

## The electrooxidation of cysteine on Pt electrodes, a spectroscopical point of view.

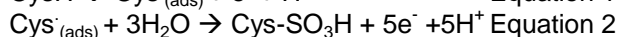
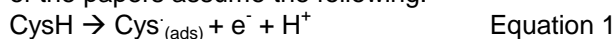
**André H.B. Dourado (PG)<sup>1\*</sup>**, Susana I.Cordoba de Torresi (PQ)<sup>1</sup>, Márcia L.A. Temperini (PQ)<sup>1</sup>, Paulo T.A. Sumodjo (PQ)<sup>1</sup>

<sup>1</sup>Instituto de Química da Universidade de São Paulo, Av. Prof. Lineu Prestes, 748, 05508-000, São Paulo, Brazil

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### Introdução

Cysteine (cys) is an aminoacid important for understanding the adsorption of proteins and their interaction with metallic substrates. Also, this molecule has been studied for a long time; however, even the most detailed works on its mechanism of oxidation<sup>1</sup> do not respond to all questions, such as, how many steps are on this reaction? Which species are formed? And how can we control it? The majority of the papers assume the following:



The first step is probable; it is a one electron transfer oxidation, but the second one is a multi-electron process, an improbable reaction. Just one work suggested an intermediate step<sup>1</sup>, but the presenting species were until now, not proved by any characterization technique.

The present work studied the adsorption/oxidation behavior of cys on different pH values.

### Resultados e Discussão

A Pt disk was used ( $r=5\text{mm}$ ) as working electrode, a Pt grid as counter and Ag|AgCl ( $\text{KCl}_{\text{sat}}$ ) as reference electrodes. The supporting electrolyte was  $\text{Na}_2\text{SO}_4$   $0.5 \text{ mol L}^{-1}$ , pH adjusted by the addition of  $\text{H}_2\text{SO}_4$  or NaOH.

For the first experiment (null pH, full protoned) the potential was fixed at 0.4 V, for adsorption of cys, and at 0.6-1.2V for its oxidation while the IR spectra were recorded. To evade  $\text{CO}_2$  contaminations, the system was continually purged by  $\text{N}_2$  and the sample was desaturated. Also, after each oxidation potential, the electrode was cleaned by piranha solution imertion.

The adsorption spectra presented a band at  $599 \text{ cm}^{-1}$ , that was assigned to C-S stretch of adsorbed cys, some vibrations related to  $-\text{COO}^-$  can be seen, suggesting that this group was closer to the surface than  $-\text{NH}_3^+$ . Similar structure was proposed by Brolo *et al.* for the same molecule on  $\text{Ag}^2$ . The spectra at potential of 0.6 V did not differ from the observed at 0.4 V, the subtraction of the adsorption spectrum gave just the base line.

At 0.8 V some new bands can be seen, probably, due to the  $-\text{NH}_3^+$  group, what suggests that at this potential this group can interact more with the surface, and a new conformation could be seen.

Also, a band at  $1324 \text{ cm}^{-1}$  was observed. This region is characteristic of sulfones ( $-\text{SO}_2-$ ), so a new oxidized species could be detected. This new functional group corroborates the suggestion of Pardac and Koryta<sup>1</sup>.

Higher potential values also showed vibrations related to  $-\text{SO}_3\text{H}$ , as expected by equation 2. At 1.0 and 1.2 V, a band appeared at  $2341 \text{ cm}^{-1}$  which was not expected. By the wave number and its shape, it could be due to  $\text{CO}_2$ . This could not be due contaminations, so that, a Kolbe or a non-Kolbe reaction could take place, consuming the  $-\text{COO}^-$  to generate  $\text{CO}_2$ .

The same experiment was performed at pH=3 (carboxylic group deprotonates) and 7 (same situation). At both pHs, it was possible to detect  $-\text{NH}_3^+$  bands form the adsorption potential onwards, which could be due to a major contribution of a conformation with this group close to the surface and alternating with  $-\text{COO}^-$ . Bands due to sulfone species were just seen at more positive potentials, such as 1.0 V, suggesting that its formation involves proton dependent steps. Also, at pH=3,  $\text{CO}_2$  formation was expressive just at 1.2 V and it was much lower than the observed at pH=0. At pH=7 the same behavior was observed.

Some of the bands observed on oxidation spectra are not so clear at the three pH values used until now, other oxidation states of S could be expected. No literature data on this field was found.

### Conclusões

It was possible to observe that the pH is an important chemical variable for the cys oxidation, due to strong dependence of the production of some species that were not presented on spectroelectrochemical literature until now.

A side reaction (Kolbe reaction mechanism) is also detected. The pH dependence of it can be a strong tool to control it.

### Agradecimentos

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<sup>1</sup> Pardac, J.; Koryta, J. *J. Electroanal. Chem.* **1968**, 17, 167.

<sup>2</sup> Brolo, A.G.; Germain, P.; Hager, G. *J. Phys. Chem. B* **2002**, 106, 5982.