

The effect of adsorption of thiourea on the particle size of supported platinum nanocatalysts synthesized by chemical reduction

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Abstract

In this work, carbon-supported platinum nanoparticles were synthesized in the presence of varying concentrations of thiourea (TU). Because of the presence of the sulfur atom, thiourea adsorbs strongly on the forming Pt nuclei during the synthesis, affecting the rate and the extent of growth. High-intensity X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM) were used to probe the effect on the crystallite size and particle size, respectively, revealing a decrease in both mean crystallite and the mean particle size for increasing concentrations of thiourea during the synthesis. An adsorption isotherm for the adsorption of thiourea on platinum nanoparticles is also discussed. Cyclic voltammetry was used to check the effect of TU on the particles as well as to obtain further knowledge on both adsorption and electrochemical oxidation behavior of thiourea on Pt surfaces. Thermal treatment effectively cleaned the electrode surface, thus providing an easy way to remove adsorbed species from the Pt surface.

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1. Introduction

The growing interest in low temperature fuel cells has been a great motivation for the development and study of supported catalysts based on platinum. A variety of low temperature methods to synthesize platinum and platinum alloy nanocatalysts unsupported or supported on carbon have been explored. As early as 1977, Kinoshita and Stonehart [1] reviewed different methods for the preparation and characterization of electrocatalysts, including the impregnation and thermal decomposition methods, among others. To date, one of the main problems with these methods is the difficulty in obtaining monodisperse nanoparticles of adequate size.

In this laboratory, extensive use has been made of the reduction of suitable precursors with formic acid or formate anions (formic acid method, FAM) [2–4], mainly for the preparation of carbon-supported platinum-based nanocatalysts. Basically, the principle of the method is the use of formic acid or formate as the

reducing agent at 80 °C. This method has allowed the synthesis of Pt/C and bimetallic materials, such as Pt–Ru/C [4], Pt–Sn/C [3], Pt–Co/C [5,6], among others. Although the particle sizes obtained are in general satisfactory, it is no doubt of interest to study the possibility of controlling that parameter. Size and shape controllable synthetic routes of nanoparticles have been described in several publications [7–9] in the nanoscience technology but in general these methods are considered “dirty” to prepare electrocatalysts. Besides, most methods are presented as a way of obtaining smaller particle sizes, with respect to some standard chosen for comparison, without a physicochemical analysis that may advance our knowledge of the problem of nanoparticle formation.

Because of the presence of a sulfur atom that enhances adsorption, the adsorption of thiourea (TU) has been studied on several metal surfaces. This makes TU an ideal probe molecule to study adsorption phenomena. The earliest report is probably the work of Schapink et al. [10], who studied the adsorption of TU on Hg in a NaF electrolyte. The results of this work were elegantly used by Parsons [11] to get a first estimate of the thickness of the double layer Hg/aqueous solution. A more complete work on the adsorption of thiourea on Hg was presented later

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by Parsons and Symons [12]. Also, the principles of the adsorption of thiourea as a probe at the Hg/phosphoric acid interface were used by Gonzalez et al. [13] to show that the thickness of the double layer increases with the concentration of phosphoric acid, an important finding in the context of the oxygen reduction reaction in phosphoric acid fuel cells. Other metal surfaces, such as gold [14], silver [15], iron [16], and polycrystalline platinum [17] were also used to investigate the adsorption of TU. In practical systems, TU is generally used as inhibitor of the corrosion of copper.

In the present work, the adsorption of TU was used to control the rate and the extent of growth of platinum nanoparticles synthesized by chemical reduction with formic acid. The work is complemented by considering some physicochemical aspects of the adsorption of TU on the platinum nanoparticles that led to the formulation of an adsorption isotherm. Also, limitations in the usual methods of determining small particle sizes and the voltammetric behavior of the prepared catalysts are discussed.

2. Experimental

Carbon-supported Pt nanoparticles were synthesized by the following procedure: carbon powder (Vulcan XC-72 heat treated at 850 °C under argon) was dispersed in a 0.5 mol L⁻¹ solution of formic acid at 80 °C and then a 5 g/100 mL solution of H₂PtCl₆ was added slowly. The final solution was made to contain different concentrations of TU in the range 1–5 mmol L⁻¹. X-ray measurements were carried out at the XRD beam line at the Brazilian Synchrotron Light Laboratory (LNLS), Brazil. The diffractograms were obtained in the reflection mode, at room temperature, in a 2θ interval from 20° to 100°, using the Cu Kα energy (λ = 0.1541 nm) with a resolution of 4.5 eV, calibrated using Si(1 1 1).

The samples for the HRTEM characterizations were prepared as follows: a carbon film was deposited onto a mica sheet that was placed onto the Cu grids (300 mesh and 3 mm diameter). The material to be examined was dispersed in water by sonication, placed onto the carbon film and left to dry. Histograms of particle sizes were constructed using an average of about 250 particles. This technique was implemented in the Microscopy Laboratory of the Brazilian Synchrotron Light Laboratory (LNLS) using a HRTEM microscope JEOL, JEM 3010, URP, operating at 300 kV and having a resolution of 0.17 nm.

