XPS study of the displacement of a Cu monolayer on Pt by mercaptopyridines

A.Gutiérrez*, M. F. López, C. García-Alonso and M. L. Escudero

Departamento de Corrosión y Protección, CENIM
Avda Gregorio del Amo, 8, E-28040 Madrid, Spain

C. Alonso and A. B. Salomón

Departamento de Química-Física Aplicada, Universidad Autónoma de Madrid
E-28049 Cantoblanco, Madrid, Spain

I. Introduction

Mercaptopyridines (MP) are organic molecules composed of a pyridine ring (C_5H_5N) with an SH radical, whose position with respect to the N atom determines the chemical properties of the molecule, and gives them name: 2-MP and 4-MP. These molecules are used in biochemical applications, to promote charge transfer between gold or platinum electrodes and cytochrome *c*, which is the generic name of a group of hemoproteins [1]. Due to their electroactive character, it is necessary to perform electrochemical experiments to study the chemistry of these proteins in the physiological medium. The poor charge transfer between the proteins and the electrodes makes necessary the use of charge transfer promoters. On the other hand, MP's have been reported to inhibit electrodeposition of metals on a Pt electrode when previously deposited on it [2,3]. It is, thus, important to study the effects of MP on the surface chemistry of Pt electrodes.

Electrodeposition of metals from an electrolyte is usually performed by applying an electrostatical potential higher than the equilibrium potential between the metallic ions in the solution and the metallic atoms on the electrode. In some cases, electrodeposition can occur for potentials below this equilibrium potential. In this case only one monolayer or submonolayer adsorbs on the electrode surface and the process is called *underpotential deposition* (upd) [4]. The phenomenon of *upd* occurs when the adsorbate adatoms are more strongly bound to a foreign substrate than to a substrate of their own kind. Recently, it has been suggested that the valency of *upd* Cu on Pt is close to +1 [5]. In order to better understand the mechanisms of *upd* deposition of Cu we have investigated the effects of 2-MP and 4-MP in solution on a predeposited *upd* monolayer of Cu on Pt.

2. Experimental

A Cu monolayer was first deposited in the *upd* regime onto a polycrystalline Pt electrode by exposing it to a $1\cdot10^{-3}$ M $CuSO_4$ solution in 0.5 M H_2SO_4. This solution was then substituted by a 2-MP or 4-MP solution in water, which was led interact with the electrode at open circuit. The Pt electrode is then transported to the XPS chamber in a glass cell under nitrogen atmosphere while immersed in the MP solution. By transferring the samples to the UHV chamber, they are briefly exposed (5-10 seconds) to the atmosphere. A direct contact with the air was, however, avoided by leaving a solution drop on the samples surface. This remanent solution was removed during pumping in the vacuum chamber. XPS measurements were performed using a VG-CLAM hemispherical analyzer, with an energy resolution of ~0.6 eV. The base pressure in the UHV chamber during measurements was 1×10^{-9} mbar.

Results and Discussion

Fig. 1 shows XPS spectra at the Cu-2p core level of one monolayer of Cu electrodeposited on a polycrystalline Pt electrode in the *upd* regime (top) and the same electrode after interacting with a solution of 4-MP in water. The same was obtained in a 2-MP solution. As can be observed, the previously deposited Cu monolayer has been completely removed after interaction with the MP solution. This suggests that the MP molecules are more strongly bound to the Pt surface than the Cu atoms.

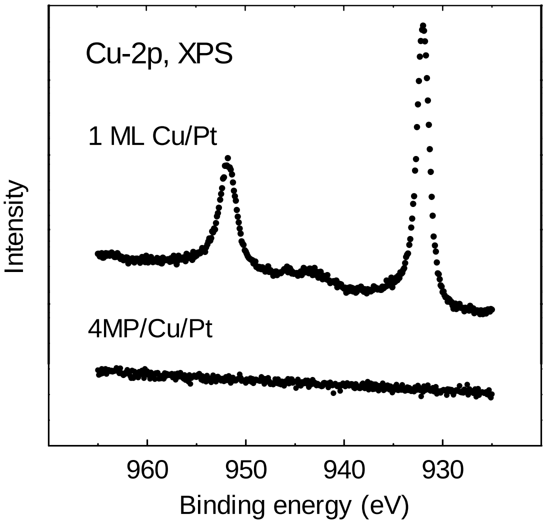

Figure 1: XPS spectra at the Cu-2p core level of one monolayer of Cu electrodeposited on a polycrystalline Pt electrode in the *upd* regime (top) and the same electrode after interacting with a solution of 4-MP in water.

Fig. 2 shows XPS spectra at the S-2p core level of 2-MP and 4-MP adsorbed on the Pt electrode after the Cu monolayer has been removed. From voltammetric experiments, the amount of adsorbed 2-MP and 4-MP has been determined to be one monolayer in all cases. A least-squares fitting procedure was employed to analyze the experimental data. As can be seen in the figure, all spectra can be decomposed into three components. The dash-dotted subspectrum, at ~169 eV, can be assigned to sulphates. They probably originate by oxidation of the MP molecules by oxygen diffusion through the water drop during sample transport to the UHV chamber. In order to identify the other two components we have measured some reference compounds, shown in Fig. 3. In Fig. 3a, XPS spectra of pure, polycrystalline 2-MP and 4-MP are shown. They have been previously mixed with either water or ethanol in order to fix them to the sample-holder. Oxidation occurs at

