

G. Horányi

Anion adsorption in the course of dichromate reduction on a smooth gold electrode in aqueous acid solutions

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Abstract The specific adsorption of anions (HSO_4^- , Cl^-) present in low concentration ($c < 10^{-3} \text{ mol dm}^{-3}$) was studied by radiotracer techniques in the course of the reduction of dichromate (chromate) species in $1 \text{ mol dm}^{-3} \text{ HClO}_4$ supporting electrolyte. In accordance with the results of preliminary studies reported earlier, enhancement of the anion adsorption was found, induced by some adsorbed intermediates of the reduction process. Potential dependence of the induced adsorption and its correlation with the reduction rate was investigated. The role of adsorption competition between various anions is discussed. It is concluded that study of the induced anion adsorption could be a tool for the investigation of the sorption of intermediates formed in the course of the reduction.

Key words Anion adsorption · Dichromate reduction · Gold electrode · Radiotracer technique

Introduction

The reduction of chromium(VI) species in acid solution at a gold electrode is considered an intriguing example of electrocatalytic behaviour [1]. The mechanistic problems of the reduction process at noble metal electrodes have been discussed by several authors quite recently (see [1–6] and literature cited therein).

It has been shown [7] by radiotracer techniques that the reduction of dichromate ions on a gold electrode proceeds through the formation of surface species containing anions present in the solution phase. Although this observation was confirmed [8], no special attention

was paid in the literature to these phenomena by discussing the mechanistic aspects of the reduction. In the present communication, using radiotracer techniques an attempt will be made to give a detailed phenomenological description of the “induced” anion adsorption in the course of the reduction of Cr(VI) species.

Experimental

The cell and apparatus used have been described previously [7, 9, 10]. Gold-plated plastic foil forming the bottom of the cell served as the main electrode. ^{35}S -labelled H_2SO_4 (specific activity $185 \text{ MBq mmol}^{-1}$) and ^{36}Cl labelled HCl (specific activity 26 MBq mmol^{-1}) were used in the radiotracer experiments.

The supporting electrolyte used was $1 \text{ mol dm}^{-3} \text{ HClO}_4$. The reference and auxiliary platinized platinum electrodes were immersed in the supporting electrolyte under continuous H_2 bubbling. Through the central compartment of the cell, Ar was bubbled. Potential values quoted in this paper are given on the RHE scale. The concentration of the Cr(VI) species was adjusted by addition of CrO_3 to the solution phase.

The real surface area (roughness factor) of the electrode was estimated from the charge associated with the reduction of the oxide film formed on the gold [11, 12].

Results

Figure 1 shows the voltammetric behaviour of the gold electrode in the presence of Cr(VI) species (in low concentration) at 10 mV s^{-1} sweep rate over a wide potential range. These voltammetric patterns are very similar to those reported previously [7].

It may be seen from this figure that a (diffusion) limiting current can be observed during the anodic sweep up to 800 mV, while during the cathodic sweep the picture is more complicated. A significant hysteresis between the cathodic and anodic sections can be observed. On the other hand, the sections above 1000 mV completely coincide with that of the cyclic voltammetric curves obtained with the gold electrode in the absence of chromate species (see Fig. 3). This indicates that the

G. Horányi (✉)
Institute of Chemistry, Chemical Research Center,
Hungarian Academy of Sciences,
P.O. Box 17, H-1525 Budapest
e-mail: hor34@ludens.elte.hu
Tel.: +36-1267-0820; Fax: +36-1266-3899

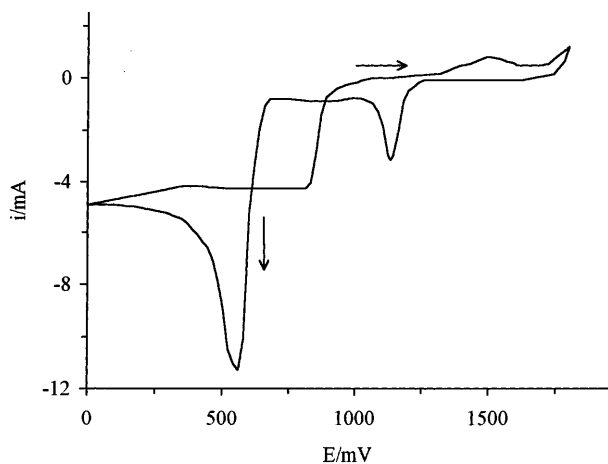


Fig. 1 Cyclic voltammogram curve at a smooth gold electrode in the presence of $1 \text{ mol dm}^{-3} \text{ HClO}_4 + 2 \times 10^{-4} \text{ mol dm}^{-3} \text{ Cr(VI)}$ species. Sweep rate 10 mV s^{-1}

formation and reduction of the oxide layer has nothing to do with the reduction of chromate species and the hysteresis observed. The problem of hysteresis and the role of the gold surface oxide layer can be studied by changing the sweep rate and the upper limit of the potential range studied. The results of these studies are reflected by the curves presented in Figs. 2 and 3.