Electrochemical experiments were carried out at room temperature in 0.5 mol L⁻¹ H₂SO₄ using an Ecochemie AUTOLAB PGStat 30 potentiostat. Potentials were measured using a reversible hydrogen electrode in the same solution. The working electrode was prepared by applying a thin layer (around 1 μm thickness) of the supported catalyst (50 μg cm⁻²) dispersed in water on a glassy carbon disk according to a method already described [18,19]. Briefly, a drop (approximately 45 μL) of a re-dispersed aqueous suspension containing about 1 mg mL⁻¹ of catalyst was pipetted on top of a glassy carbon disc of 0.348 cm² embedded in PTFE, yielding around 50 μg Pt cm⁻². After water evaporation, 40 μL of a diluted Nafion[®] solution (0.05 wt%, in a solution of 1:1 water/methanol) was placed onto the dried cata-

lyst material. The electrode was protected by a pure water droplet and then transferred to the electrochemical cell.

3. Results and discussion

3.1. X-ray diffraction (XRD) and high-resolution electron microscopy (HRTEM) experiments

Fig. 1 shows the X-ray diffractograms of the materials obtained. For concentrations of TU up to 4 mmol L⁻¹ the characteristic peaks of the fcc structure of Pt are distinguishable, although losing gradually their shape. On the other hand, for larger concentrations of TU (5 mmol L⁻¹), the diffractograms are almost featureless, characteristic of a microcrystalline or amorphous material.

Because of the gradual disappearance of the Pt peaks for increasing concentrations of TU and the large background signal related to the amorphous carbon support, the lattice parameter and the mean crystallite size could not be determined quantitatively with confidence. More specifically, the mean crystallite size, hereafter denominated by “*d*”, is generally estimated by the well-known Scherrer equation, $d = 0.94 \lambda_{K\alpha} / \beta_{(2\theta)} \cos \theta$, where $\lambda_{K\alpha}$ is the wavelength of the X-ray radiation, θ the angle of the (2 2 0) peak (which has the lowest contribution from the carbon support), and $\beta_{(2\theta)}$ is the width in radians of the diffraction peak at half-height. Despite the cited difficulty to obtain structural parameters from XRD, the results presented in Fig. 1 agree qualitatively to the behavior expected from Scherrer’s equation, which predicts that broader peaks are related to smaller crystallite sizes. Therefore it is clear that the presence of thiourea in the synthesis medium acts as a crystallite size modulator, that is, the higher the concentrations of TU the smaller the crystallite size.

X-ray diffraction provides more statistically reliable data than other local tools such as high-resolution electron microscopy (HRTEM), but there are some problems associated to the use of Scherrer’s formula for nanoparticle systems, as discussed by Cohen [20]. On the other hand, the use of high-intensity X-ray sources obtained from synchrotron sources, as in this work, can increase the XRD sensibility, but special procedures to analyze the data need to be applied [20]. Considering the difficulties

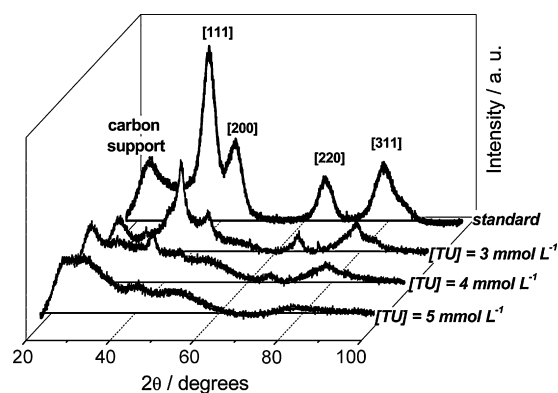


Fig. 1. Powder XRD pattern of Pt/C synthesized with different concentrations of thiourea in solution. $\lambda_{(Cu K\alpha)} = 0.1541$ nm, 25 °C. Some reflections are indicated in the figure.

mentioned above no attempt was made at obtaining quantitative information from XRD measurements. So, in order to obtain further insights regarding particle size and dispersion, the materials were analyzed by HRTEM, which allowed the determination of the distribution and shape of Pt nanoparticles in the carbon support, the histograms of particle size distribution and the mean particle size. Fig. 2 shows the HRTEM micrographs for Pt/C prepared using the more concentrated thiourea solutions.

Although the diffractogram for the material obtained with 5 mmol L^{-1} TU is featureless (cf. Fig. 1), HRTEM micrographs show clearly that the Pt nanoparticles are present in the material, Fig. 2c.

