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Investigation of the electrochemical behavior of L-cysteine in acidic media

André H.B. Dourado *, Rodrigo Queiroz, Marcia L.A. Temperini, Paulo T.A. Sumodjo †

Instituto de Química, Universidade de São Paulo, Av. Prof Lineu Prestes, 748 São Paulo, SP, Brazil

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ABSTRACT

Cysteine is an important organic molecule in electrochemistry. It can be used as an electrode modifier and is responsible for the adsorption of many proteins. Although it is a well-studied molecule, cysteine's behavior and mechanism of oxidation remain unclear in the literature. The current study is focused on investigating the electrochemical behavior of this molecule in acidic media on a Pt electrode using electrochemical techniques and Raman spectroscopy. The adsorption process appears to be similar to the one proposed in the literature (i.e. a monoelectronic oxidation). The adsorbed species appear to strongly interact with one another, and therefore, this adsorption is more suitably described by a Temkin model. The Raman spectra indicate that the adsorption is most likely due to the thiol group on the side chain of the amino acid. In addition, the carboxyl group interacts more with the electrode than the amino group. The oxidation of these adsorbed species is achieved by 5 electrons, and supports the formation of the previously proposed species. Other experiments suggest that the adsorption does not occur in a single step. Using voltammetry and pseudocapacitance adsorption model interpretations, a monoelectronic rate-limiting step was detected, which indicates the existence of a more complex mechanism for the oxidation of cysteine on platinum.

1. Introduction

The study of the electrooxidation of cysteine (cys) on solid electrodes is important due to cysteine's use as an electrode modifier in biosensors [1] and its involvement in protein chemisorption processes [2], this process also being influenced by the pH of the system, since this variable controls the protonation state of the biomolecule; that is to say, its charge and its attraction or repulsion with surfaces [3]. Most studies with a fundamental approach on the electrooxidation reaction and mechanisms are dated from the 80s or before (e.g. Davis and Bianco's in the 60s [4]), where voltammetric and chronoamperometric techniques indicated that the adsorption of this molecule involved the thiol group on its side chain. Therefore, authors reported a mechanism consisting two steps as follows: a monoelectronic oxidative adsorption followed by multielectronic oxidation of the adsorbed species [4].

$$R-SH+Pt\rightarrow R-S^{\cdot}Pt_{(ads)}+e^{-}+H^{+} \tag{1}$$

$$R-S^{\cdot}Pt_{(ads)}+3\ H_2O\rightarrow R-SO_3^{-}+5\ e^{-}+6\ H^{+} \tag{2}$$

$$R-S^{\cdot}Pt_{(ads)}+2\ H_2O\rightarrow R-SO_2{}^{\cdot}Pt+4\ e^{-}+4\ H^{+} \tag{3}$$

$$R=H_3N^{+}C_{\alpha}(COO^{-})CH_2-.$$

Davis and Bianco performed their experiments in full protonated media [4] and proposed a pre-equilibrium step involving; the deprotonation of the carboxylic acid group, which suggested that the adsorbed species was a negatively charged molecule [4].

Because the transfer of more than one electron most likely does not occur due to a tunneling effect, the oxidation of the adsorbed species cannot occur in a single step. Therefore, Pardac and Koryta [5] proposed a new step, in one of the few studies of cysteine on Pt electrodes reported in the literature, where a sulfone species is generated (step 3). More recent studies (e.g. Johnson's group [6–8]) did not propose new steps but sulfones were not identified in the ex situ mass spectrometry experiments, which only provided information about cystine and cistenic acid, as oxidized species [6].

Currently, there are a few studies on the electrochemical behavior of cys on different noble metals, such Pd [9]. This study was based on previous ones performed on Au and also suggested the possibility of the generation of sulfone species; but, different from Pardac and Koryta [5], the authors assume that instead of a S–Pt bond, a S–H one would be formed. This idea was only supported by cyclic voltammetry measurements. This organic function was not detected by ex-situ characterization carried out by Johnson's group [6] or by Cabrera et al. [9]. In fact, during the last two decades, most publications dealt with cys as corrosion protector [10] or about its adsorption using DFT calculations [11, 12] or about the structure of these adsorbed species using Raman spectroscopy [13,14]. Therefore, the literature about the electrochemical behavior of cys, it still contradictory and new reaction steps are still possible to be postulated; so, the aim of the current study was to gain

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* Corresponding author.
E-mail address: dourado@iq.usp.br (A.H.B. Dourado).
† In memoriam.

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further insight into the adsorption and electrooxidation of cys on Pt electrodes in acidic media to determine a more accurate mechanism that explains the behavior of this amino acid on platinum surfaces.

2. Experimental

2.1. Chemicals

Chlorohydrated cysteine (Sigma-Aldrich) and sulfuric acid were used without further purification.

2.2. Electrochemical measurements

All of the experiments were performed at room temperature under a N_2 atmosphere. The electrochemical cell was a conventional three electrode one, a Pt black (0.02 cm^2, geometric area) disk was used as the working electrode, a Pt wire was employed as the counter electrode, and all of the potentials are referred to the Ag|AgCl (KCl_{sat}) electrode. The experiments were performed with a Princeton Applied Research potentiostat/galvanostat 273A. For some experiments, the electrode was activated by a step potential program ($E_1 = -0.2$ V, $t_1 = 5$ s, $E_2 = 1.5$ V, $t_2 = 5$ s, this was repeated three times, finishing with E_1). All of the potential perturbation programs are shown in the figures.

