On the electrochemical behavior of formamidine disulfide on gold electrodes in acid media

William Cheuquepán, José Manuel Orts *, Antonio Rodes

Departamento de Química Física e Instituto Universitario de Electroquímica, Universidad de Alicante, Apartado 99, E-03080 Alicante, Spain

ABSTRACT

The adsorption and reactivity of formamidine disulfide (FDS) were studied at gold single crystal and thin film electrodes in perchloric acid solutions and the results of cyclic voltammetry and in situ infrared spectroscopy (SNIFTIR and ATR-SEIRAS) experiments compared with those previously obtained with thiourea (TU). In addition, optimized geometries and theoretical harmonic vibrational frequencies were obtained for adsorbed FDS, TU and thioureate from plane-wave DFT calculations using periodic surface models. These results were compared in the case of TU and thioureate to those previously obtained with a model Au cluster surface with (111) orientation. In the case of FDS, weak adsorption takes place with the S–S bond essentially parallel to the metal surface. No specific bands for adsorbed FDS can be identified in the experimental ATR-SEIRA spectra. These latter spectra suggest that adsorbed thioureate species are spontaneously formed upon dissociative adsorption of FDS when dosing this molecule at open circuit. Some of the adsorbed thioureate species undergo reductive protonation giving rise to a mixed adlayer formed by adsorbed thioureate and thiourea in a surface process which is faster when a controlled potential of 0.70 V is applied. In agreement with the observations reported when dosing TU, the ratio between TU and thioureate adsorbates is found to depend on the electrode potential, being higher for potentials close to the hydrogen evolution limit and decreasing for higher potential values.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Formamidine disulfide (FDS, $(NH_2)(NH)CS-SC(NH)(NH_2)$) has been reported as the main product of thiourea (TU, NH_2CSNH_2) electrooxidation on gold and platinum electrodes when working at moderate potentials in diluted acidic TU solutions [1–4].

$$2 \quad \longrightarrow \quad + \quad 2H^+ \quad + \quad 2e^- \qquad (1)$$
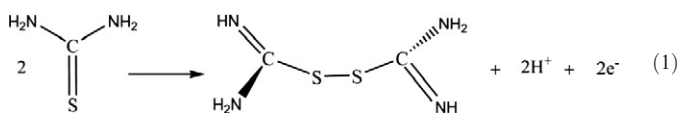
In the case of gold electrodes, the formation of FDS is paralleled by the oxidative dissolution of gold that takes place at high TU concentrations via the formation of gold-TU complexes [5–7].

The electrochemical behavior of FDS has been studied in connection with that of thiourea [2,8–11]. Several authors reported that the presence of FDS has a strong catalytic effect on the gold dissolution reaction in acidic thiourea solutions [9,11]. The presence of adsorbed TU and FDS species at metal electrodes and their role in the processes described above is a point still open to discussion. As expected from the strong sulfur-metal interaction, a variety of surface techniques has allowed the detection of irreversible adsorbed TU on gold and platinum electrodes in contact with TU-containing solutions [4,6,12–16]. Surface-Enhanced Raman Scattering (SERS) spectroscopy experiments proved the bonding of TU to the metal surface through the sulfur atom [12,13, 16–18]. Moreover, both external reflection infrared spectra [6] and surface-enhanced infrared reflection–absorption spectra obtained under attenuated total reflection conditions (ATR-SEIRA) [17] showed bands assigned to the symmetric and asymmetric NCN stretching modes of adsorbed TU. The observation of the latter band implies a significant tilting of the S–C axis with respect to the surface normal. The conclusions on the adsorption geometries of adsorbates (namely, TU and related species) derived from the analysis of spectroscopic data can be supported by theoretical calculations. In this respect, the stability and the interaction with water of TU [19] and thioureate [20], as well as the interaction of TU with anions [21], metallic cations [22], and coordination compounds [23] has been addressed in the past. Regarding the interaction with bulk metals, the only theoretical study dealing with the adsorption of TU, thioureate and FDS is due to Patrito et al. [24], who studied these species on cluster models of the Ag(111) surface, using DFT and MP2 methods. In that study, the effects of external electric field and solvation were also addressed. Regarding the interaction of TU and related species with gold surfaces, we are not aware of any theoretical study other than the DFT study carried out by our group

* Corresponding author.
E-mail address: JM.Orts@ua.es (J.M. Orts).