High-resolution TEM images reveal that the Pt/C material synthesized with different concentrations of thiourea presents well-dispersed particles on Vulcan XC-72. In general, the shape displayed by the particles is cubooctahedral, as can be seen in

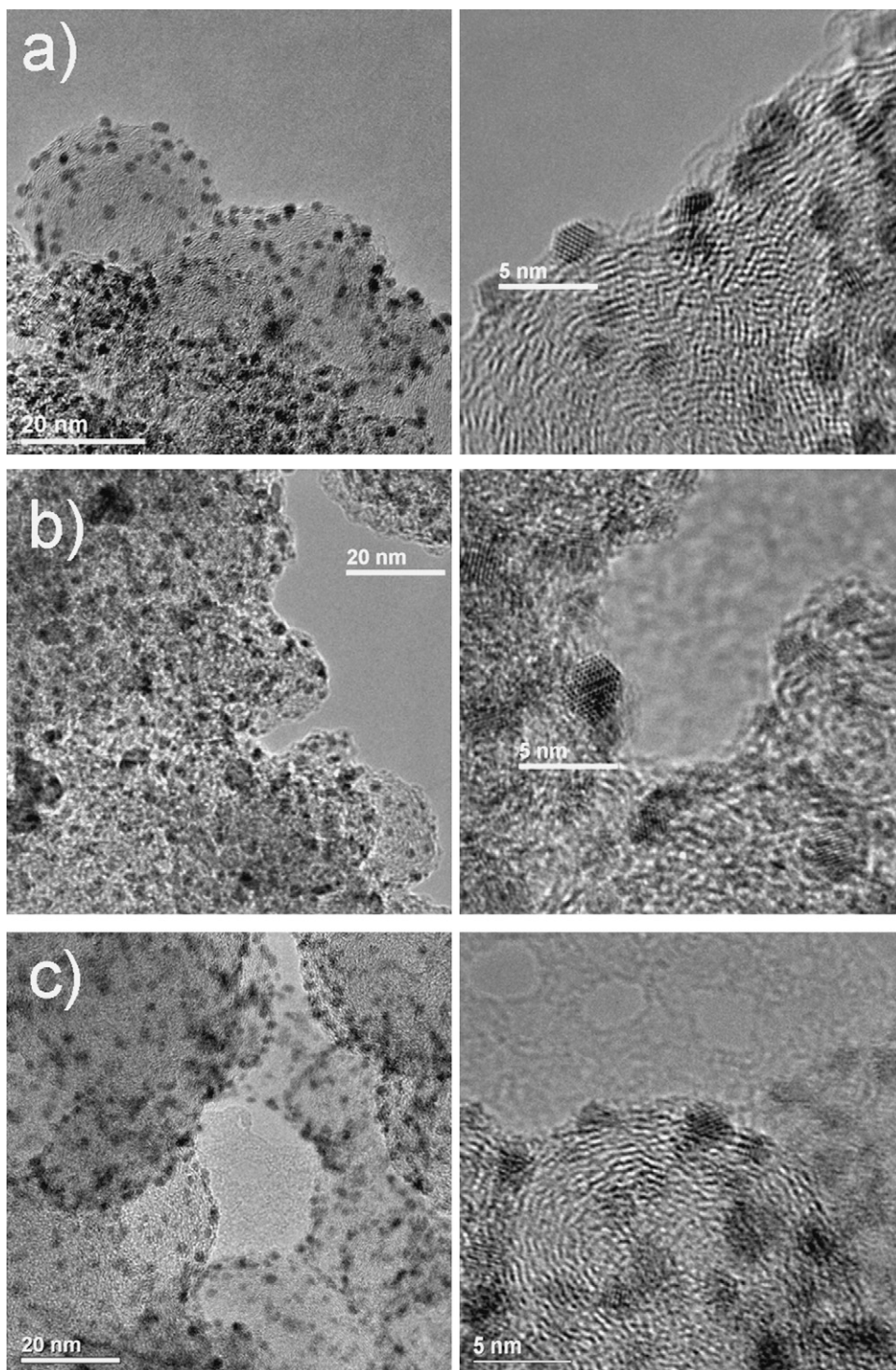


Fig. 2. HRTEM Micrographs of Pt/C nanoparticles synthesized using the FAM with (a) 3 mmol L^{-1} , (b) 4 mmol L^{-1} and (c) 5 mmol L^{-1} of thiourea.

Fig. 2a–c. From the HRTEM images, histograms of particle size distribution were built and shown in Fig. 3. Specially for those materials synthesized in the more concentrated solutions of thiourea, the distribution profiles (nearly a log-normal shape) indicate that the mechanism by which the crystal growths is by coalescence rather than by Ostwald ripening [21,22].

All the histograms in Fig. 3 are in the same scale, allowing an easy comparison among them. Considering the strong adsorption of sulfur atoms on metal surfaces, such as platinum, and comparing the different concentrations of thiourea during the synthesis, it is expected that by increasing the thiourea concentration in the synthesis media, the amount of large particles (>5 nm) will diminish and at the same time, the number of small particles will increase. From Fig. 3 it is clear that, indeed, the amount of large particles vanishes as the concentration of thiourea is increased. In general, the adsorption of thiourea on Pt nuclei clearly decreases the mean particle size of supported platinum nanoparticles, as shown in Fig. 4, where the mean particle size of Pt nanoparticles is plotted as a function of the concentration of thiourea used in the synthesis.