2.3. Spectroscopic measurements

The substrates consist of surface-enhanced Raman spectroscopy (SERS) active Au electrodes with a Pt thin film over layer. This type of substrate has been adopted because it presents the same borrowing SERS effect [15,16]. To prepare this substrate, a Au electrode (Au, area = 0.11 cm^2) was mechanically polished with sand paper, chemically cleaned with $KMnO_4$ and polished with an Al_2O_3 suspension (0.30 and 0.05 μm). This substrate was electrochemically activated by cyclic voltammetry sweeping the potential from −0.25 V to 1.2 V, for 25 cycles at 100 mV s^{-1} followed by modification via the electrodeposition of a thin Pt film. The procedure was based on the one proposed by Weaver et al. [15], except for the Na_2HPO_4 supporting electrolyte replaced by K_2HPO_4 0.7 mol L^{-1} because potassium ions provide more uniform films [17]. The Pt film was galvanostatically prepared by applying a cathodic current density of 40 mA cm^{-2} for 40 s.

The SERS spectra were obtained using a Renishaw InVia spectrometer coupled to a Leica microscope with a water immersion objective lens with 63× magnification and NA = 0.9.The laser excitation was 785 nm and its power was 17 μW at the sample, and the illuminated area by the laser is 5 $μm^2$.

3. Results and discussion

3.1. Adsorption evidence

Fig. 1 shows the voltammogram obtained after electrode activation in a cys 0.1 mol L^{-1} solution.

The anodic current starts to increase at 0.4 V and does not reach a diffusion limit. In addition, the anodic current is not substantially affected by switching the potential sweep in the reverse direction. The oxidation current continues until a potential is more negative than 0.4 V, the same where the oxidation begins. Since this oxidation current was not observed in the blank, it can be only due to cys oxidation but it was not possible to verify an oxidation peak or get more information from it. Because of this, the approach was changed, and instead of simultaneously studying all the processes that occur in the entire potential range, they were divided. After the activation process the first attempt involved the polarization of the electrode at 0.4 V for 800 s, which led to an anodic transient current that was related to Eq. ((1). Then, the electrode was rinsed with distilled water, and it was placed in a cell containing only the supporting electrolyte to record the voltammogram, which is shown in Fig. 2.

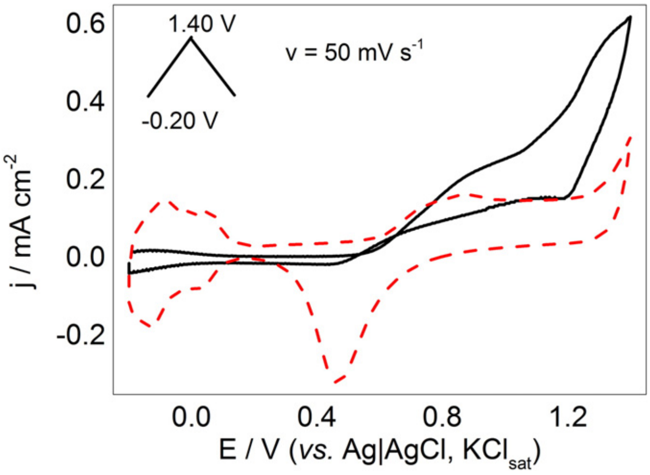

Fig. 1. j/E potentiodynamic profiles of a Pt electrode in a 0.1 mol L^{-1} cys solution in 0.5 mol L^{-1} H_2SO_4 (solid line) with blank (dashed line). The E/t applied program is depicted in the figure.

Since the electrode was rinsed, all species from the cys solution that were not chemisorbed on the electrode were removed. That's why the intensification of the anodic current observed as a peak placed at 1.1 V can be only due to the presence of strong adsorbed species (SAS), which would corroborate the formation of $cys^{\cdot}_{(ads)}$, as expected by Eq. ((1).

Using these adsorption conditions, the cys concentration (C) was varied, and by sweeping the potential towards negative values, the measured charge of the hydrogen adsorption blocking (Q_{block}) was estimated as the coverage degree of the surface (Fig. 3).

The data were first fitted by a Langmuir type isotherm. However, better results were obtained with a Temkin model, which suggests that SAS interacts strongly with itself. The heterogeneity or Temkin factor (r) was positive, indicating repulsion [18], and its magnitude indicates a coherent strong interaction [18], which may be due to the repulsion of the protonated amine functions. This result is in agreement with the one proposed by Samec and co-workers [19].

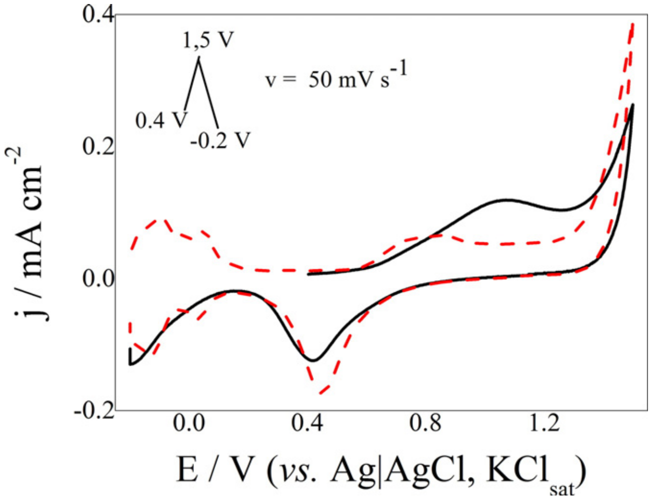

Fig. 2. j/E potentiodynamic profiles of a Pt electrode after the adsorption procedure (black line) in a cys free H_2SO_4 0.5 mol L^{-1} electrolytic solution. The blank experiment (red line) is also shown along with the E/t applied program.