

Platinum nanoparticles spontaneously formed on glassy carbon substrates

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Abstract Platinum nanoparticles (Pt NPs) can be obtained successfully on glassy carbon (GC) substrates by spontaneous deposition taking place upon immersion of the GC electrode, at open circuit, in a 1 mM H_2PtCl_6 + 0.5 M H_2SO_4 solution. The metallic deposits were characterized by ex situ atomic force microscopy (AFM) and scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM-EDX) analysis. At long immersion times, AFM and SEM images show hemispherical Pt NPs of varying sizes (20–390 nm), and heights (50–185 nm), distributed mainly on the GC polishing lines. These deposits coexist with larger Pt clusters, including dendritic structures with sizes in the order of several micrometers, suggesting that both primary and secondary nucleation processes occur on the carbon surface. EDX spectrum confirmed that Pt indeed composes both types of deposits. Cyclic voltammetry was used to evaluate their catalytic activity, qualitatively, towards the hydrogen evolution reaction (HER). The voltammetric response of the GC electrode modified with Pt NPs generated at long immersion times evidenced a behavior similar to that of polycrystalline Pt electrodes, and an enhancement in the catalytic activity regarding HER.

Keywords Platinum nanoparticles · Spontaneous deposition · Glassy carbon · HER · Carbon electrode

Introduction

Platinum nanoparticles (Pt NPs) dispersed onto carbon surfaces have been studied extensively to analyze their potential as catalyst materials, particularly for fuel cell applications (Singh et al. 2014; Ong et al. 2017; Samad et al. 2018). In the fabrication of this type of modified substrates, it is important to optimize the catalytic activity with the use of a lower metal load to reduce the production costs. To achieve this goal, it is necessary to control particle size, distribution, and dispersion due to the existing dependence between the catalytic activity and these parameters (Cherstiouk et al. 2003; Antolini 2016; Cao et al. 2016)

Efforts have been made to produce particular structures and shapes of Pt NPs on carbon substrates, employing different methods, among which electrodeposition and chemical reduction are the most commonly used (Rao and Trivedi 2005). On the other hand, it has been found that Pt nanoparticles could be formed spontaneously on highly ordered pyrolytic graphite (HOPG) surfaces (Zoval et al. 1998; Shen et al. 2001; Lu and Zangari 2006; Juarez et al. 2014). In this case, the complete mechanism of this phenomenon is not yet fully understood, since spontaneous metal deposition involves surface sensitive reactions. It has been proposed by Zoval et al. (1998) that the driving force of the spontaneous deposition process is the presence of

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oxidized functionalities such as aldehydes, ketones, and alcohols on the HOPG surface, and these functionalities work as reducing equivalents to Pt ions present in solution. The surface functional groups present at the carbon surfaces might also influence the dispersion, agglomeration, and surface diffusion of Pt nanoparticles (Rodríguez-Reinoso 1998). However, Juárez et al. (2014) have recently confirmed by a theoretical approach that, besides this hypothesis, there are another involved interactions which make this phenomenon more complicated to study thoroughly. These facts have served as a starting point to investigate the spontaneous deposition of Pt on glassy carbon (GC) substrate; this is a low-cost alternative, whose surface also contains carbon-oxygen functional groups similar to those of HOPG (Randin and Yeager 1975; Collier and Tougas 1987; Ray and McCreery 1999); the surface functional groups can undergo some phase transitions spontaneously, and therefore, the formation of metal nanoparticles could be expected at open circuit conditions.

We have reported previously, the spontaneous deposition of Pt nanoparticles on HOPG surfaces (Arroyo Gómez and García 2015), and demonstrated that, at long immersion times (2 h), large Pt clusters constituted mainly of different sized hemispherical particles were formed. In this case, the deposits covered almost entirely the electrode surface and exhibited sizes up to 250 nm and heights between 125 and 200 nm. Therefore, if this deposition process is also feasible on the GC surface, it could provide a useful method to obtain well-controlled amounts of Pt particles on GC varying the time of immersion for a given concentration of $[\text{PtCl}_6]^{2-}$ ions in the solution, and could significantly simplify the preparation of new metal/GC catalyst materials.