Analyzing the histograms, it was not observed a significant amount of very small nanoparticles, in the 0–1 nm range. One problem on acquiring images from very small- and therefore unstable-nanoparticles using TEM is the relatively high-intensity electron beam generally used in the transmission electron microscope, ca. 300 kV. The energy of the beam could be large enough to promote cluster aggregation, as recently shown to occur with Pt nanoparticles supported on carbon nan-

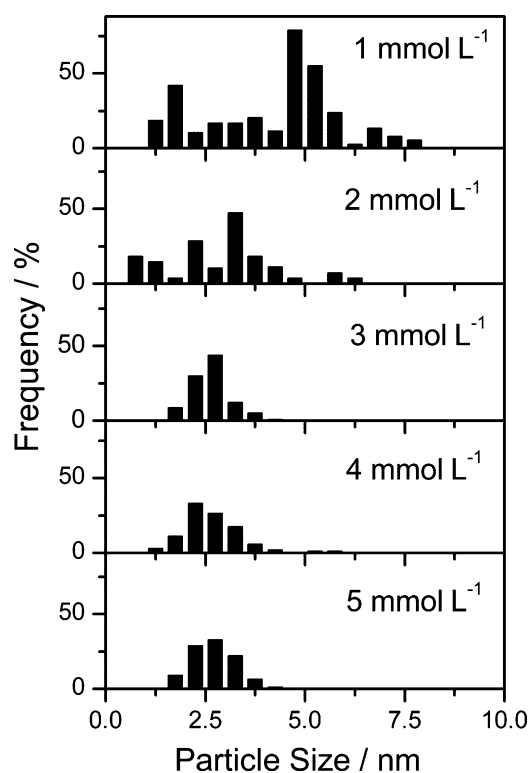


Fig. 3. Particle size distribution histograms determined from the HRTEM micrographs. The different thiourea concentrations used during synthesis are indicated in the figure.

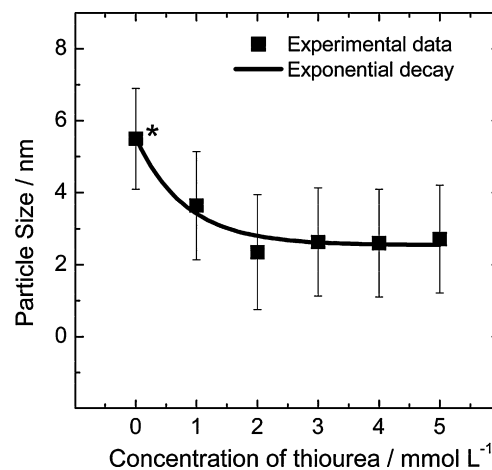


Fig. 4. (■) Particle sizes and the standard deviations, determined by HRTEM as a function of the concentration of thiourea used during synthesis. (—) Exponential fit to the experimental values. (*) Value extracted from Pt/C prepared by the FAM [2].

otubes [8]. This phenomenon, to which not much attention has been paid, is a limiting factor in HRTEM analysis. The so called “surface melting” and “quasimelting” are size-dependent processes and have been found to occur in some metals, such as Pb [23], Au [24] and Pt [8].

In the results presented here, the possibility of cluster aggregation (surface melting and/or quasimelting) due to the energy of the electron beam cannot be ignored. In this sense, it is clear that if the clusters of very small nanoparticles want to be “seen” by HRTEM, their size cannot be determined accurately. Indeed, crystal growth can occur even at room temperature as shown by Leite et al. [25], who studied the growth mechanism of SnO₂ nanoparticles in colloidal systems. They showed that SnO₂ particles in the size range 1–3 nm present coalescence when two or more grains assume the same orientation (Grain-Rotation-Induced Grain Coalescence model [26]). This results in a single crystalline cluster or chain at room temperature, formed with very low activation energy. Despite of the fact that the authors do not comment about the possible aggregation effect caused by the energy of the electron beam, at 300 kV, the growth of very small nanoparticles is expected because of the high surface area and high surface energy. Consequently, stabilization occurs by crystal growth, as predicted by the Ostwald–Freundlich equation [25].

Fig. 4 shows that the mean particle size diminishes as the concentration of thiourea in the synthesis medium is increased up to a value where a further increase in the concentration of thiourea does not produce significant changes in the particle size, i.e., 3–5 mmol L⁻¹ of thiourea in solution. This behavior closely follows an exponential decay, as indicated in Fig. 4. It is believed that thiourea molecules adsorbed on the just-formed nuclei are responsible for the inhibition of particle growth, as shown in the histograms in Fig. 3 complemented by the discussion in the previous sections. Furthermore, by considering the particle size dependence on the concentration of thiourea in solution (exponential decay-like) and the inhibition of particle growth by adsorbed thiourea, it seems that the amount of

thiourea adsorbed on Pt sites (the degree of coverage of thiourea, θ_{TU}) is proportional to the amount of thiourea in the bulk of the solution. In other words, the particle size (p) can be considered as inversely proportional to θ_{TU} :

$$\frac{1}{p(C_{TU})} = k\theta_{TU}, \quad (1)$$

where k is a constant of proportionality. However, it is more convenient to define another variable, τ , given by Eq. (2), which gives the relative size change due to the presence of TU:

$$\tau = \frac{1}{p(C_{TU})} - \frac{1}{p(C_{TU} = 0)} \quad (2)$$

The plot of τ versus the concentration of thiourea shows that τ increases as the synthesis solution is made more concentrated in thiourea. Taking into account that the parameter τ is related to the thiourea surface coverage, the plot shown in Fig. 5 is an adsorption isotherm-like plot. Note that for the higher thiourea concentrations in the synthesis media, τ tends to a limiting value, around 0.2 nm^{-1} . Recalling that τ is inversely proportional to the particle size and the later is a function of the thiourea surface coverage, θ_{TU} , this limiting value of τ is directly related to the maximum surface coverage of thiourea (θ_{TU}) on the platinum nuclei formed during synthesis.

