by a slow linear increment till cycle 100 attaining a value of 1.37.

Additionally, the charges corresponding to the formation and reduction of Pt—O domains were calculated and plotted vs. the number of cycles (Fig. 2, red dots). In a general way, a similar behavior to that of H-desorption is noticed, i.e., an abrupt decrease of the charges in the first 10 cycles (2.25 → 1.75) followed by a more subtle lowering, reaching 1.15 in cycle 100. These results aid to elucidate the sort of processes taking place during cycling and to confirm the qualitative concepts brought out earlier on the basis of voltammograms of Fig. 1. Furthermore, it must be recalled that "Pt—O" involves different O-containing species formed on Pt surface, namely, PtOH, PtO, PtO$_2$, etc., [13]. In addition, a value of the ratio Pt—O oxidation domain charge/Pt—O reduction charge larger than 1 can be explained by considering that the electrode is made of Pt NPs containing carbon Vulcan XC72® and deposited on a gold support. Hence, it is possible to find contributions arising from the gold substrate, oxidation of carbon, irreversible oxidation of Pt and perhaps a very little amount of remaining impurities.

3.3. Physical characterization

TEM and HR-TEM micrographs were performed with the purpose of determining the main structural and surface modifications induced by the potential cycling.

Fig. 3 shows detailed images of the Pt NPs before and after the electrochemical cleaning. Size distribution histograms have been drawn taking the information of several images before and after the potential cycling (Fig. 4 and Tables A1 and A2). From the histograms it was possible to determine that the typical sizes were 2.74 ± 0.08 nm and 3.61 ± 0.07 nm (95% confidence interval) for unclean and clean NPs, respectively. The histograms confirm that the Pt NPs grow with the cycling. Anyway, TEM observations of the Pt NPs after cycling do not show any specific faceting, that is, that any plane grew preferentially at the expense of others, having approximately the same shape after and before the cleaning procedure. Besides, as it was expected, TEM images confirmed that the NPs studied constitute essentially monodomains.

In an article devoted to the electrochemical stability of Pt NPs [14], the authors use a two-pronged approach to investigate
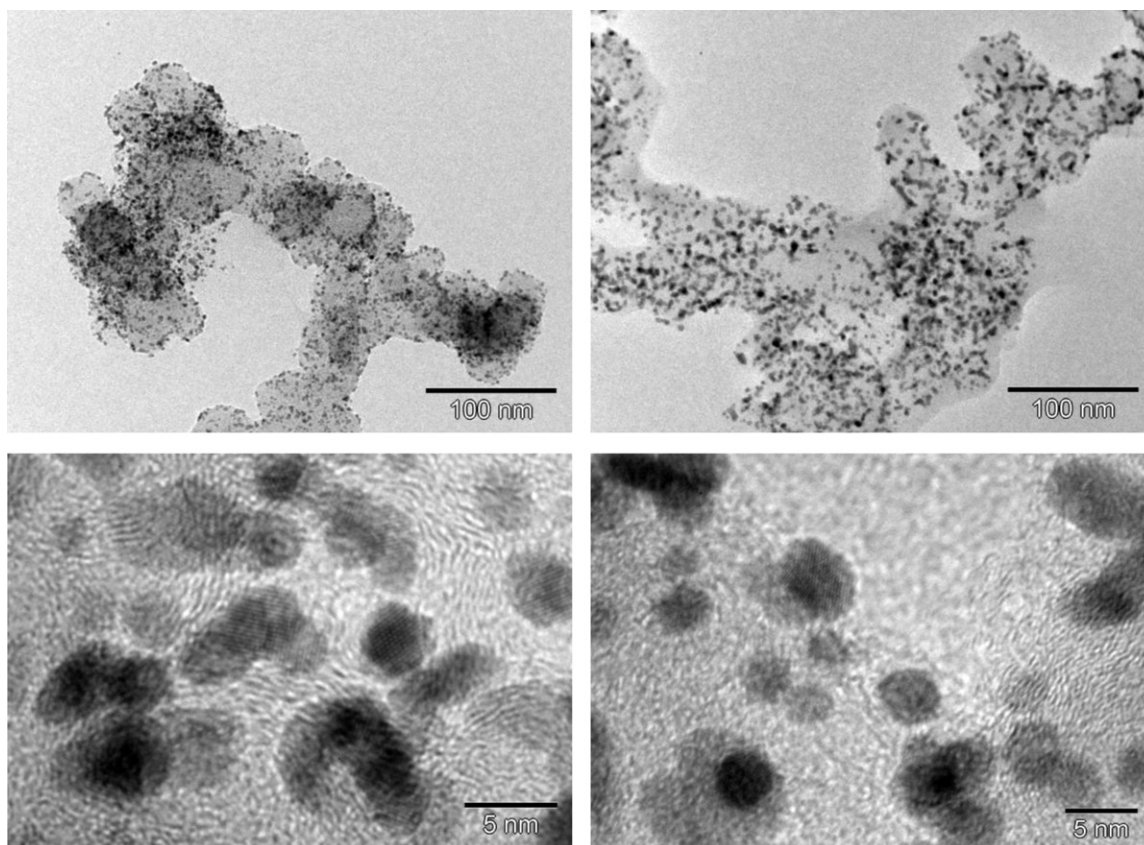
Fig. 3. Tem images for unclean (left) and electrochemically cleaned NPs (right).