In the present work, the surface modification of a GC electrode by spontaneously deposited Pt was investigated, taking into account the influence of the electrode surface conditions (surface morphology and surface roughness) on this phenomenon. This behavior was compared to that obtained using HOPG electrodes. The dependence of the open circuit potential (OCP) with immersion time was carried out to understand the deposition mechanism that takes place on the substrate surface. AFM and SEM-EDX techniques together with cyclic voltammetry were used to characterize the Pt deposits formed on GC. The catalytic effect for the hydrogen evolution reaction was analysed qualitatively by voltammetric measurements.

Experimental

The GC substrates (HTW, Germany) used as working electrodes, were rods ($\phi = 3$ mm) sealed into a Teflon holder, with an exposure area of 0.0707 cm². The electrode surface was mechanically polished to a mirror-like finish with an emery paper of progressively finer grain size, followed by 0.3 μm alumina paste and then, rinsed thoroughly with tri-distilled water.

The spontaneous formation of the Pt nanoparticles on GC was performed immersing the electrode in a 1 mM H_2PtCl_6 + 0.05 M H_2SO_4 solution, prepared with suprapure chemicals (E. Merck, Darmstadt) and tri-distilled water. All the experiments were carried out at a temperature of $T = 298$ K using a conventional three-electrode electrochemical cell. The counter electrode was a Pt sheet (1 cm²), and the reference electrode was a saturated calomel electrode, (SCE, $E_{\text{ECS}} = 0.2415$ V vs. SHE). All electrode potentials mentioned in this work, are referred to this electrode. The deposition took place at open circuit potential (OCP), and in order to evaluate the morphological changes of the Pt nanoparticles, different immersion times were used.

All the experiences were recorded using a computer-controlled EG&G Princeton Applied Research model 273A potentiostat-galvanostat. The characterization of Pt nanoparticles on GC was carried out by ex situ AFM, using a standard nanoscope III microscope (Digital Instruments, Santa Barbara, USA), operated in contact mode using a scanner of 15 μm and oxide-sharpened silicon nitride probes (Veeco Probes), and by SEM using a JEOL 35CF microscope integrated with an EDX DX-4 analyzer.

Results and discussion

Temporal OCP evolution

It has been well established that Pt is spontaneously deposited in HOPG substrates (Zoval et al. 1998; Shen et al. 2001; Lu and Zangari 2005; Juárez et al. 2014) but until now, this phenomenon has not been reported to occur on GC surfaces. The oxidized functionalities at surface defects on HOPG electrodes are the driving force for the process (Zoval et al. 1998), the higher quantity of surface defects and the electrochemical performance of GC, compared to HOPG (Zittel and Miller 1965), are enough reasons to suspect that this

phenomenon may also take place at the GC surface without any chemical or electrochemical pretreatment of the carbon electrode. To evaluate this hypothesis, open circuit potential (OCP) was measured for a GC electrode immersed in a 1 mM H_2PtCl_6 + 0.05 M H_2SO_4 solution.

It is well known that the spontaneous deposition of metals on certain materials is accompanied by changes in the surface potential of the substrate, which are related to the charge transfer due to the oxidation of the substrate and the reduction of the metal ion (Brankovic et al. 2001a, b). Figure 1 shows the typical OCP-time evolution after an immersion time of 2 h. In all experiences, the recorded OCP ranged between 520 and 550 mV. These values are slightly above to those reported for the $\text{PtCl}_6^{2-}/\text{Pt}$ and $\text{PtCl}_4^{2-}/\text{Pt}$ couples (Lu and Zangari 2005) (502 and 516 mV vs. ECS, respectively), indicating that Pt reduction could occur through these processes together with some influence of the anions present in solution. In our case, the difference of the potential values may be related to the presence of SO_4^{2-} anions in the supporting electrolyte, which promote the reduction processes and increase the electrolyte conductivity (Lu and Zangari 2005). This difference could also be interpreted regarding the substrate activity, related to the amount of surface defects which contain functional groups that may be oxidized and provide the electrons necessary for the reduction of Pt from the plating solution. Anyway, the OCP data obtained in this work are similar to those reported for HOPG electrodes employing solutions with and without supporting