According to the work of Bolzan et al. [17] the maximum degree of coverage of thiourea on platinum surfaces is 0.75, which is in agreement to value found for the adsorption of thiourea on Au(111) surfaces [14]. Taking into account that the maximum value of the parameter τ is 0.21 at a concentration of thiourea of 5 mM, it is possible to find a correlation between the two variables. In other words, it is possible to calculate θ_{TU} by means of a correlation factor, where $\theta_{TU} = 3.6\tau$. Using this relation, a plot of θ_{TU} versus C_{TU} , that is, an adsorption isotherm plot, can be build. This plot is shown in Fig. 6.

The adsorption of thiourea on Hg surfaces was studied by Parsons and Symons [12] and by Baars et al. [27]. They found that the adsorption process can be described by a Frumkin isotherm. In cases where adsorbate–adsorbate interactions take place, it is expected that the adsorption energy depends on the surface coverage. More specifically, if the adsorption energy depends linearly on the surface coverage and considering a Frumkin-type adsorption isotherm as discussed by Bolzan et al. [17], the

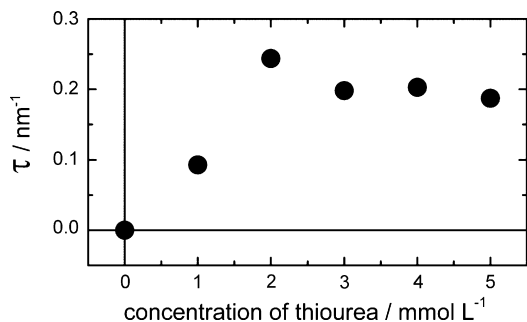


Fig. 5. Dependence of the parameter τ as function of the concentration of thiourea.

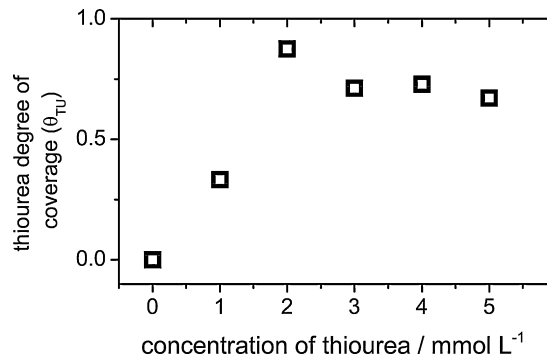


Fig. 6. Surface coverage of thiourea as a function of the concentration in the solution.

adsorption process can be described by the isotherm:

$$\frac{\theta}{1-\theta} = \frac{c_i}{55.6} \exp\left(-\frac{\Delta G_{\text{ads}}^{\circ}}{RT}\right) \exp(-a\theta)_{298} \quad (3)$$

where $\Delta G_{\text{ads}}^{\circ}$ is the standard Gibbs free energy of adsorption, c_i the concentration of species in solution and a is the Frumkin interaction factor, being positive for attractive adsorbate–adsorbate interactions and negative for repulsive interactions. The standard state related to this adsorption isotherm is given by [17,28]:

$$\frac{\theta}{1-\theta} \exp(+a\theta) = 1 \quad (4)$$

Resulting in $\theta_0 \approx 0.25$ for the value of a found for their system, $a = -4.3$ [17].

Taking into account the relationship between the particle size and the surface coverage of thiourea discussed above, an attempt was made to apply the Frumkin isotherm to the results of this work to obtain further knowledge on the adsorption process of thiourea on Pt nanoparticles. From Eq. (3), a plot of $\ln[(\theta/(1-\theta))(55.6/c_i)]$ versus θ_{TU} should give a linear relationship, from where it can be extracted the values of the interaction parameter (a), from the slope of the linear fit, as well as the standard Gibbs free energy of adsorption ($\Delta G_{\text{ads}}^{\circ}$) from the linear coefficient, extrapolating the straight line to $\theta_{TU} = 0$. As shown in Fig. 7, it was found that the values of

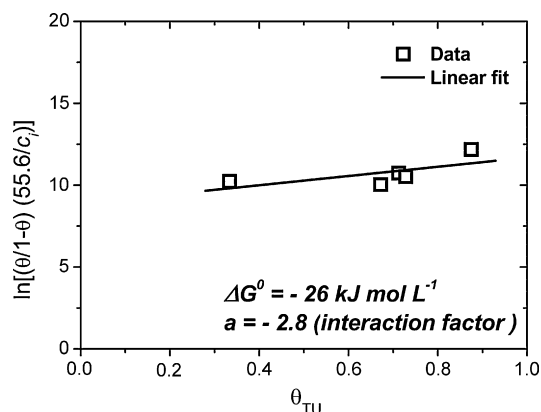


Fig. 7. Plot of $\ln[(\theta_{TU}/(1-\theta_{TU}))(55.6/c_i)]$ vs. θ_{TU} . Continuous line: linear regression using the least squares method.