In Fig. 2 it is shown that no hysteresis can be observed in the potential range from 100 mV to 700 mV; however, on shifting the upper limit of the potential range to higher values the hysteresis becomes more pronounced, and the cathodic peak at about 700 mV will be higher.

The cathodic and anodic curves, disregarding the cathodic peaks, more and more coincide on decreasing the sweep rate and increasing the concentration of

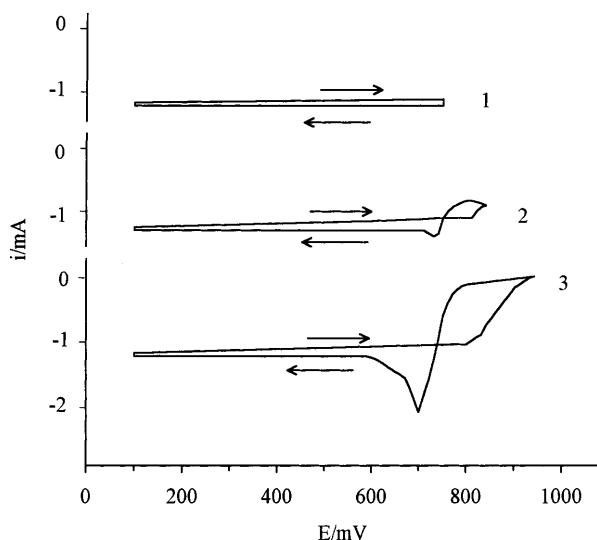


Fig. 2 Cyclic voltammogram curves obtained starting from 100 mV in the presence of $1 \text{ mol dm}^{-3} \text{ HClO}_4$ supporting electrolyte $+ 3 \times 10^{-4} \text{ mol dm}^{-3} \text{ Cr(VI)}$. Sweep rate 4 mV s^{-1} . Upper limit of the potential range: 1 700; 2 800; 3 900 mV

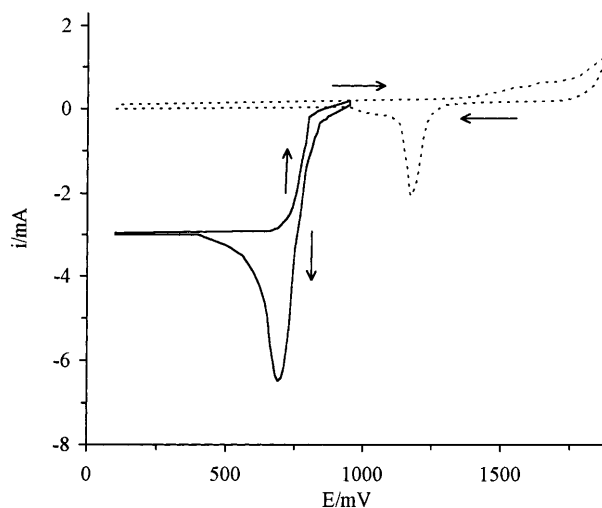


Fig. 3 Cyclic voltammogram curves in the presence (full line) and absence (dotted line) of Cr(VI) species. Supporting electrolyte $1 \text{ mol dm}^{-3} \text{ HClO}_4$. Concentration of Cr(VI): $5 \times 10^{-4} \text{ mol m}^{-3}$. Sweep rate: 2 mV s^{-1}

Cr(VI) species, as shown in Fig. 3. In the cases presented in Figs. 2 and 3 the upper limit of the potential range is far from the formation of the oxide layer; thus the phenomena observed cannot be ascribed to this process.

As was demonstrated in the previous communication [7], a significant increase of the adsorption of labelled sulfate species can be observed in the course of the reduction of Cr(VI) species at potentials where no adsorption of HSO_4^- (SO_4^{2-}) ions takes place in the absence of chromate ions (see, for instance, Fig. 4 in [7]).