electrolyte (Lu and Zangari 2006; Arroyo Gómez and García 2015; Quaino et al. 2005).

Surface analysis

Different amounts of Pt were found to deposit spontaneously on GC surfaces, after varying the immersion time, t_i , in the chloroplatinic acid solution, and characterized by ex situ AFM and SEM-EDX analysis. Initially, the topography of the Pt-free substrate shows a rough surface with typical lines originated by the polishing treatment (mean roughness $R_a < 2$ nm). After a relatively short immersion time ($t_i = 200$ s), a small amount of metal deposits with a mean particle size of 32 nm, was observed on the substrate (Fig. 2a), indicating that the driving force for metal adsorption is not enough to produce considerable nucleation of Pt clusters. However, with increasing the immersion time to $t_i = 7200$ s (2 h), highly covered regions of Pt crystals were evidenced (Fig. 2b).

Figure 2b, c shows a representative AFM image of the Pt-decorated GC electrode and the corresponding size distribution, respectively. Indeed, the hemispherical Pt nanoparticles are distributed over the surface, mainly on the polishing lines of the substrate; with sizes ranged between 20 and 390 nm. Despite the wide range of diameters observed, the predominant Pt particle size was below 150 nm (Fig. 2c). Unlike the HOPG where the active sites are preferably distributed at the step edges of the surface, the Pt clusters are located randomly on the substrate. Size diversity of metal deposits is consistent with a progressive nucleation and growth mechanism. This growth and the coalescence of Pt crystals is promoted by the presence of the supporting electrolyte, which allows the nanoparticles to reach a critical size and then move on the substrate surface to grow in a hemispherical shape (Lee et al. 1998). A cross-sectional analysis of the marked lines in the AFM image was carried out, indicating a maximum particle height of 0.185 μm (Fig. 2d).

Analysis of the AFM images from different regions of the samples also shows aggregates of interconnected particles (Fig. 3a). These are similar to Pt deposits observed by Zoval et al. (1998) as diffuse rings on the HOPG electrode after 1 min immersion in a chloroplatinic solution using 0.1 M HCl as supporting electrolyte, and those generated via sol-gel impregnating a silica surface (Mizukami et al. 1994). The higher surface non-uniformity lead to the aggregation of the Pt,

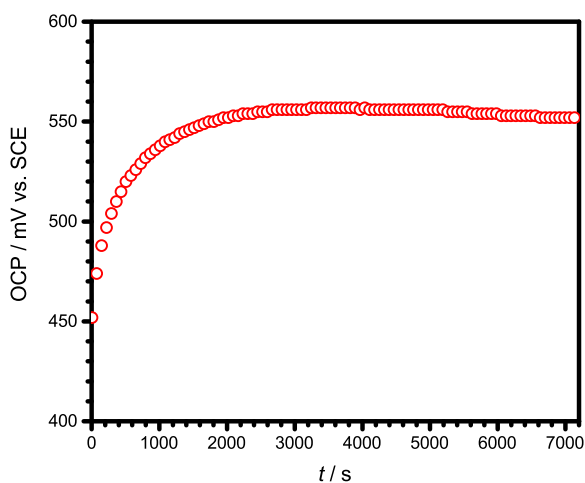


Fig. 1 Time evolution of the open circuit potential (OCP) of a GC electrode immersed in a 1 mM H_2PtCl_6 + 0.05 M H_2SO_4 solution