how the electrochemical stability of Pt particles changes as a function of size. Experimentally, using electrochemical scanning tunneling microscopy (ECSTM), the authors directly examine the behavior of Pt nanoparticles dispersed onto an Au(1 1 1) substrate as a function of the applied potential. The results demonstrate that in 0.1 M H₂SO₄, smaller Pt particles are less stable to dissolution than larger ones. In addition, using ab initio methods, the authors compute the total energy of Pt particles of various sizes equilibrated for adsorption with oxygen and hydroxyl species and formulate their electrochemical equilibrium with an acidic solution to obtain the dissolution potential [15]. Such approach determines the total energy of a nanosystem directly without relying on simplifying approximations. Both approaches independently point towards a substantial decrease in stability as the particle size decreases [14,15]. These articles can explain the Ostwald ripening occurring during cycling. Thus, during the positive going potential scan, as well as the processes described above, the partial dissolution of Pt NPs is a fact that certainly occurs forming Pt^{2+} entering into the solution. When the potential scan is reversed those ions are deposited preferentially on larger Pt NPs. In addition, it should be taken into account that some ions diffuse towards the bulk solution generating an irreversible dissolution and a net loss of Pt mass. This process is undoubtedly explained taking into consideration that dissolution is favored in smaller NPs than in larger ones due to the lower stability of the former.

Fig. 5 shows the X-ray diffraction pattern corresponding to the small unclean NPs supported on carbon. The X-ray spectrum shows both the peak corresponding to the VULCAN XC72® and the peaks corresponding to the Pt nanoparticles. The peak corresponding to the (0 0 2) reflection of the carbon structure is clearly seen in the diffractogram. It confirms the presence of graphitic planes in the

structure of carbon VULCAN XC72®. All the other peaks correspond to the Pt NPs. From the Bragg equation, we calculated the Pt lattice parameter as 0.393 nm (Reflection 220). This value is in reasonable accordance with the reported value of the Pt lattice parameter [16]. Here we assume that the broadening of the peaks is mainly due to the small particles size. In consequence, from the broadening of the peaks combined with the Scherrer equation it was possible to estimate the crystallite size. By using the reflection 220 again, a value of 2.63 nm was obtained. This result is consistent with the values obtained from the TEM images corresponding to the same unclean samples.

3.4. GER and electrocatalytic activity

Cyclic voltammograms (CV) were performed in 0.255 M glycerol and 0.1 M H₂SO₄ aqueous solution in the potential domain 0.05 V < E < 1.45 V at 0.1 V s^{-1}. In Fig. 6, four consecutives voltammograms obtained with unclean (Fig. 6A) and electrochemically cleaned NPs (Fig. 6B) are shown. Using the same amount of catalyst for two independent experiments is very difficult, even if the same volume of catalyst dispersion is always taken, which is our usual procedure. This method, widely used in this field is not as reproducible as performing the electroactive area calculation. Therefore, we chose to normalize the values obtained for electroactive area, which, in the case of Pt can be easily calculated in a reproducible way.