A simultaneous steady state study of the potential dependence of the sulfate adsorption and reduction current gives some interesting information about the processes taking place at the electrode surface. The potential dependence of the adsorption obtained by steady state measurements during two consecutive runs with increasing and decreasing potential is shown in Fig. 4 (first run: 1 and 1'; second run: 2 and 2'). It may be seen from this figure that there is a significant hysteresis in the potential dependence of the adsorption of sulfate species. Figure 5 shows the results of the simultaneous measurement of the potential dependence of the adsorption and current starting from high potential values. It may be seen from this figure that the reduction process starts only at potentials where a relative high coverage with respect to adsorbed species is attained.

The attainment of the steady state at certain potential values requires a long time. For instance, Fig. 6 demonstrates the transients observed following potential switches from 1600 to 0 mV and from 0 to 800 mV. In the latter case the decrease in current is connected with an increase in the induced adsorption.

The effect of Cl^- ions on the sorption of labelled HSO_4^- species is clearly demonstrated by Fig. 7. Although the addition of Cl^- ions results in a decrease in the adsorption of HSO_4^- ions, the extent of this decrease is significantly less than that observed in the absence of Cr(VI) species

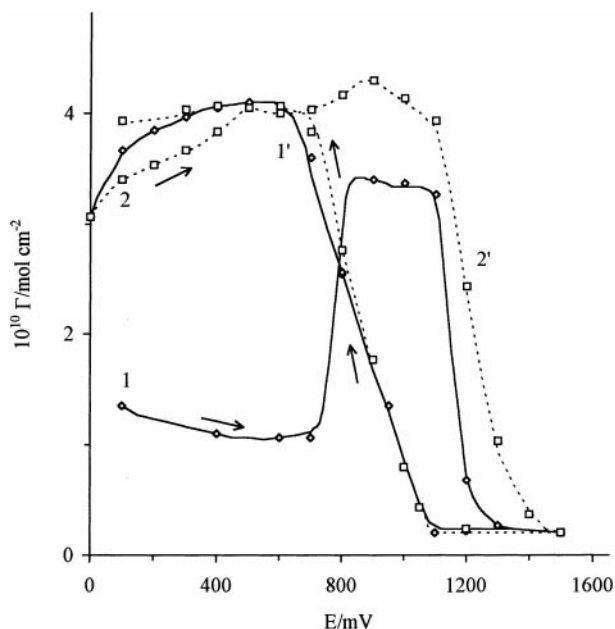


Fig. 4 Potential dependence of the adsorption of labelled HSO_4^- (SO_4^{2-}) species ($5 \times 10^{-4} \text{ mol dm}^{-3}$) in the presence of chromate ions ($4 \times 10^{-4} \text{ mol dm}^{-3}$) in $1 \text{ mol dm}^{-3} \text{ HClO}_4$ supporting electrolyte. Steady state measurements by point-by-point method. First run (full line): starting from 100 mV and shifting the potential by step-by-step method to 1600 mV (1); returning to 0 mV (1'). Second run (dotted line): the same procedure as above, returning to 100 mV

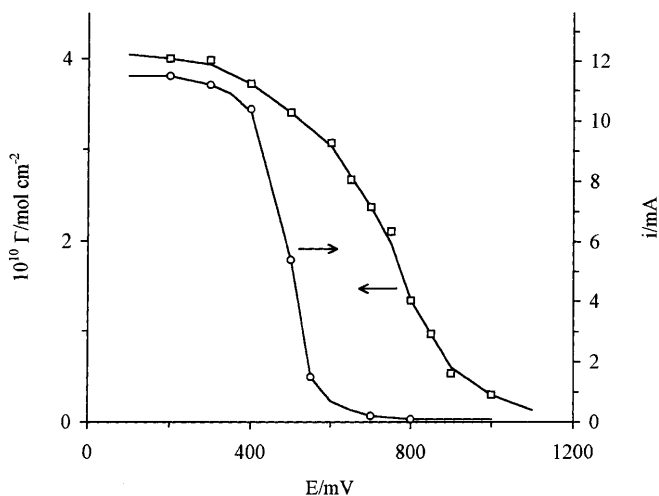


Fig. 5 Simultaneous measurement of adsorption and reduction current starting from 1000 mV. Other data as in Fig. 4

(complete displacing), as reported previously [15]. It follows from this result that the induced adsorption of Cl^- ions should be observed on studying the adsorption of labelled chloride ions in the presence of Cr(VI) species. The results of this study are presented in Fig. 8.

