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ORIGINAL PAPER

The oxidation of trivalent chromium at the reconstructed Au(100) electrode

P. Skołuda

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Abstract The electro-oxidation of Cr(III) to Cr(VI) species at the reconstructed Au(100) electrode has been investigated in a highly alkaline solution. The subsequent comparison of the results obtained with those at Au(111) electrode points to the structural sensitivity of this oxidation process related to different adsorbability of OH^- anions on both electrodes. Finally, it was found that the addition of Cr(III) ions does not shift the reconstruction peak to less positive values of potential indicating that for Au(100) electrode the oxidation process under consideration has no impact on the lifting of the surface reconstruction.

Keywords Electro-oxidation · Chromium · Au(100) electrode · Surface reconstruction

1 Introduction

The chromium contamination of the natural environment in various parts of the world has been well documented. The main sources of chromium pollution in ground water are plating industries, cooling towers, leather tanning and wood preservation. Chromium in solution may be present as Cr(III) and Cr(VI), and these two oxidation states have a different influence on the environment and human health. While chromium(III) is a required trace element for humans, chromium(VI) can be highly toxic and carcinogenic. Therefore, due to this contrasting impact of these oxidation states the electrochemistry of chromium has attracted much interest in recent years. Of particular interest in this context is the reduction of the hexavalent chromium [1] as well as the oxidation of trivalent chromium species [2–4]. This latter process has been studied by e.g. Compton and co-workers [4] in a highly alkaline solution at the polycrystalline gold electrode and the following mechanism was proposed for the overall electrode reaction:

$$CrO_2^{\,-} + OH^- \rightarrow e^- + H^+ + CrO_3^{\,2-}$$
$$\text{rate-determining step (RDS)}$$

$$CrO_3^{\,2-} \rightarrow e^- + CrO_3^{\,-} \quad \text{fast}$$

$$CrO_3^{\,-} + OH^- \rightarrow e^- + H^+ + CrO_4^{\,2-} \quad \text{fast}$$

Recently, we have done some preliminary work on structural sensitivity of the electro-oxidation of Cr(III) ions applying the thermally and potentially reconstructed surface of the Au(111) electrode [5]. Usually, the occurrence of surface reconstruction has a marked impact on electrochemical processes e.g. adsorption and phase transition in organic adlayer [6–8]. In the course of these studies, it has been noticed additionally that the lifting of the reconstruction can be due to the co-adsorption of the anions (OH^-) from the supporting electrolyte and the anions ($CrO_4^{\,2-}$) supplied from the electro-oxidation process under consideration.

The subsequent studies [9] conducted with the Au(210) and Au(311) stepped surfaces have not only assessed the structural effect of this process but also permitted explanation of the differences obtained with these electrodes in terms of the blocking effect of the strongly adsorbed $CrO_4^{\,2-}$ anions and different ability of the electrode surface to adsorb OH^- anions.

We have described below the electro-oxidation of Cr(III) ions on the Au(100) single crystal electrode. We have chosen Au(100) single crystal electrode as it undergoes surface reconstruction [10] similarly as Au(111) and

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P. Skołuda (✉)
Zakład Chemii Fizycznej, Wydział Chemii, Uniwersytet im.A.Mickiewicza, ul.Grunwaldzka 6, 60-780 Poznan, Poland
e-mail: pskoluda@main.amu.edu.pl; pskoluda@amu.edu.pl

for which the data on the adsorption of OH^- anions is available in literature [11]. Thus, it is expected that the results obtained will allow further estimation of the influence of the adsorbability of OH^- anions on differently oriented Au surfaces on the oxidation of Cr(III) ions as well as the impact of this latter process on the surface reconstruction/lifting phenomena.

2 Experimental

The working electrode was an Au(100) 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 [12]. Namely, the crystal was annealed for 3 min in a Bunsen burner flame and then cooled down to room temperature in a stream of nitrogen. Contact with the electrolyte was achieved by the hanging-meniscus method [13]. The counter electrode was a Pt wire. The reference electrode was a saturated calomel electrode (SCE), and throughout this work, all potentials are reported versus SCE. The voltammetric measurements were performed using an AUTOLAB system (Eco Chemie).

All solutions were prepared from Milli-Q water. NaOH (Suprapure) was obtained from Merck, whereas $Cr(NO_3)_3$ (99.99%) was purchased from Aldrich.

All electrolytes were deaerated (for 50 min) by nitrogen. Nitrogen was allowed to flow over the solution at all times. All experiments were carried out at room temperature 25 ± 1 °C.

3 Results and discussion

In the voltammetric measurements, throughout this work, a scan rate of 50 mV/s has been chosen for the sake of comparison with the results obtained for the (111) single crystal gold electrode [5].