[17]. The optimized adsorption geometry for TU on clusters modeling the Au(111) surface was found to correspond to a unidentate configuration for adsorbed TU on top surface sites via the sulfur atom and with the C–S bond tilted by 45° from the normal. This result confirmed the conclusions derived from the observation of the asymmetric NCN band in the in situ infrared spectra [6,17].

Another point of interest that can be addressed by combining spectroelectrochemical data and a theoretical analysis regards the potential-dependent processes undergone by adsorbed thiourea and the eventual formation of adsorbed FDS. Cyclic voltammograms for gold electrodes in diluted TU solutions are characterized by the presence of surface redox processes in the so-called double layer region of the bare electrode for which different origins have been proposed. Those observed in neutral solutions between − 1.10 and 0.40 V SCE were related by Azzaroni et al. [25] to the changes in the in situ STM images as a function of the electrode potential. These authors interpreted the observed ladder-like structures as due to adsorbed FDS, which can be reduced to adsorbed TU or oxidized yielding adsorbed sulfur. On the other hand, a surface redox process at potentials between 0.60 and 0.90 V RHE for gold electrodes in acidic TU-containing solutions has been related to the deprotonation of adsorbed TU to form adsorbed thiourate species [17]. Note that this proposal is connected to previous suggestions regarding the existence of a deprotonation process leading to the formation of adsorbed thiourate on platinum [26], copper [27, 28] and gold [29] electrodes that would involve the tautomeric form of the TU molecule.

$$(2)$$
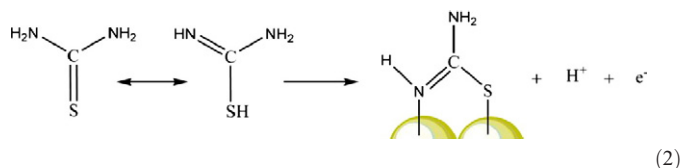
The presence of adsorbed thiourate at gold electrodes has been inferred from the observation of potential-dependent changes in the characteristic infrared frequencies of the adsorbate formed in TU-containing solutions [17]. Namely, a new band around 1550 cm^{-1} appearing in the ATR-SEIRA spectra collected in water solutions was assigned, according to DFT calculations, to the asymmetric NCN stretching of adsorbed thiourate species. None of the theoretical calculations with adsorbed TU yielded vibrational frequencies near this value. The same holds for the observed band at ca. 1322 cm^{-1} in the spectra collected in D_2O solutions that can only be ascribed to the symmetric NCN stretching of adsorbed deuterated thiourate. The observation of both symmetric and asymmetric NCN bands can be related to the optimized adsorption geometry derived from the DFT calculations for adsorbed thiourate [17], which implies bidentate bridge bonding via both the S atom and the N atom of the NH group, with the molecular plane perpendicular to the surface and the C–S bond tilted around 60–70° from the surface normal. Finally, the presence in the spectra collected in D_2O solutions of a band at 1380 cm^{-1} characteristic of deuterated TU, at potentials as high as 0.90 V indicates the presence of significant amounts of coadsorbed TU coexisting with thiourate at this potential.