The character of the two Γ vs. E curves presented in Fig. 8 differs significantly: at low potentials in both cases there is an increase in the adsorption, while at higher potentials the presence of Cr(VI) species results in a

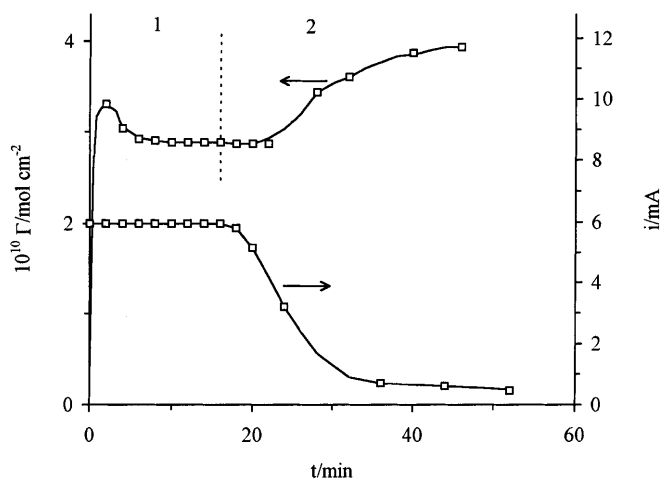


Fig. 6 Γ and current transients following potential switches: 1 from 1600 to 0 mV; 2 from 0 to 800 mV. Other data as in Fig. 4

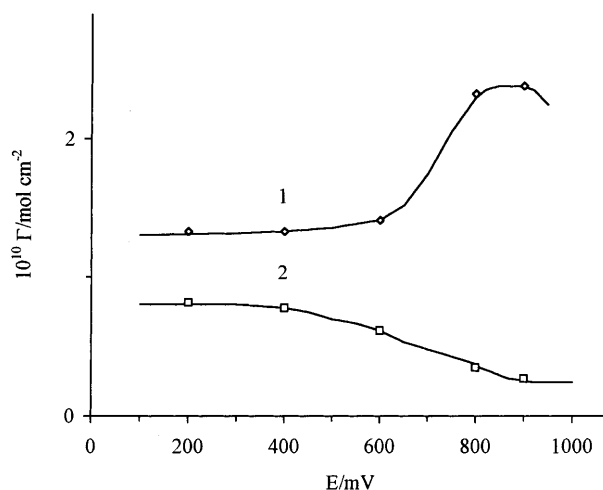


Fig. 7 The effect of Cl^- ions on the adsorption of labelled sulfate species. The potential dependence of HSO_4^- adsorption 1 in the presence of $3 \times 10^{-4} \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ and $2 \times 10^{-4} \text{ mol dm}^{-3} \text{ Cr(VI)}$ species in $1 \text{ mol dm}^{-3} \text{ HClO}_4$ and 2 after the addition of $2 \times 10^{-4} \text{ mol dm}^{-3} \text{ HCl}$

decrease in the extent of Cl^- adsorption. The latter decrease can be connected with the adsorption competition with unreduced $\text{Cr}_2\text{O}_7^{2-}$ or CrO_4^{2-} species.

Really, as Fig. 9 shows at 1000 mV where no reduction takes place, the addition of Cr(VI) species leads to a decrease in Cl^- adsorption. This is very interesting information, proving that the adsorption strength of Cr(VI) species is very high as a significant decrease in the relatively strongly adsorbed Cl^- species can be observed.

On the basis of this result a more pronounced effect should be expected in the case of the displacement of HSO_4^- (SO_4^{2-}) ions by Cr(VI) species. In accordance with this expectation, a similar experiment in the case of labelled HSO_4^- species (at 1100 mV) proves that the competitive adsorption of HSO_4^- and Cr(VI) species is also a reality, as shown by Fig. 10. It may be seen from