Figure 1a and b displays the cyclic voltammograms (CVs) for the oxidation of 100 μM Cr(III) in 0.1 M NaOH on the thermally and partly potentially reconstructed Au(100) electrode, respectively. As can be seen, both voltammetric responses consist of the large anodic wave with two separate peaks (denoted as I and II). Not the whole current wave, however, can be exclusively attributed to the oxidation process as in the vicinity of peak II; this process overlaps with the lifting of the reconstruction. It can be concluded from the voltammetric curves recorded in 0.1 M NaOH (supporting electrolyte), which are also depicted in Fig. 1. These curves show either a well-developed peak (Fig. 1a) or, at less positive potentials, a smaller peak (Fig. 1b) associated with the lifting of the thermally and potential-induced reconstruction, respectively [10]. From the ratio of the charge under the above mentioned peaks, we can learn that only ca. 43% of the surface is reconstructed again by potential during the subsequent scan; therefore it is obvious that a noticeable difference between peaks II in Figs. 1a and b is due to a much greater contribution of the charge associated with the lifting of thermally than potentially induced reconstruction.

All this indicates that only peak I is solely associated with the electro-oxidation of Cr(III) ions. Further inspection of Fig. 1 reveals that for the thermally reconstructed surface the onset of electro-oxidation potential ca. −0.190 V is less negative than for the potentially reconstructed surface, which already indicates that the electro-oxidation of Cr(III) ions is structure sensitive. This conclusion is corroborated, as follows from the inset of Fig. 1a, by the difference in the oxidation onset potentials which is ca. 60 mV less negative for the reconstructed Au(111) electrode than for Au(100) one. This structural effect of the electro-oxidation of Cr(III) similar to the one that arises from the mechanism [4] may be explained by the involvement of the hydroxide anion in the RDS, whose chemisorption and electrosorption valence are strongly surface structure dependent [11]. Therefore, the more negative value of the oxidation onset potential obtained for Au(100) electrode can be explained by the greater charge associated with OH^- chemisorption on this electrode (120 $\mu C\ cm^{-2}$) than on Au(111) one (15 $\mu C\ cm^{-2}$) [11].

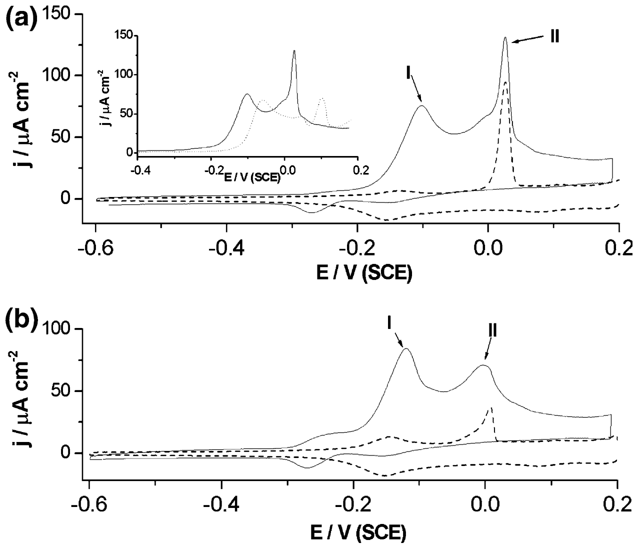

Fig. 1 Cycling voltammograms illustrating the oxidation of 100 μM Cr(III) in 0.1 M NaOH (———) and lifting of the reconstruction in 0.1 M NaOH alone (– – – – – –) for thermally (**a**) and potentially (**b**) reconstructed Au(100) electrode. *Inset* The comparison of the CVs for the thermally reconstructed Au(111) (- - - -) and Au(100) (———) electrodes in 100 μM Cr(III) + 0.1 M NaOH

The structural sensitivity of the oxidation process is further supported by the Tafel analysis based on the voltammograms plotted as potential versus log (current) which produced larger value of slope. ca. 110 mV/decade for the thermally reconstructed Au(100) than for Au(111) ca. 102 mV/decade [5].

Incidentally, these values of the Tafel slope are very close to the theoretical one i.e. 118 mV/decade, which corresponds to a three-step reaction with the rate determining step being the initial irreversible electron transfer.