This paper reports a spectroelectrochemical study of FDS adsorption on gold electrodes. The nature of the adsorbed species formed from diluted FDS solutions is investigated in potential and FDS concentration range selected in order to minimize further FDS oxidation and/or the dissolution of the gold electrode via the formation of TU complexes, these processes being out of the scope of this paper. Voltammetric and spectroscopic data obtained in acidic media with Au(111) and Au(100) single crystal electrodes are compared to those for gold thin-film electrodes and with the previously published results for adsorbed TU. As in previous studies recently published by our group [17,30–37], infrared spectroscopy is used to gain molecular level information on the bonding of these adsorbed molecules. The reported experiments

combine the use of single-crystal electrode surfaces (in external reflection infrared experiments) and gold thin film electrodes (for ATR-SEIRAS). The use of ordered gold thin films with a preferential (111) orientation as electrodes in the so-called Kretschmann's configuration (ATR-SEIRAS experiments) allows comparisons with the behavior of gold single crystal electrodes while keeping the enhanced surface sensitivity. This characteristic behavior facilitates the detection of adsorbates at low coverages (thus allowing the use of low FDS concentrations for which solution or surface dissolution processes are not significant) as well as the study of interactions between adsorbed species and interfacial water molecules [38,39]. In order to better support the assignment of experimental vibrational frequencies, DFT calculations will be used for obtaining optimized adsorbate geometries and theoretical harmonic vibrational frequencies of adsorbed FDS, TU and thiourate species. We have selected in this case a slab model with periodic boundary conditions for modeling the metal surface, in order to allow for the calculation of the FDS adsorbate, that would require too big a cluster, which makes the cluster calculation extremely costly. Moreover, the slab model with nonlocalized basis sets provides a much better description of the metallic properties of the solid. In order to allow for comparisons within the same computational framework, we have also carried out slab calculations with adsorbed thiourea and thiourate species which give results that are basically similar to those previously obtained from cluster models [17] and are presented as supplementary materials.

2. Model and computational details

All the DFT calculations in this paper were carried out using the Vienna Ab-initio Simulation Package (VASP, v-4.6) [40–43], using the GGA exchange-correlation functional of Perdew, Burke and Ernzerhof (PBE) [44,45], which is known to be a good compromise for describing both metal surfaces and molecular systems, as well as adsorbates. As a basis set we used a system of Projector Augmented Waves (PAW) [46, 47] with a cutoff energy of 400 eV. The selection of k-points for sampling the Brillouin zone was done with the automatic Monkhorst–Pack method [48], using a centered ($3 \times 3 \times 1$) set. For smearing, we chose the second order Methfessel–Paxton method [49] with a sigma value of 0.2 eV.

The simulation cell used for modeling the Au(111) surface consisted of four layers of gold atoms with the (4×4) structure (16 atoms each), with a vacuum region of more than 1.2 nm, that ensures that no significant coupling exist between periodic replica in the Z-direction. The cell dimensions amounted to 1.1808 nm × 1.1808 nm × 2.1693 nm, that are in all the three axis sufficiently greater than the longest distance between two atoms in FDS (0.691 nm). This rules out the possibility of hydrogen bonding between FDS adsorbates in neighboring replica that could arise because of the periodic boundary conditions. In order to keep modest the computational costs, and as our main interest in these calculations is obtaining the optimized geometries and harmonic vibrational frequencies of the adsorbate in the range accessible in our experiments, in the optimization procedure we have only allowed the molecular adsorbate to relax (starting from a number of different starting geometries), while the metal nuclei are kept at fixed positions, with a lattice constant of 0.41748 nm (nearest-neighbor distances of 0.29520 nm). This value was obtained from a series of bulk energy calculations with different lattice constant, and fitting to the Murnaghan equation of state. This value coincides with the calculated values reported by other authors for the PBE functional, and compares well with the experimental value of 0.40789 nm [50]. We also carried out some test calculations allowing the relaxation of one metal layer, with minor differences in the adsorbates' optimized geometries and calculated frequencies.

The convergence criteria were: 10^{-5} eV for the electronic step, and 0.2 eV/nm for the forces on the atoms in the geometry optimization. All calculations were carried out with a total zero charge. Frequency calculations were done with a value of POTIM = 0.02. The assignment of the vibrational normal modes to the calculated frequencies has been