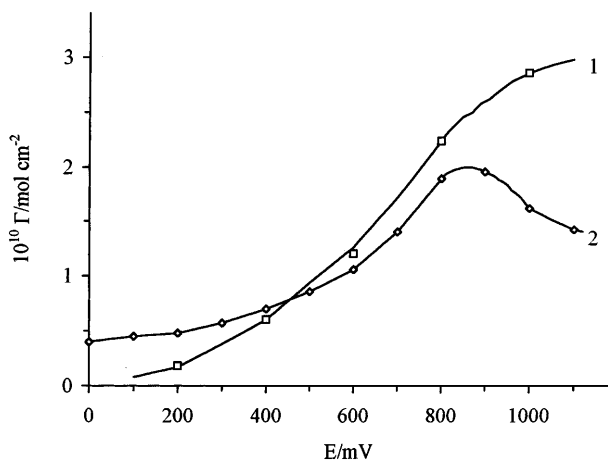


Fig. 8 Study of the potential dependence of the adsorption of ^{36}Cl -labelled chloride ions ($4 \times 10^{-5} \text{ mol dm}^{-3}$) in $1 \text{ mol dm}^{-3} \text{ HClO}_4$ in the absence (1) and presence (2) of Cr(VI) species ($2 \times 10^{-4} \text{ mol dm}^{-3}$)

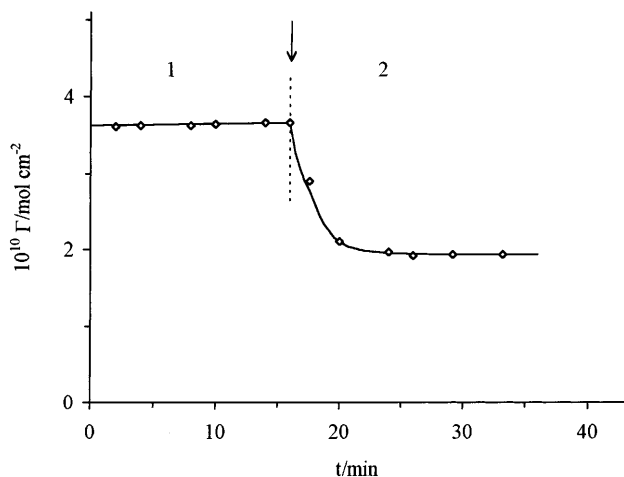


Fig. 9 Displacement of adsorbed Cl^- ions by Cr(VI) species at a potential where no significant reduction of the latter ions takes place. $E = 1000 \text{ mV}$; $c_{\text{Cl}^-} = 4 \times 10^{-5} \text{ mol dm}^{-3}$. Chromate ($4 \times 10^{-4} \text{ mol dm}^{-3}$) was added to the solution phase at the moment indicated by the arrow

this figure that labelled HSO_4^- ions adsorbed at 1100 mV on the gold surface are almost completely displaced by Cr(VI) species. On shifting the potential to a value where at least a slow reduction of the chromate ions takes place, an increase in the sulfate adsorption occurs indicating that a change in the state of the adsorbed molecule or the formation of some adsorbed intermediate leads to the induced adsorption of the anion.

Another comparison of the adsorbability of HSO_4^- and Cl^- on the surface species formed by the reduction process proves that the adsorption of HSO_4^- species leads to the partial displacement of adsorbed Cl^- ions. This is shown in Fig. 11 (the opposite case was shown in Fig. 7). Further information proving the role of competitive adsorption of anions is furnished by Fig. 12, where the effect of H_3PO_4 on the adsorption of HSO_4^- is shown.

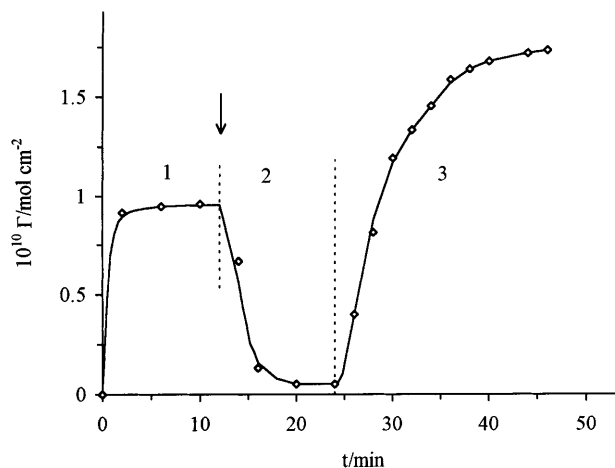


Fig. 10 Displacement of adsorbed sulfate ($4 \times 10^{-4} \text{ mol dm}^{-3}$ in $1 \text{ mol dm}^{-3} \text{ HClO}_4$) by chromate ions at a potential where no reduction of the latter species takes place. 1 Adsorption of sulfate at 1100 mV . 2 Addition of chromate at 1100 mV (at the moment indicated by the arrow); $c = 3 \times 10^{-4} \text{ mol dm}^{-3}$. 3 Potential switch to 800 mV