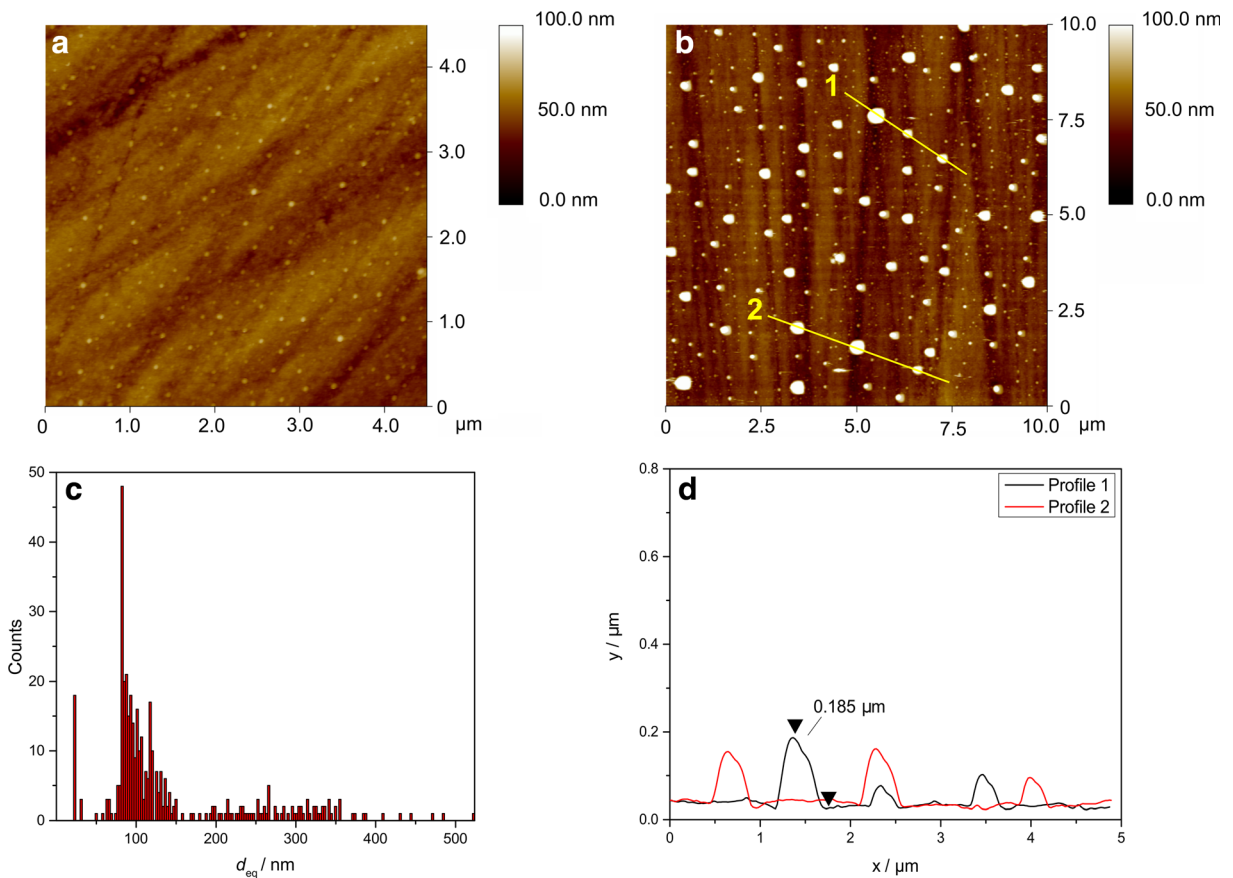


Fig. 2 Ex situ AFM images of Pt deposits generated after an immersion time of **a** 200 s and **b** 2 h, **c** particle size distribution, and **d** cross section of Pt deposits ($t_1 = 2$ h) on two different regions of the surface