The general behavior of this system is reported elsewhere [2]. It is important to notice the huge differences between both performances (Fig. 6). With this aim, we discuss how the maximum current peak is modified with the cycle number for each kind of NPs. While the maximum of the peaks centered at 0.64 V and 0.84 V increases with the number of cycles for unclean NPs, those peaks
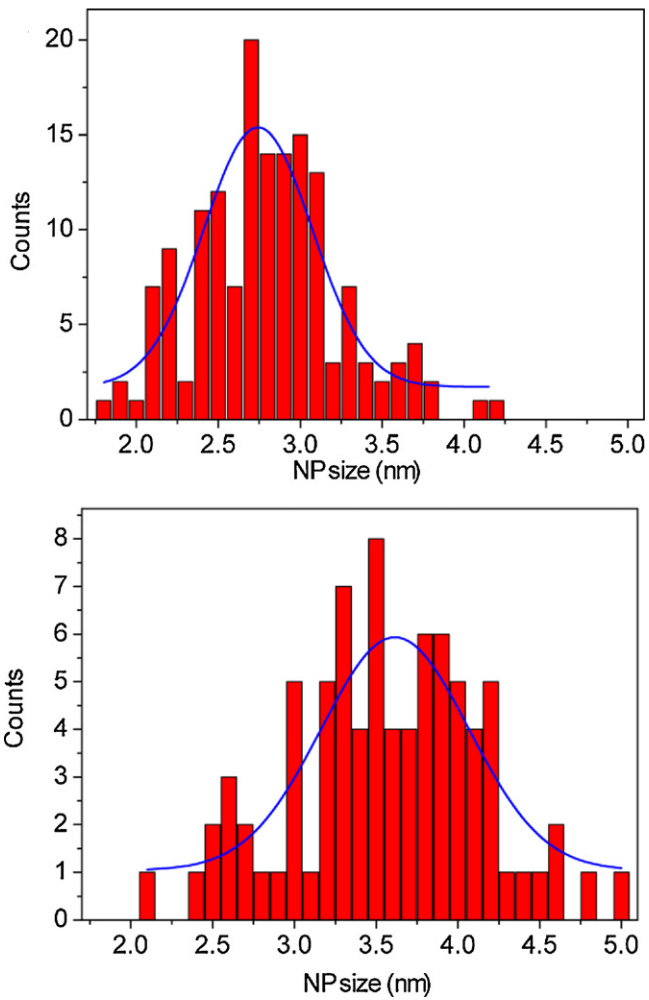
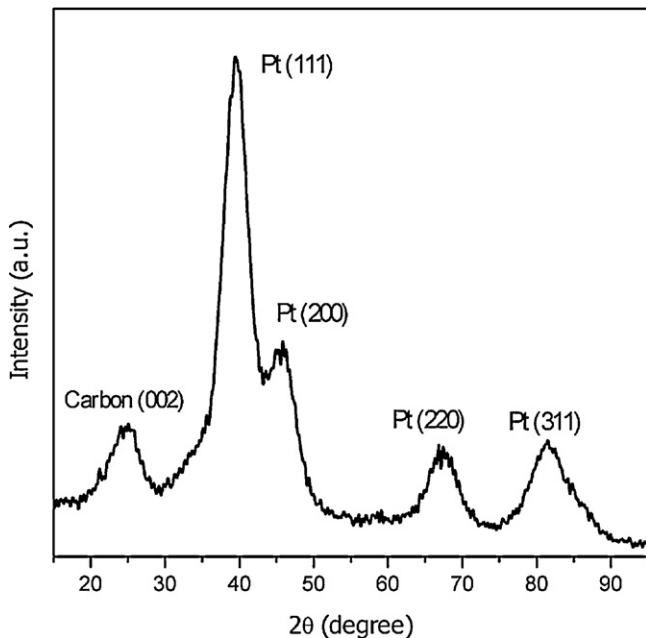**Fig. 4.** Histograms for unclean (above) and electrochemically cleaned NPs (below).