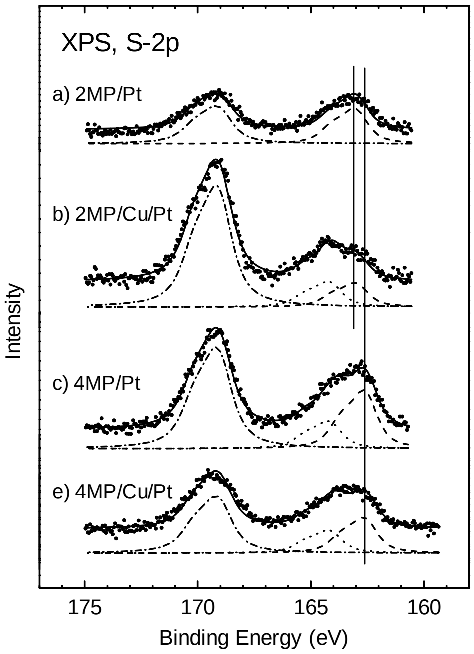

Figure 2: XPS spectra at the S-2p core level of 2-MP and 4-MP adsorbed on the Pt electrode after the Cu monolayer has been removed. The solid line through the data points is the result of a least-squares fitting procedure, giving the three components shown as subspectra.

the surface, as evidenced by the small sulphate component observed in all cases. The solid subspectrum can be assigned to an intermediate oxide. The dashed component corresponds to a sulphur atom in an organic environment, i.e., to MP. Fig. 3b corresponds to aldrithiol adsorbed on Pt and to sulphides, respectively. Aldrithiol is an organic molecule composed of two 4-MP rings bound by the S atoms. In this case both the dashed and dotted components are observed. The dotted component can be, thus, associated to S-S bonds in the organic matrix. We can exclude the presence of sulphides in the spectra of Fig. 2 because the sulphide spectrum of Fig. 3 can not be decomposed in two subspectra, and its binding energy position and width are slightly different to the components observed in Fig. 2.

Taking into account the obtained results on the reference compounds, we can assign the dashed component in Fig. 2 to MP molecules directly bound to Pt through the S atom. This adsorption geometry has already been reported in previous works on 4-MP deposited on Pt studied by surface techniques like EELS, Auger, or Raman Scattering [6,7]. The binding energy shift observed in this component between 2-MP and 4-MP (see vertical lines) is probably associated to the different electronic environment around the S atom due to the proximity or not of the N atom. In the case of 2-MP, the N atom is close to the Pt surface, allowing the formation of chelate structures of type S-Pt-N, which can lead to the observed binding energy shift. On the other hand, the dotted component observed in Fig. 2 can be assigned to organic complexes made of more than one MP molecule, in which S-S bonds are possible, since the same component is observed in the spectrum of aldrithiol together with the S-Pt component (Fig. 3b). In a very recent work, the formation of such organic complexes has been suggested to occur through an oxidation reaction of two MP molecules adsorbed on Pt [8].

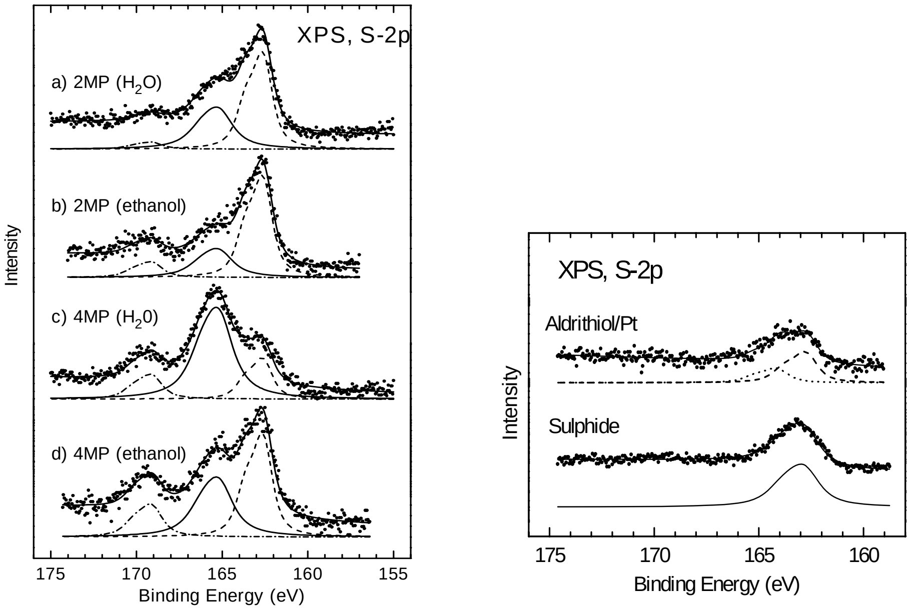

Figure 3: XPS spectra at the S-2p core level of: (a) polycrystalline 2-MP and 4-MP, previously mixed with water or ethanol in order to fix them to the sample-holder; (b) aldrithiol and sulphides electrodeposited on Pt.

In summary, we have performed an XPS study of the effects of 2-MP and 4-MP on a Cu monolayer electrodeposited on a Pt electrode in the *upd* regime. The Cu monolayer is completely displaced both by 2-MP and 4-MP, suggesting a stronger bonding of the MP through the S atom as compared to Cu. Two components are observed in the S-2p spectra (additionally to a sulphate component), and assigned to R-S-Pt bonds and R-S-S-R bonds, respectively, where R represents the pyridine ring. The chemical shift observed between 2-MP and 4-MP in the first of these components suggests the formation of structures of type Pt-S-N in the case of 2-MP, changing in this way the electronic environment around the S atom with respect to 4-MP

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