generating large dendritic structures (Fig. 3), and this formation could be assumed as a secondary nucleation process on the surface of previously deposited Pt (Sherstyuk et al. 2000). A Pt dendrite consists of a central stem with wide side branches decorated by some small nanoparticles; the branch length can reach a width of $11.4 \mu\text{m}$ and a length higher than $12 \mu\text{m}$ (Fig. 3b). This characteristic morphology of Pt crystals could be explained by the anisotropic surface diffusion of the adsorbed Pt atoms, and the relatively long deposition time used. The three-dimensional growth morphology from hemispherical nanoparticles to form larger structures depends on coalescence and mobility of Pt on the surface, as it was pointed out before.

SEM images also corroborate the formation of large dendritic deposits surrounded by smaller ones (Fig. 4a). It could be suggested that the particles, which exist near the dendritic structures would be predominantly incorporated in their branches, thus leading to a denuded zone for small clusters. Higher magnification of this region

(Fig. 4b) reveals that, around the large dendrites, the islands with smaller size exhibit also a dendritic shape, whereas the most remote crystallites, even smaller, evidence a more compact structure. In this case, the dendritic structure could be associated with the generation of Cl^- anions as a result of the formation of metallic Pt. These anions could be adsorbed on Pt crystals, blocking active sites for subsequent Pt reduction, and could influence the morphology of the deposits (Lee et al. 1998). The EDX spectrum (Fig. 4c) confirmed that Pt indeed composes both compact nanoparticles as well as dendritic structures, also showing the presence of the C and O signals corresponding to the substrate and superficial oxides, respectively.

Anyway, taking into account the observed microstructure of Pt deposits, it could be assumed that both primary and secondary nucleation processes occur on the carbon surface, i.e., growth of isolated nuclei forming islands, which come into contact and coalesce, and those that grow beyond a certain size due to anion

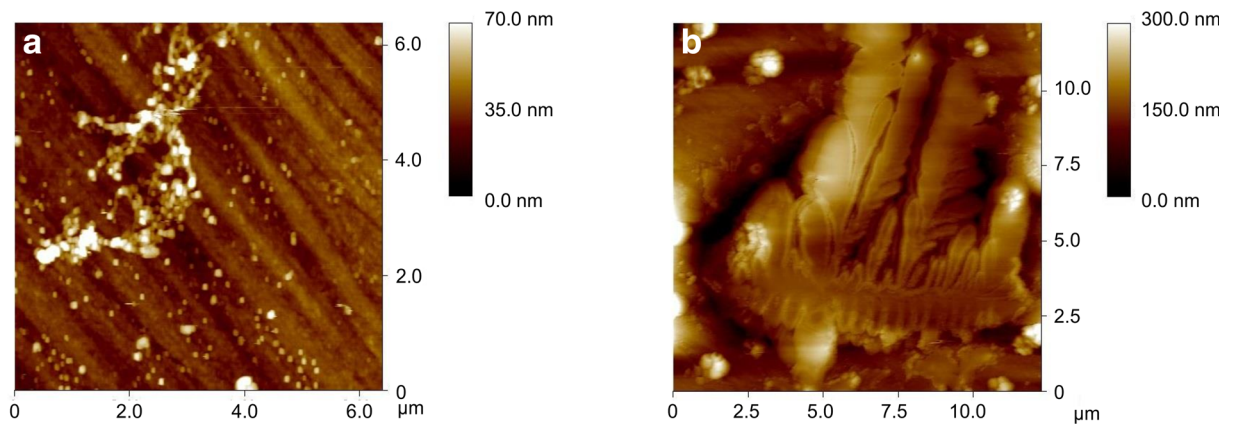


Fig. 3 Pt deposits obtained after an immersion time of 2 h. AFM images of **a** aggregates of interconnected particles and **b** dendritic structures

adsorption causing a secondary nucleation of Pt crystals. A formation mechanism can be proposed considering primary and secondary nucleation on the GC surface, as shown in the schematic illustration of Fig. 5.