Fig. 5. XRD spectra for carbon supported Pt NPs are shown. Electrochemical active areas were calculated before cycling in 0.1 M H_2SO_4.
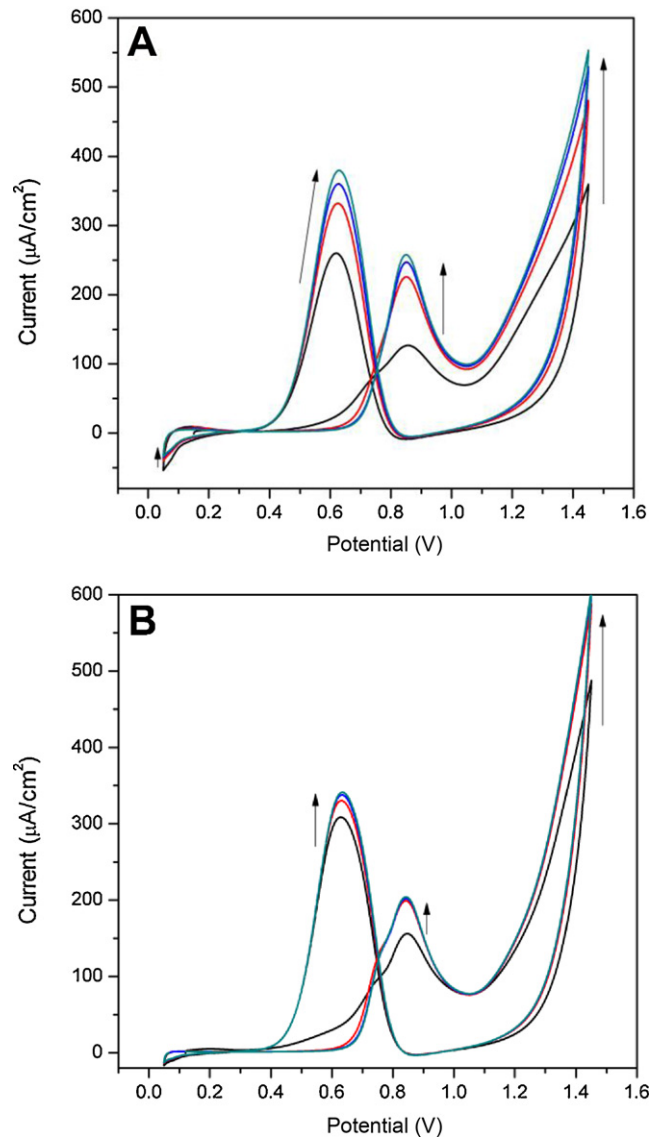

Fig. 6. Voltammetric response of unclean (A) and clean (B) Pt NPs in 0.255 M Gly and 0.1 M H_2SO_4. $v = 0.1\,V\,s^{-1}$.

registered using the electrochemically cleaned NPs are almost constant. An exception is found for the first cycle, which is run under different conditions in both cases. Thus, second, third and fourth voltammograms start at 0.05 V after the negative potential sweep of the previous one, which starts after holding the potential at 0.12 V during 10 min.

These results can be explained taking into account that the surface cleaning continues during the cycling in the presence of glycerol. The fact that the oxidation current peaks are progressively similar could be ascribed to NPs electroactive areas which attain a maximum value. Anyway, it is well-known that during cycling in the presence of glycerol, besides the cleaning of the NPs (due to the oxidation of impurities and also through their displacement by glycerol or partially oxidized glycerol species which adsorb on the Pt surface [2]) and the own oxidation of the alcohol, a quantity of processes can take place, namely, (i) NPs poisoning due to very stable glycerol fragments, PVP [17] and glycolate residues accumulation at the Pt active sites, (ii) catalyst degradation, by loss of active material (Pt irreversible dissolution) and carbon oxidation [18,19] (iii) Ostwald ripening.