The response of the reconstructed Au(100) electrode towards increasing additions of trivalent chromium in 0.1 M NaOH was recorded next. The set of CVs obtained is displayed in Fig. 2 (not to complicate the graphical representation only positively going sweeps of the CVs are presented). The curve recorded in the absence of Cr(III) is also shown. As can be seen, the first oxidation peak (at negative potentials) significantly increases with the concentration of Cr(III), while the second peak is present on the voltammetric curves only for small concentrations (till 300 µM). For the highest Cr(III) concentration (1200 µM), these features are no longer visible and we observe only one large oxidation peak. Moreover, the increase in the oxidation peak current as follows from the inset of Fig. 2 was found to be linear with the concentration of Cr(III) and the gradient was equal 0.0664 AM^{-1} dm^{3} ($R = 0.998$). This allowed us to calculate the number of electrons transferred corresponding to this peak from the following equation for the electrochemically irreversible reaction in which the first electron transfer is rate determining step:

$$I_{\mathrm{peak}} = \left(2.99 \times 10^{5}\right) n \left(\alpha_{\mathrm{an}} n'\right)^{1/2} A D^{1/2} V^{1/2} C$$

where n is the total number of electrons involved in the reaction, D the diffusion coefficient (cm^{2} s^{-1}), A the area of the electrode (cm^{2}), V the potential scan rate (V s^{-1}), C the bulk concentration of analyte (mol cm^{-3}) and $\alpha_{\mathrm{an}} n'$ calculated from Tafel slope coefficient. The obtained value of n is 2.42 which indicates that this peak can be related to the three electrons transfer. It is worth mentioning that for the (111) gold electrode n was higher and equal 2.91 [5] which confirms again the structural sensitivity of the process investigated.

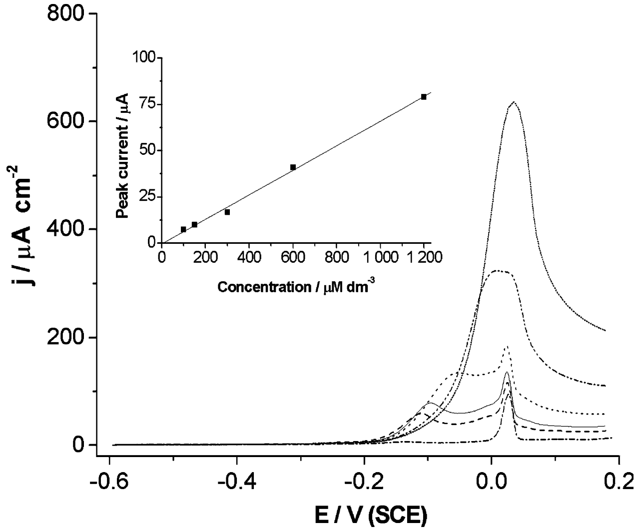

Fig. 2 Positive sweeps of cyclic voltammograms for Au(100) in 0.1 M NaOH alone (– - - -) and after addition of 100 (— — — —), 150 (———), 300 (– – – –) 600 (- - — - -) and 1200 (- - - -) µM of Cr(III). *Inset* The oxidation peak current against concentration of chromium (III) in 0.1 M NaOH for Au(100) (■ ■ ■ ■)

In our earlier work Skoluda [5] has reported that the electro-oxidation of Cr(III) influences the lifting of the surface reconstruction of the Au(111) electrode, and therefore, it seems worthwhile to consider this point also for Au(100) one. Inspection of Fig. 1 reveals that although this former process commences (ca. 212 mV) at more negative potentials than the latter one, similarly to the Au(111) electrode, but, as follows from Fig. 2, there is no shift of the reconstruction peak to less positive values of potential as the concentration of Cr(III) increases. This means that in contrast to the Au(111) electrode [5], the oxidation process under consideration has no impact on the lifting of the reconstruction of the Au(100) electrode. This difference is probably due to the coincidence of the reconstruction and second oxidation peaks for Au(100) electrode, while for Au(111) electrode [5] the former peak is distinctly followed by the latter one. In other words, while for Au(100) electrode the lifting of the reconstruction overlaps with the oxidation process, for Au(111) one it occurs at potentials at which this latter process is almost completed. As a result for Au(100) electrode, the adsorption of OH^{-} anions alone lifts the reconstruction, while for Au(111) coadsorption of OH^{-} + $CrO_4{}^{2-}$ being the final product of the oxidation process (see scheme in [4])] species is responsible for the lifting of the reconstruction.

4 Conclusions

In this study, the electro-oxidation of trivalent chromium at the reconstructed Au(100) electrode has been described providing the values of such parameters as the potential of the onset of the oxidation, Tafel slope and the number of electrons transferred.

A comparison of the results presented with those of our previous study performed at Au(111) electrode [5] shows some differences indicating the structural sensitivity of the process under consideration. These differences appear to be caused by the strongly surface dependent chemisorption of OH^{-} anions that have to be present on the surface of the electrode during the oxidation of Cr(III) [11]. Therefore, for example, the potential at which the oxidation of Cr(III) ions begins is more negative for the Au(100) electrode than for Au(111) one due to much higher number of chemisorbed OH^- anions on the surface of this former electrode.

Moreover, in the course of the studies it was noticed that the increase in Cr(III) concentration does not shift the reconstruction peak to less positive values of potential. It indicates that for Au(100) electrode, in contrast to Au(111) one, the oxidation process under consideration has no impact on the lifting of the surface reconstruction.

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