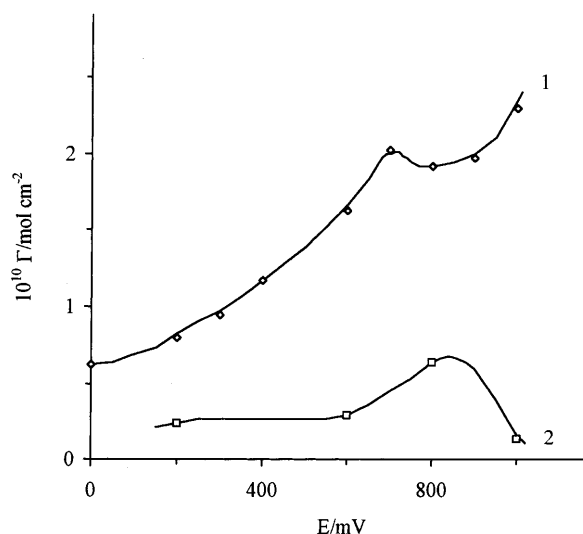


Fig. 11 Effect of sulfate ions on the adsorption of labelled Cl^- ions ($c = 5 \times 10^{-5} \text{ mol dm}^{-3}$ in $1 \text{ mol dm}^{-3} \text{ HClO}_4 + 2 \times 10^{-4} \text{ mol dm}^{-3} \text{ Cr}_2\text{O}_7^{2-}$). 1 Γ vs. E curve in the absence of HSO_4^- ions. 2 Γ vs. E curve following the addition of $1 \times 10^{-2} \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$

Finally, it should be emphasized that exhaustive reduction of Cr(VI) species, i.e. after their complete transformation into Cr(III) ions, leads to the elimination of induced anion adsorption. The simultaneous decrease of current and adsorption in the course of an exhaustive reduction is shown in Fig. 13. Following the exhaustive reduction, no adsorption of anions can be observed at low potentials; however, the addition of a small amount of Cr(VI) species results in an increase in the adsorption.

On the basis of the steady state or transient adsorption measurements presented above, it can be expected that a periodical change in the adsorption of anions

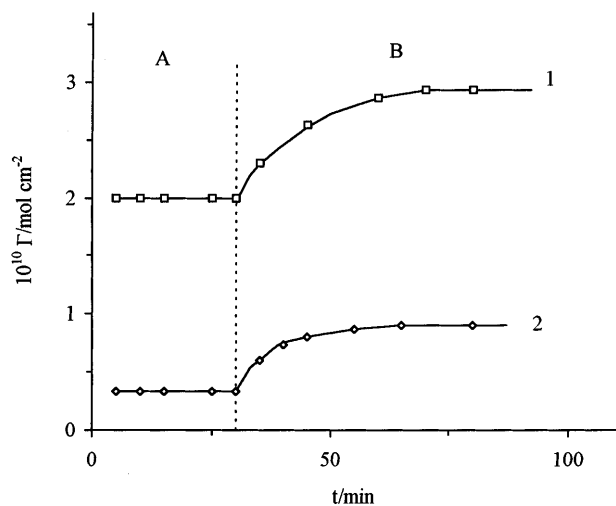


Fig. 12 Effect of H_3PO_4 on the adsorption HSO_4^- ions. Transient phenomena following 1 a potential switch from 0 (A) to 800 mV (B) in the presence of $5 \times 10^{-4} \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ in $1 \text{ mol dm}^{-3} \text{ HClO}_4 + 4 \times 10^{-4} \text{ Cr(VI) species}$. 2 The same procedure following the addition of $2 \times 10^{-2} \text{ mol dm}^{-3} \text{ H}_3\text{PO}_4$