On the contrary, Pt nucleates on the HOPG substrate forming irregular agglomerates on step edges, which

transforms, at the same immersion time (2 h) used in this work, to large clusters, mainly constituted by hemispherical particles of different sizes (Arroyo Gómez and García 2015). Therefore, the influence of the substrate structure on the nucleation behavior of the spontaneously deposited Pt crystals can be clearly evidenced.

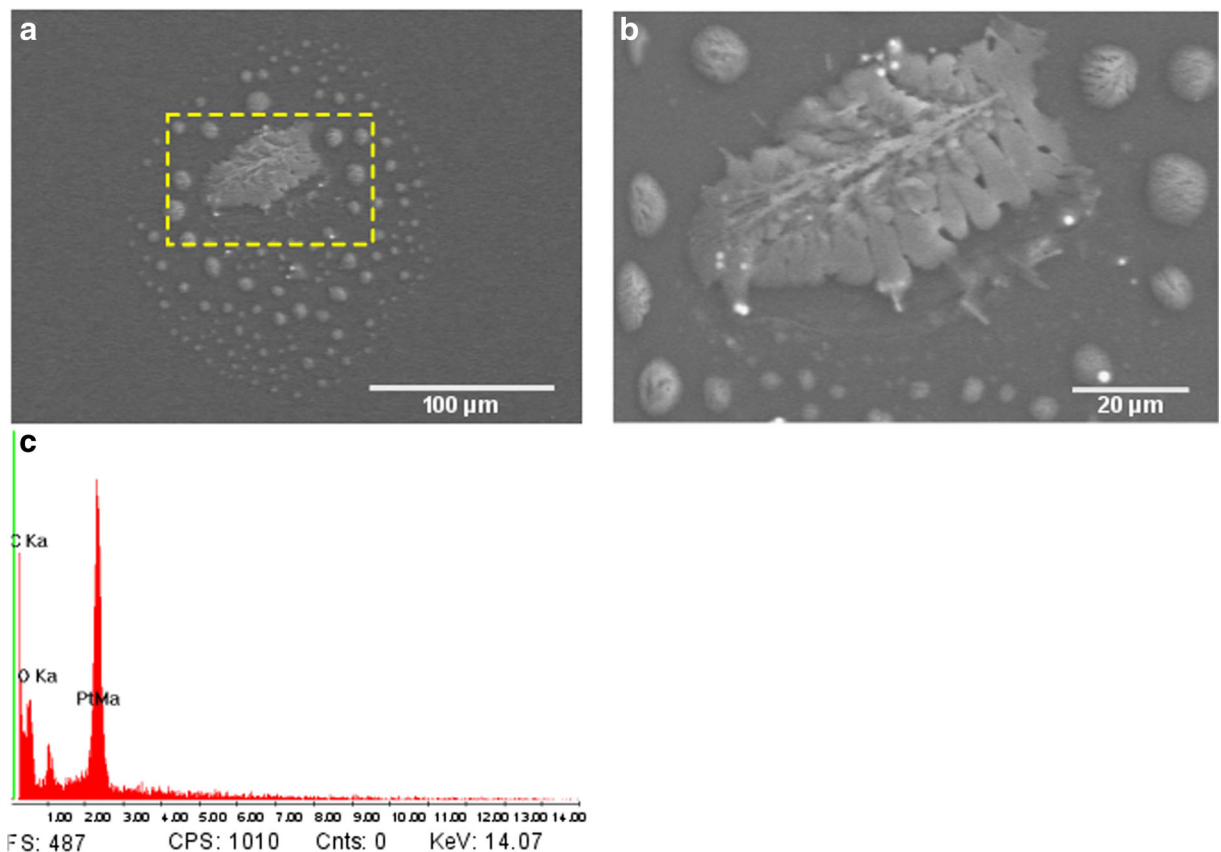


Fig. 4 SEM micrographs of the Pt deposits obtained after an immersion time of 2 h. **a** $\times 300$, **b** $\times 1500$, and **c** EDX spectrum