Chronoamperometric experiments were performed at 0.7 V (after CV runs). This potential was chosen in order to have well

measurable currents for both catalysts. Sometimes, when the potential is too low, different catalysts presents very low currents, with variations within the experiment uncertainty. The general response for this kind of systems was observed in our experiments. Stationary state currents values for unclean and electrochemically cleaned NPs were $37 \pm 12\,\mu A\,cm^{-2}$ and $44 \pm 3\,\mu A\,cm^{-2}$, respectively (Fig. A1a and A1b). Taking into account the development of the five CV cycles in presence of glycerol, unclean NPs appear to be almost cleaned. This conclusion has been drawn because the CV current peaks grow with the number of cycles and seem to reach a maximum value, a fact that was corroborated by performing 50 cycles (Fig. A2). At this stage, the fact that the uncertainty in the stationary state current obtained with unclean NPs is four times larger than that obtained for the clean ones is not surprising. Four CV cycles performed in glycerol do not produce exactly the same cleaning for two electrodes prepared independently, and this non-reproducibility is quite reasonable, as the several processes occurring into the porous electrode depends on "macro" parameters, i.e., the transversal area and the thickness of the porous frame, that are not exactly reproducible in this kind of experiments. Clearly, different CV runs, i.e., independent experiments with unclean NPs, demonstrate that in the fourth cycle each electrode is in a different cleaning stage meaning that not all the electrodes need the same number of cycles to approach the stationary state (total cleanliness). It can be easily perceived taking into consideration the current peak differences by observing each cycle. Thus, if the electrode is close to achieve the stationary state the last two cycles must be quite similar as in the case of clean NPs (Fig. 6B).

Therefore, bearing our above discussion in mind, it is very difficult in principle, to make a comparison between the electrochemical behavior of the two kinds of particles. Then, if we think that stationary state currents measured with unclean NPs were divided by an electroactive area (EAA) which was calculated before performing CV runs in glycerol, where an important quantity of impurities is oxidized, we can assume that the CA experiments were made on a EAA larger than that which was actually considered. This line of reasoning allows us to conclude that unclean NPs are less electroactive. However, it is very difficult to account for this behaviour. As unclean NPs have some amount of residues on the surface, it is possible the existence of some PVP-NPs or glycolate-NPs interaction that could diminish the electrocatalytic performance. On the other side, it must not be forgotten that the electrochemically cleaning process changes the NPs size, without producing any faceting. As there is not any study, at least to our knowledge, devoted to the dependence of the electrocatalytic activity of Pt NPs with size for glycerol electro-oxidation in acid medium, it is not possible to connect these observed differences with size modifications. Besides, this kind of investigation in different systems have produced contradictory results, and it is very difficult to find categorical results in papers dedicated to associate the electrocatalytic behavior of NPs with their shape or size [10]. Therefore, the most important conclusions of this part of the article are: (i) it is possible to have reproducible measurements only with completely clean NPs; (ii) the electrochemical method is suitable for this purpose and (iii) the uncertainty in the measurements made with unclean NPs is principally due to the fact that at the same time at which the reaction is occurring the catalyst is getting cleaner and accordingly the EAA continuously changing.

4. Conclusion

Polyols method using PVP allows us to obtain well dispersed Pt NPs with a narrow size distribution. Several "soft" cleaning processes prevent to obtain very clean NPs, which is essential to evaluate the real electrochemical behavior of the as-prepared material. However, by using electrochemical cycles, we obtained and characterized (CV and HR-TEM) Pt NPs free of impurities. The cleaning process can be monitored following the very sensitive CV response of Pt NPs in sulfuric acid media. The electrochemical behavior towards the GER was evaluated for clean and unclean NPs. Electrochemical experiments confirm that the clean NPs show better catalytic performance by active site or EAA than the unclean ones. Moreover, we demonstrate that at the same time that the GER is occurring, some surfactant molecules are going away from the NPs surface, letting free active sites and generating a larger EAA. These facts generate major dispersion and less reproducibility in data obtained with unclean NPs than with the clean ones.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.electacta.2013.02.129.

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