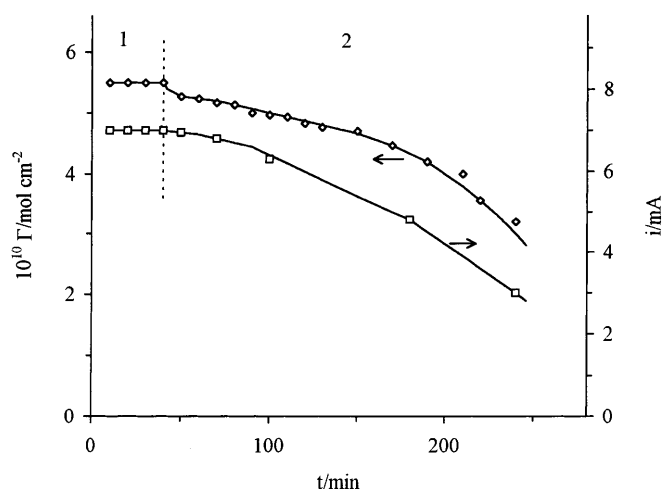


Fig. 13 Simultaneous measurement of the reduction current of Cr(VI) species and the adsorption of labelled sulfate following a potential switch from 750 mV (1) to 0 mV (2). Initial data as in Fig. 4

should occur during a potential cycling like in the case presented in Fig. 1. Simultaneous voltammetric and voltradiometric measurements confirm the validity of this expectation. Figure 14 shows the periodical changes in the adsorption of labelled sulfate species during cyclic voltammetric measurements in the presence of chromate species.

Discussion

The experimental results presented confirm without any doubt that induced specific anion adsorption occurs in the course of the reduction of Cr(VI) species in acid

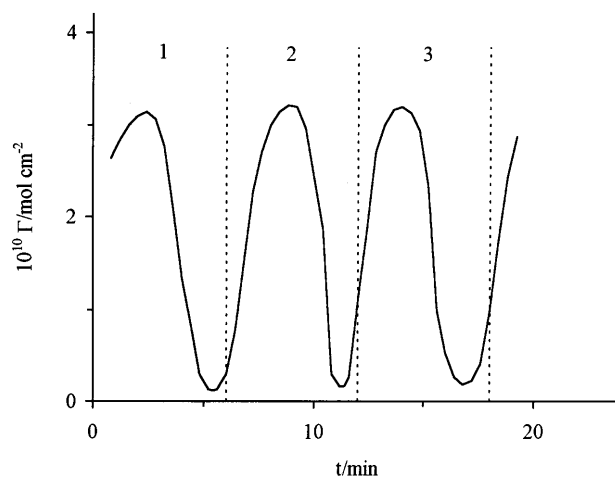


Fig. 14 Periodical changes in the adsorption of sulfate ions in the course of potential cycling between 100 and 1900 mV. Sweep rate: 10 mV s^{-1} . $c_{\text{H}_2\text{SO}_4} = 5 \times 10^{-4} \text{ mol dm}^{-3} + 3 \times 10^{-4} \text{ mol dm}^{-3} \text{ Cr(VI) species}$ in $1 \text{ mol dm}^{-3} \text{ HClO}_4$

medium. It is very important to emphasize that owing to the great excess of ClO_4^- ions the enhancement of HSO_4^- (SO_4^{2-}) or Cl^- ions cannot be ascribed to electrostatic interactions; thus the phenomenon can be approached only in terms of specific adsorption.

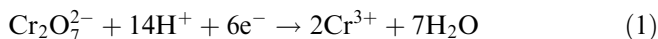
The experimental results obtained at potentials where the rate of the reduction of Cr(VI) species can be neglected prove, at least indirectly, that the specific adsorption of $\text{Cr}_2\text{O}_7^{2-}$ or CrO_4^{2-} species on a gold electrode could be significant and their adsorption strength is commensurate with that of Cl^- ions.

On the other hand, it follows from the results that the final products of the reduction, Cr(III) ions, do not exert any induction effect on the adsorption of anions. Thus the main conclusion is that the induced adsorption of anions should be ascribed to the formation of an adsorbed intermediate of the reduction process.

In this respect the potential dependence of the induced anion adsorption reflects the behaviour of some adsorbed (more or less reduced) Cr-containing species similar to some other cases [13, 14], where the study of induced adsorption of labelled species served as an indirect tool for the investigation of the behaviour of some adsorbed species (escaping the detection with other methods). The adsorbed layer formed by reduction at least partly inhibits the reduction process and this inhibitory effect depends on the potential.