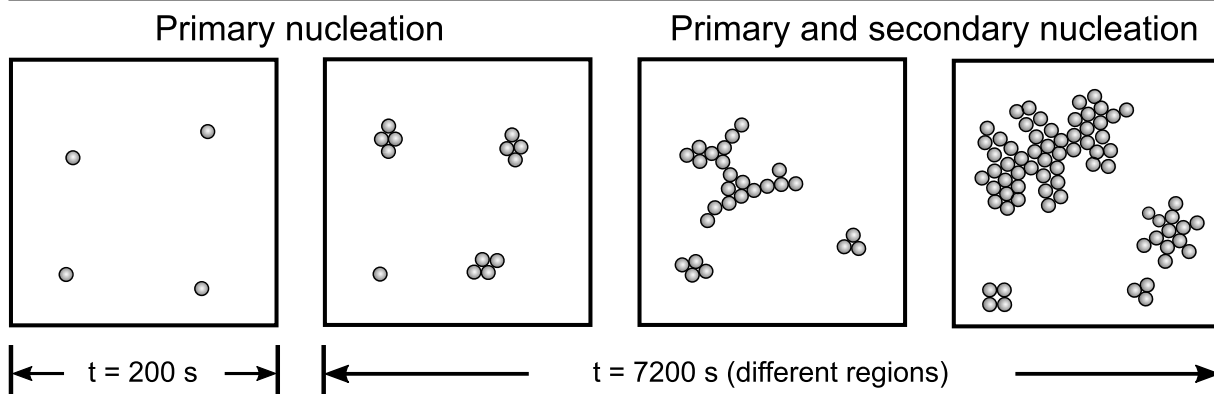


Fig. 5 Schematic illustration of the spontaneously Pt deposits formation

Electrochemical characterization

The characterization of the Pt NPs modified GC substrate was carried out in a 0.5 M H_2SO_4 solution. After an immersion time of 2 h, the cyclic voltammogram of the Pt-modified electrode showed similar features to those of polycrystalline platinum, as presented in Fig. 6a. The differences between the two voltammograms could be associated with a low surface area related with large sized Pt particles observed by AFM and SEM (Mukerjee 1990). Nevertheless, the Pt-modified electrode showed the main voltammetric features, i.e., the reduction of Pt oxide during the cathodic sweep, which is observed at $E \sim 500$ mV, followed by the hydrogen adsorption at $E < 0$ mV. In the anodic direction, the corresponding desorption of the adsorbed

hydrogen and the Pt oxide formation processes are shown. The voltammetric response is similar to that reported for Pt-modified HOPG electrodes (Zoval et al. 1998; Lu and Zangari 2006; Fortuin et al. 2018).

The catalytic activity of the Pt-modified surfaces was evaluated qualitatively by cyclic voltammetry. Figure 6b shows the voltammetric results for the GC electrode modified with Pt deposits, using different immersion times. The current observed in the hydrogen evolution region is increased with immersion time, and the onset potential (E_{onset}) value for the HER becomes 400–420 mV more positive than that of the unmodified GC substrate. This behavior can be attributed to an increase in the Pt load at higher deposition times, leading to an enhanced catalytic activity. Table 1 summarizes the values of the HER