$\ln(\theta_{TU}/(1 - \theta_{TU}))(55.6/c_i)$ versus θ_{TU} fit reasonable well a linear relationship.

The value of the Frumkin interaction factor a determined by linear regression was $a = -2.8$, smaller than the value obtained by Bolzan et al. [17], -4.3 . The negative value indicates that repulsive adsorbate–adsorbate interactions prevail, probably because of the interactions among protonated neighbor $-NH$ groups [17]. Using the obtained interaction factor a in equation (4), the surface coverage in the standard state (θ_0) is found to be 0.3. Indeed, a value of θ lower than 0.5 was expected, since $\theta = 0.5$ describes the coverage at the standard state for the Langmuir adsorption isotherm, where no interaction between adsorbed molecules is assumed to occur. From the linear coefficient, the value found for the standard Gibbs free energy of adsorption ΔG_{ads}° was -26 kJ mol^{-1} , which is also lower (in modulus) than the value obtained by Bolzan et al. [17], $\Delta G_{ads}^\circ = -40 \text{ kJ mol}^{-1}$. The difference appears to be large but it should be bear mind that the experimental conditions were quite different, that is, different supporting electrolytes and mainly different temperatures at which the adsorption took place (80°C , the temperature of the synthesis) in contrast to the experiments conducted by Bolzan et al., at 25°C in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$. Besides, the substrates in this work are platinum particles in the nanoscale range, where more than 30% of the atoms are surface atoms, in which the electronic properties could be very different from those of large polycrystalline surfaces. Also the Pt–Pt distances may be different, as observed by X-ray absorption [29]. Another point that should be stressed is that the results of this work were obtained in a non-electrochemical environment, different than that used by Bolzan et al. It is reasonable to expect that these differences, specially the temperature, will influence the energy of adsorption of thiourea and therefore the interaction factor (a) is expected to be smaller as the temperature is increased. The application of the Frumkin isotherm derived from experimental data indicates that the assumptions made on the relationship between the particle size and the amount of thiourea adsorbed on the Pt nuclei during synthesis seem to be valid. However, more accurate experiments need to be made in order to get more precise values of the parameters for the adsorption of thiourea on Pt nanoparticles in acid media and at temperatures above 25°C . Such experiments, however, are out of scope of the present work.

3.2. Cyclic voltammetric experiments

Regarding the synthesis of supported catalysts, such as Pt/C, for fuel cell applications, it is better to look for a clean method, in the sense that the species eventually used in the preparation procedure are easily removed after the synthesis unless they do not interfere in the electrochemical response. Cyclic voltammetry (CV) experiments were used to study the surface state of the materials prepared in the presence of thiourea.

Fig. 8 shows that the first cycle of a Pt/C catalyst synthesized in the presence of $1 \text{ mmol L}^{-1} \text{ TU}$ in a $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution is almost featureless, that is, without evidence of the characteristic voltammetric peaks of platinum in acid solution. This is due to the presence of strongly adsorbed TU on the Pt

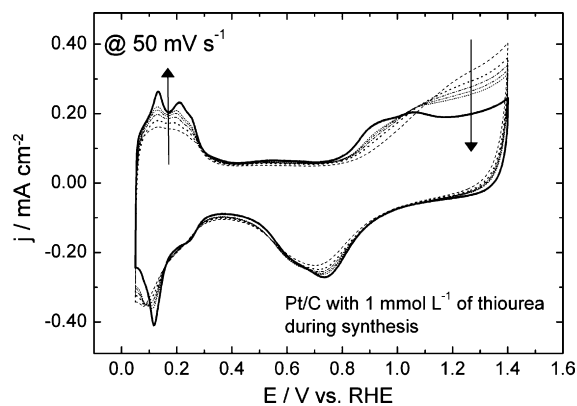


Fig. 8. Cyclic voltammograms obtained in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ at 50 mV s^{-1} for Pt/C (20 wt%) prepared with the FAM with 1 mmol L^{-1} of thiourea. Arrows indicate increasing number of cycles.

surface (or other adsorbates produced by dissociative adsorption of thiourea). The procedure employed in the electrode preparation, involves the attachment of the supported particles on the glassy carbon surface by means of a drop (approximately $40 \mu\text{L}$) of a diluted Nafion[®] solution (0.05 wt% in a 1:1 water/methanol solution) and Nafion[®] impurities, always present, produce some ill-defined profile on the first cycles of the voltammogram, so the effects shown above could be related to two processes, that is, the presence of Nafion[®] impurities and thiourea molecules adsorbed on the Pt surface. The latter, which we believe to be the main factor responsible for the voltammetric profile shown in Fig. 8, could be a drawback to the use of thiourea to control the size of Pt nanoparticles. However, the surface can be cleaned by potential cycling.

