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Influence of tetrabutylammonium cations on phase transition within adsorbed adlayer and lifting of reconstruction at Au(111) electrode in sulfate solution and in presence of coumarin

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The effect of tetrabutylammonium (TBA) cations on phase transition within adsorbed adlayer and lifting of reconstruction at Au(111) electrode in sulfate solution and in presence of coumarin (CUM) has been studied by means of the cyclic voltammetry and differential capacity measurements. TBA cations retard the adsorption of sulfate anions which is responsible for the lifting of the reconstruction. Next, the presence of TBA cations in sulfate solution induces the appearance of phase transition in CUM adlayer for twice lower coumarin concentration and at much more negative potentials. Moreover, the protection against the sulfate anions adsorption which lifts the reconstruction is higher for CUM molecules than for TBA cations.

1. Introduction

Quaternary ammonium salts are of widespread use in everyday life, industry and pharmacy because of their fungicidal, germicidal, algaecides and even veridical properties. They have become also the subject of considerable attention in electrochemistry. Investigation of adsorption of tetraalkylammonium cations (with a small organic tail group) started at the mercury electrode (see Ref. [1] and references cited therein) and later-on has been extended to solid electrodes such as Bi or Cd single crystal electrodes [2,3] from non-aqueous solutions in order to understand the role of surface structure in processes occurring in non-aqueous supercapacitors [4]. Literature also provides results of impedance measurements for a polycrystalline gold electrode in aqueous tetraalkylammonium electrolyte solutions [5]. Moreover, as follows from electrochemical literature also quaternary cationic surfactants at single crystal electrodes [6,7] have been intensively investigated.

We have done some preliminary work [8] on the adsorption of tetrabutylammonium (TBA) cations on Au (100) and Au(111) electrodes from perchlorate solution, which was found to be structure sensitive and from electrochemical point of view resembled more simple organic molecules rather than ions. Recently, the influence of TBA cations on lifting of reconstruction and phase transitions within the adsorbed adlayers at Au(100) electrode in halide electrolytes i.e. containing anions of much stronger adsorbability has been studied [9].

To pursue the investigation, in the following, the influence of TBA cations on the phase transitions within adsorbed layer of organic molecules and subsequently on the lifting of the reconstruction has been examined. This former transition has been of special interest as we do not know of any precedent in the literature for such a specific impact of organic cations on similar process. From the few organic compounds which undergo phase transition at low-index Au electrodes [10–13] coumarin (CUM) has been chosen mainly due to it much less complicated adsorption behaviour in comparison with e.g. uracil [10]. This process has been carefully analyzed and described for the reconstructed Au (111) electrode [13]. Namely, for Au(111) in sodium sulfate electrolyte containing highest possible coumarin concentration of about 0.01 M a pair of sharp current spikes at negative potentials on cyclic voltammogram (CV) has been seen. On the basis of current spikes potential dependences on the CUM concentration and temperature, the appearance of these spikes has been proposed to be related to a structural transition (disorder-order) within the CUM adlayer. Further inspection of this CV reveals, at positive potentials, a well developed peak assigned to another phase transition i.e. lifting of the reconstruction. This creates the possibility to compare the protection of TBA and CUM against the sulfate anions adsorption which lifts the reconstruction.

Therefore, the objectives of this work have been: (i) to describe the unexpectedly large influence of TBA cations on phase transition within the adlayer of CUM (ii) to compare the protection of TBA and CUM against the sulfate anions adsorption which lifts the reconstruction (iii) to present the overall picture of the behaviour of TBA cations at Au (111) electrode in sulfate solution being the necessary step in interpreting the above processes.

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2. Experimental

The working electrodes was an Au(111) single crystal disc, 4 mm in diameter and 4 mm thick, and oriented to < 1° (MaTecK, Jülich). Before each experiment the electrode was prepared according to the well-known procedure for preparation of well-ordered gold surfaces [14]. Namely, the crystal was annealed for 3 min in a Bunsen burner flame, then cooled down to room temperature in a stream of nitrogen. Contact with the electrolyte was achieved by the hanging-meniscus method [15]. The counter electrode was an Au sheet. The reference electrode was a saturated calomel electrode (SCE) and throughout this work all potentials are reported versus SCE. The voltammetric and capacity measurements were performed using an AUTOLAB system (Eco Chemie). All the voltammograms were obtained at a scan rate of 50 mV s^{-1}. In capacity measurements the potential was stepped in 10 mV divisions with ac voltage of 6 mV amplitude and a frequency of 19 Hz.

The supporting electrolyte solution was prepared from Na_2SO_4 (suprapure, Merck). Tetrabutylammoniun perchlorate purisse (from Fluka) and coumarin (from Aldrich) were used without further purification. All solutions were prepared from Milli-Q water.

All solutions were deaerated by nitrogen before each experiment and a constant flow was maintained over the solution at all times. All experiments were carried out at room temperature 20 ± 1 °C.

3. Results and discussion

3.1. *Overall picture of the interfacial behaviour of TBA cations at Au(111) electrode in sulfate solution*

The overall picture of the interfacial behaviour of TBA cations in the broad potential range $-0.730 \leq E \leq 1.200$ V at Au(111) single crystal electrode is given in Fig. 1 which depicts CVs recorded in $5{\cdot}10^{-2}$ M Na_2SO_4 + $5{\cdot}10^{-4}$ M TBAP (solid line) and, for comparison, in the absence of TBA cations (dotted line). The CV presented for the supporting electrolyte ($5{\cdot}10^{-2}$ M Na_2SO_4) alone shows a small peak R associated with the lifting of the reconstruction [13,16] which occurs before the formation of surface oxides. The addition of TBAP, as follows from Fig. 1, produces the peaks A and a broad and split peak DR at positive potentials. Further polarization of the electrode to more positive potentials (ca. 0.720 V) gives rise to the high faradic current which brings about the appearance of a large wave (OX) related to the oxidation of gold. As can be seen the current profile for formation an oxide monolayer is practically the same as in the supporting electrolyte, which simultaneously indicates not only the absence of TBA cations at the surface but confirms the good quality of the surface of the Au(111) electrode [16].