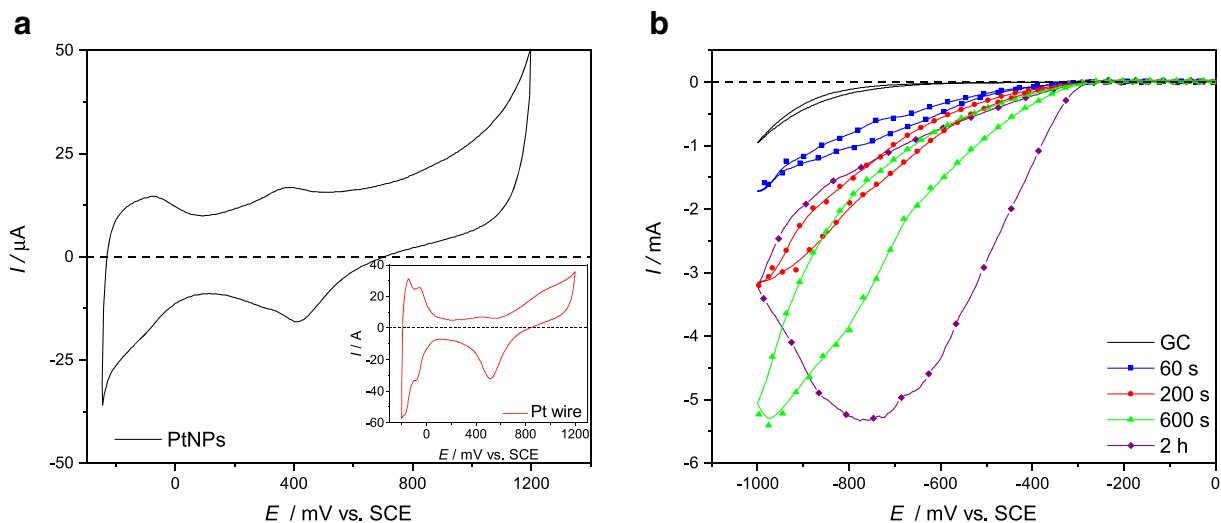


Fig. 6 Cyclic voltammograms in 0.5 M H_2SO_4 of **a** Pt-modified GC electrode (2 h immersion time), inset: polycrystalline Pt, $|dE/dt| = 50$ mVs^{-1} , and **b** freshly polished and Pt-modified GC surfaces using different immersion times, $|dE/dt| = 10$ mVs^{-1}

Table 1 HER Onset potentials and maximum cathodic current for Pt NPs obtained at different deposition times

Deposition time (s)	HER	
	E_{onset} (mV)	I_{max} (mA)
0*	-710	0.95
60	-343	1.71
200	-320	3.15
600	-300	5.29
7200	-290	5.32

*Pristine glassy carbon electrode

onset potential and the maximum cathodic current obtained in the potential region considered, for Pt nanoparticles deposited at different immersion times on GC surfaces. It is indicated that the Pt nanoparticles generated with an immersion time of 7200 s, exhibit the most positive onset potential value which may favor the proton reduction kinetics, with a maximum cathodic current (I_{max}) of 5.32 mA. These results suggest that the GC substrate modified with spontaneously deposited Pt NPs could be a promising electrocatalyst material for the HER. Further work is in progress to evaluate the kinetic parameters through Tafel plots to study the mechanism of HER.

Conclusions

It was demonstrated that platinum nanoparticles were formed on GC substrates by a spontaneous deposition process. The OCP vs. immersion time profiles revealed potential values higher than those of the $\text{PtCl}_6^{2-}/\text{Pt}$ and $\text{PtCl}_4^{2-}/\text{Pt}$ couples, suggesting that some of these processes could take place and be influenced by the presence of SO_4^{2-} anions.

Pt deposits with different shapes and sizes were generated spontaneously on GC surfaces at long immersion times, i.e., hemispherical nanoparticles with a broad size distribution, and large dendritic structures observed on different regions of the substrate, the latter being regarded as a secondary nucleation process. The voltammetric data of the GC electrode modified with Pt NPs generated at an immersion time of 2 h, evidenced a behavior similar to that of polycrystalline Pt electrodes. The voltammetric response

regarding HER showed an enhancement in the catalytic activity with the deposition time, showing a pronounced effect for Pt NPs formed on GC electrodes after an immersion time of 2 h.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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