Upon repeated cycling between 0.05 and 1.4 V versus RHE, the characteristic profile of Pt gradually emerges as the surface becomes cleaner. In fact, as observed by Arvia and co-workers [30] as the potential is made more positive, thiourea oxidizes and generates soluble species. No alterations are observed in the double layer region showing that the cleaning of the surface is the only effect promoted by repeated cycling.

As shown in Fig. 9, using more concentrated thiourea solutions during synthesis, the first cycle of the as-prepared supported catalyst does not show the main features of the hydrogen

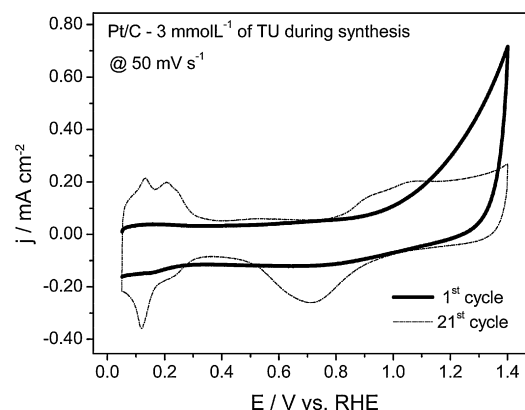


Fig. 9. Cyclic voltammograms of Pt/C (20 wt%) (FAM), $56 \mu\text{g cm}^{-2}$; $v = 50 \text{ mV s}^{-1}$; $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$; 3 mmol L^{-1} thiourea during synthesis.

region, obviously indicating the blocking effect of thiourea on the adsorption of hydrogen. By cycling these catalysts repeatedly the surface is practically cleaned, revealing a voltammetric profile very similar to that well known for Pt/C in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ electrolyte.

To complement the voltammetric study of the system, a different experiment was performed. For this experiment a 1 mmol L^{-1} thiourea solution was prepared in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ and the cyclic voltammetry of Pt/C prepared with the standard formic acid method (without thiourea) was recorded (Fig. 10). Cycling the electrode several times between 0.05 and 1.4 V clearly reduces the degree of coverage of adsorbed thiourea on the surface. This can be seen by the increasing currents in the hydrogen adsorption/desorption region and the decreasing currents above 1 V, probably due to the oxidation of thiourea. The first cathodic sweep reveals almost an absence of the platinum “oxide” reduction currents probably due to the blocking effect of TU on H_2O adsorption. This may indicate that the adsorption energy of TU molecules is higher than that of water molecules, so the preferential adsorption of TU displaces adsorbed H_2O on the surface. Although these remarks may appear a little speculative they are plausible and add to the understanding of the voltammetric profile and adsorption phenomena of thiourea on Pt/C.

It is interesting to note that in spite of the presence of thiourea in solution, the voltammetric profile after several cycles approaches that of clean Pt due to the consumption of thiourea near the interface. This behavior was expected, considering both the potentiodynamic characteristic of the voltammetric techniques and the continuous oxidation of TU which increases its concentration gradient giving rise to an apparently thiourea-free surface even when TU (or its oxidation soluble products) are present in the solution. In unstirred solutions the thickness of the Nernst diffusion layer is a function of time and, therefore, after enough time, the TU molecules will arrive at the Pt surface, blocking the hydrogen adsorption/desorption region. Indeed, creating a TU flux towards the surface by means of forced convection, characteristic of the rotating disk electrode,

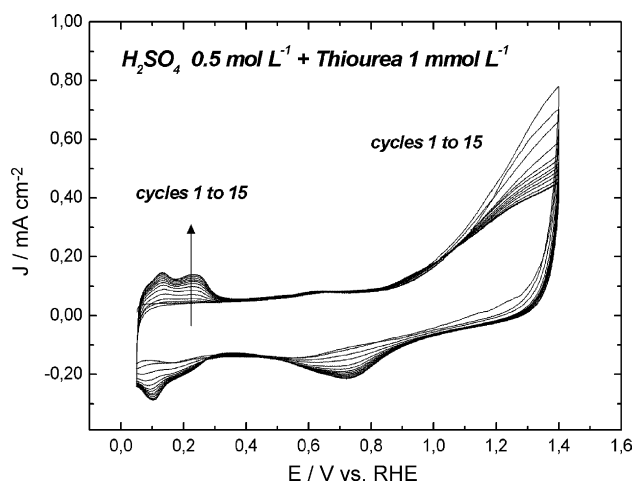


Fig. 10. Cyclic voltammograms obtained at 50 mV s^{-1} of Pt/C in a $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4 + 1 \text{ mmol L}^{-1}$ thiourea solution. Arrows indicate increasing number of cycles.