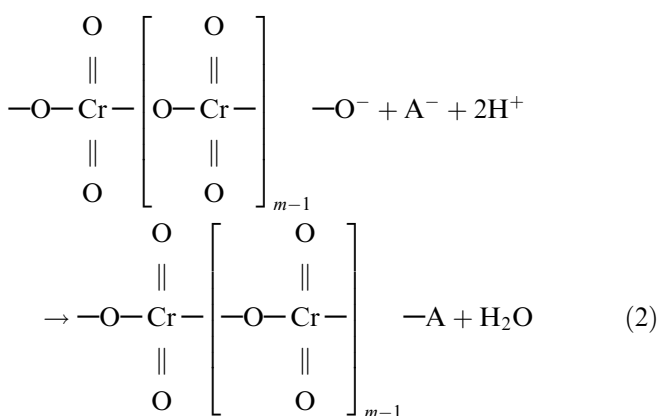
The results presented in Fig. 6 show that a slow decrease in the reduction current (following a switch from 0 to 800 mV) is connected with a slow increase in the induced adsorption of anions. This phenomenon can be explained only by the assumption that the slow accumulation of the adsorbed intermediate indicated by the anion adsorption leads to a slow decrease in the reduction current. The hysteresis phenomena observed in reduction rate and adsorption could be connected with this effect.

The electrocatalytic nature of the electroreduction of Cr(VI) species is clearly demonstrated by the fact that despite the high $E^\circ = 1.33$ V value for the reaction



the reduction takes place, through a dramatic change in its rate, at potentials $E < 1.0$ V (see, for instance, Fig. 3). This behaviour was explained [1] on the basis of the so-called incipient hydrous oxide/adatom mediator (IHOAM) approach. According to this approach the important species with regard to catalysis at the gold surface are the low coverage active gold atoms (Au^*) and the oxidized state of the latter (AuO_x^*). The reversible potential for the $\text{Au}^*/\text{AuO}_x^*$ transition is assumed to be ca. 0.95 V. Dichromate undergoes a redox reaction with Au^* , the former being reduced to Cr^{3+} (and H_2O) while the latter is oxidized AuO_x^* . This can only occur in a continuous manner at $E < 0.95$ V as only under the latter condition is Au^* regenerated electrochemically by reduction of the active oxide. AuO_x^* is rather stable in the presence of dichromate above ca. 0.95 V, so that reduction cannot continue owing to the absence of Au^* .

The results of the present work, however, do not contradict the assumptions made in [1] and cited above, but prompt us to emphasize the role of an anion-containing surface layer in the reduction mechanism, i.e. in the electrocatalytic reduction of Cr(VI) species. In this respect the results presented here seem to be in accordance with the model suggested [3] for the interpretation of the kinetics of the electroreduction of hexavalent chromium compounds on a gold electrode and to explain the effect of various additives, for instance, anions on the reduction rate. According to the model proposed, the rate of electroreduction of Cr(VI) to the trivalent state depends upon kinetic regularities governing the formation of intermediate surface complexes. It is assumed that the reduction takes place via a CE (chemical-electron-transfer) mechanism where the heterogeneous chemical step which precedes the charge transfer involves particles such as HSO_4^- and Cl^- ions, leading to the formation of complex surface species containing, for instance, anions in accordance with the following formulation:



where A^- is the added species (anion). This reaction consists of several steps that include the adsorption of polychromate ions and additives and the interaction between the adsorbed species. According to this mechanism, the role of the anions is the formation of bridges that facilitate the electron transfer from the electrode surface to the chromium atom.

The results of present study can be considered a direct proof of the existence of anion-containing surface species and their role in the reduction process. First of all we found a parallel between the potential dependence (steady state) reduction current and the extent of the anion adsorption (Fig. 5). Where no measurable anion adsorption occurs, no significant reduction rate can be observed. This phenomenon is in accordance with the assumption that anions play the bridges in the electron transfer.

On the other hand, the hysteresis phenomena occurring in the anion adsorption and the decrease of the rate of the reduction process in the course of lasting electrolysis allow us to assume that a film is formed on the surface that, with increasing thickness, exerts an inhibitive effect and slows down the mobility of anions in the film.

In order to obtain a better insight into the nature of the adsorbed surface species, the use of labelled Cr species for the sorption studies could be suggested as a next step. It would be of importance to obtain information about the thickness of the layer, i.e. whether a monolayer or a multilayer is formed. On the basis of the observed slowness of the induced adsorption processes, multilayer formation could be suggested. The investigation of these problems could be the subject of further studies.

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