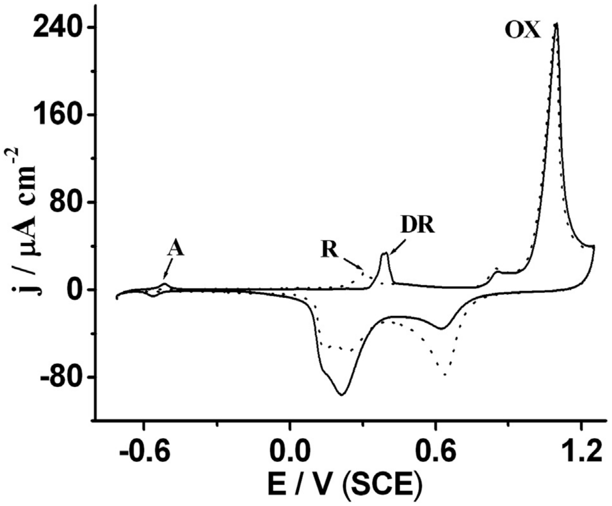

Fig. 1. Comparison of CVs for thermally reconstructed Au(111)-$(22 \times \sqrt{3})$ in $5{\cdot}10^{-2}$ M Na_2SO_4 (dotted line) and with addition of $5{\cdot}10^{-4}$ M TBAP (solid line). Description of the peaks is provided in the text.

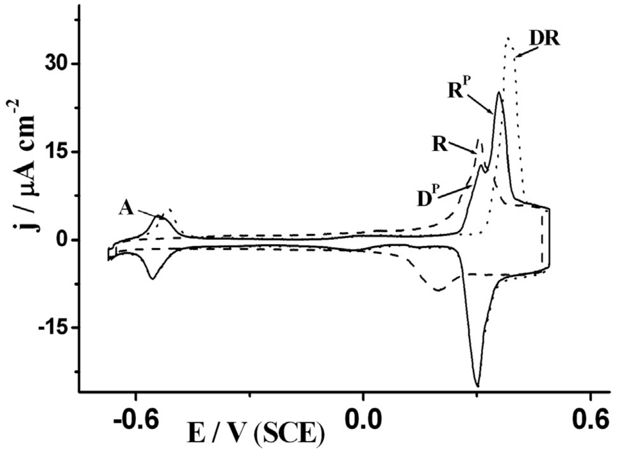

Fig. 2. CVs in the double layer region for thermally (dotted line) and potentially (solid line) reconstructed Au(111)-$(22 \times \sqrt{3})$ in $5{\cdot}10^{-2}$ M Na_2SO_4 + $5{\cdot}10^{-4}$ M TBAP and for thermally reconstructed Au(111)-$(22 \times \sqrt{3})$ in $5{\cdot}10^{-2}$ M Na_2SO_4 (dashed line). Description of the peaks is provided in the text.

The further and in more details analysis of the origin of the above mentioned peaks is performed in the potential window where the processes connected with charging only the double layer take place. Therefore, Fig. 2 shows a comparison of two CVs recorded, in the potential range before the formation of surface oxides, for a thermally-induced Au(111)-$(\sqrt{3} \times 22)$ electrode in $5{\cdot}10^{-2}$ M Na_2SO_4 + $5{\cdot}10^{-4}$ M TBAP (dotted line) and in $5{\cdot}10^{-2}$ M Na_2SO_4 alone (dashed line). The CV obtained for the $5{\cdot}10^{-2}$ M Na_2SO_4 solution agrees well with those reported previously [13,16] for the reconstructed Au(111)-$(\sqrt{3} \times 22)$ surface i.e. it depicts small and almost potential independent current followed by an increase in current leading to a large, high and slightly reversible peak R at about 0.308 V, which is assigned to the lifting of the reconstruction. Next, the CV recorded in the presence of $5{\cdot}10^{-4}$ M TBAP exhibits an anodic hump A at ca. -0.516 V corresponding to the adsorption of TBA cations. At less negative potentials, a reduction of the double layer current is observed and it retains this low value till 0.180 V, followed by large and irregular shape peak DR at around 0.390 V suggesting its mixed nature. In order to find the origin of this peak we applied the same procedure as before dealing with perchlorate solution [8]. This procedure is based on the structure sensitive adsorption of TBA cations [8] and the well-known, from STM observation [17] difference in structure between the potential- and thermally-induced surfaces of Au(111). For this purpose, after lifting of thermally-induced reconstruction, the electrode was kept at negative potential (-0.730 V) for 3 min in order to reconstruct its surface potentiostatically. The obtained CV (solid line), as can be seen from Fig. 2, depicts now two well separated peaks. Such separation which is a result of the smaller shift to less positive potential of the reconstruction peak R^P than the desorption one D^P (ca. 35 and 69 mV, respectively) confirms again the structure sensitive adsorption of TBA cations. It is worthwhile to add that for Au(100) in perchlorate solution, the reconstruction peak distinctly follows the desorption one which is in contrast to the situation in chloride solution when the opposite order is observed [9]. Moreover, as the reconstruction peak DR is shifted by about 86 mV to more positive potentials than that of R it means that the stability of the $(\sqrt{3} \times 22)$ structure increased owing to hindering the adsorption of sulfate anions by TBA cations which would be expected to lift the reconstruction, however to a lesser ca. 145 mV extent than in perchlorate electrolyte [9].