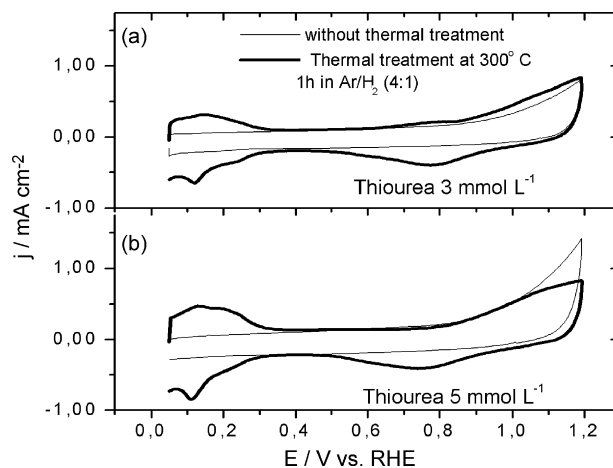


Fig. 11. Cyclic voltammograms for Pt/C synthesized with (a) 3 mmol L^{-1} and (b) 5 mmol L^{-1} of thiourea: (---) without thermal treatment and (—) with thermal treatment at $300 \text{ }^\circ\text{C}$ in (4:1, v/v) Ar/H_2 for 1 h. $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$, 20 mV s^{-1} , room temperature.

and by keeping it rotating at low potentials, i.e., 0.05 V, for a short time (around 30 s) the first cycle (not shown) clearly reveals the absence of the hydrogen adsorption/desorption region, an indicative of the presence of TU molecules adsorbed again on the platinum surface.

As an alternative to the cyclic voltammetric treatment, it was investigated the cleaning effect of a thermal treatment at $300 \text{ }^\circ\text{C}$ under a 4:1 (% v/v) Ar/H_2 atmosphere for 1 h on a Pt/C catalyst, prepared in the presence of thiourea. Fig. 11 shows the first cycle of the voltammetric profile for Pt/C synthesized in the presence of 3 and 5 mmol L^{-1} of thiourea: (i) without and (ii) with thermal treatment. The cleaning effect of the thermal treatment (TT), is evidenced by the definition of the hydrogen adsorption/desorption region in comparison to the as-prepared material. Also, there are practically no changes in the double layer region, indicating that the thermal treatment does not induce appreciable changes in the electrochemical surface area.

The effect of potential cycling was also investigated for the thermally treated materials. In general, it can be observed (Fig. 12) the same behavior described above, i.e., an increas-

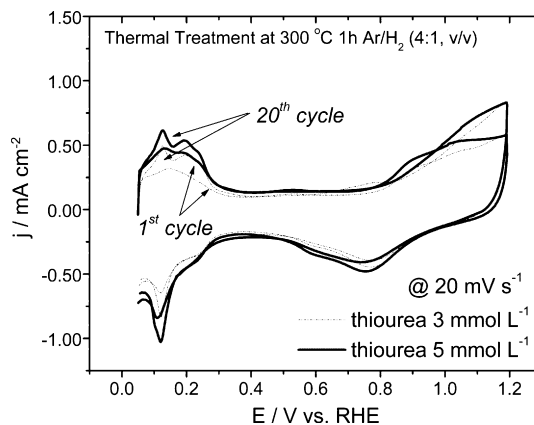


Fig. 12. First and 20th cyclic voltammograms for Pt/C synthesized by the formic acid method with different TU concentrations and submitted to a thermal treatment at $300 \text{ }^\circ\text{C}$ in (4:1, v/v) Ar/H_2 for 1 h. 20 mV s^{-1} , $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$.

ing definition of the hydrogen adsorption/desorption region with cycling, due to a cleaning of the surface. Furthermore, it should be noticed that a relative definition is already present even for the first cycle, for both Pt/C materials, synthesized with 3 and 5 mmol L⁻¹ of TU, submitted to a thermal treatment at 300 °C for 1 h in a 4:1 (v/v) Ar/H₂ mixture. After 20 cycles, the profile is very similar to that of a clean carbon-supported platinum. As a result, the thermal treatment at 300 °C in a 4:1 (v/v) Ar/H₂ atmosphere for 1 h can be employed as a convenient cleaning procedure for the materials synthesized in the presence of thiourea.

4. Conclusions

The results of this work show that the adsorption of TU decreases the mean particle size of carbon-supported Pt nanoparticles synthesized by chemical reduction. Based on the mean particle size determined by HRTEM, the degree of coverage of thiourea adsorbed on Pt nuclei during synthesis was estimated and it was found that the adsorption of thiourea on carbon-supported platinum nanoparticles can be described by a Frumkin adsorption isotherm. The inconvenience of the synthesis procedure described here is the TU that remains adsorbed on the surface of the catalyst, but it can be removed by potential cycling or by thermal treatment at 300 °C in a 4:1 (v/v) mixture of Ar/H₂. Apparently, the thermal treatment does not change the electrochemical active area, as shown by cyclic voltammetric experiments, thus providing an easy way to clean the Pt/C surface from adsorbed thiourea molecules. It must be pointed out here that thiourea was used as a convenient probe molecule to study the effect of adsorption on the growth of Pt nanoparticles. From the practical point of view of particle size control it is obvious that other molecules may be studied and eventually better candidates than TU may be found.

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