

G. Horányi

Specific adsorption of anions in the course of underpotential and bulk depositions and alloy formation of cadmium on a smooth gold support in acid medium

Received: 16 March 1999 / Accepted: 5 May 1999

Abstract The specific adsorption of ^{36}Cl -labelled Cl^- ions and ^{35}S -labelled HSO_4^- ions was studied in 1 mol dm^{-3} HClO_4 supporting electrolyte in the presence of Cd^{2+} ions at a gold support over a wide potential range corresponding to electrodeposition, alloy formation, underpotential deposition of Cd species and existence of an adatom-free surface. The distinct sections in the potential dependence of the adsorption of anions together with the potential versus time curves obtained under open circuit conditions reflect the changes in the state of the electrode surface, the dissolution of the bulk Cd phase and the slow elimination of Cd species from the Cd/Au alloy.

Key words Gold electrode · Cadmium · Electrodeposition · Alloy formation · Underpotential deposition

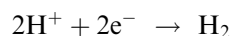
Introduction

The investigation of the specific adsorption of anions in the course of the underpotential deposition (upd) of Cd on Au and Pt supports in acid medium has been the subject of several radiotracer studies [1–3]. However, no information is available concerning the specific adsorption of anions during the course of the bulk deposition of cadmium not on alloy formation (see [4, 5] and references cited therein). The adsorption kinetics of cadmium ions on a gold electrode and the formation of Au/Cd alloys have been investigated by means of combined potentiostatic/potentiodynamic measurements in a solution of $1 \times 10^{-1} \text{ mol dm}^{-3}$ cadmium sulfate and

1 mol dm^{-3} acetate buffer [5]. The occurrence of alloy formation over a wide potential range was proved without any doubt.

In the present communication an attempt will be made to obtain information about the behaviour of an electrodeposited Cd layer on a gold support in acid medium.

The problem with Cd electrodeposition in acid medium is connected with the fact that it should be accompanied by simultaneous hydrogen evolution, owing to the low standard potential of the Cd^{2+}/Cd system (-0.403 V). Fortunately, the upd of cadmium ions on gold results in a significant increase in the hydrogen overvoltage; thus the deposition of Cd^{2+} ions can be carried out in strong acid media, although it is accompanied with H_2 evolution. A further problem is that the electrodeposited Cd layer is not stable under open circuit conditions in acid medium. Its more or less rapid corrosion takes place according to the coupled reactions:



On the other hand, this very fact could be of interest as it can be considered as a model system for sorption studies in the course of rapid corrosion.

Experimental

The study was carried out in the cell used for our previous radiotracer studies during the last two decades [1, 6, 7]. Both the counter and reference electrodes (separated from the main compartment) were hydrogen electrodes immersed in the supporting electrolyte. All potential values quoted in this paper are given on the RHE scale.

Molar perchloric acid was used as the supporting electrolyte. The concentration of labelled species remained lower than $10^{-3} \text{ mol dm}^{-3}$ and the concentration of Cd^{2+} ions was less than $2 \times 10^{-2} \text{ mol dm}^{-3}$; thus the ionic strength of the solutions was kept almost constant.

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

^{35}S -Labelled sulfuric acid (molar activity = $185 \text{ MBq mmol}^{-1}$) and ^{36}Cl -labelled HCl (molar activity = 26 MBq mmol^{-1}) were used for the tracer experiments.

The gold-plated thin plastic foil that forms the bottom of the cell served simultaneously as the main electrode for the upd and bulk deposition of cadmium and as a window for the radiation emitted by the labelled species.

It should be emphasized that unlike the previous study [1], where a porous gold electrode obtained by electrodeposition was used, in the present investigation the gold-plated foil alone served as a smooth electrode. The roughness factor of the electrode surface was estimated from the charge associated with the reduction of oxide film formed on gold [8, 9]. Roughness factor values of about 3–4 were obtained.

Results and discussion

Potential dependence of anion adsorption

Figure 1 shows the potential dependence of Cl^- ion adsorption in the presence of Cd^{2+} for a wide potential range from -0.5 V to $+0.7 \text{ V}$. The curve, obtained by steady state measurements under potentiostatic control starting from the most negative potentials where electrodeposition of Cd takes place, is composed of four distinct sections. Section 4 corresponds to the adsorption of chloride ions on the pure gold surface. The increase in anion adsorption with decreasing potentials shown by section 3 is due to the well-known enhancement of anion adsorption induced by the upd of Cd^{2+} ions. In section 2, although no bulk deposition of Cd occurs, a decrease in anion adsorption can be observed by shifting the potential to more negative values. Finally, in section 1 the massive bulk deposition of Cd takes place and the low adsorption values indicate that no specific adsorption of anions takes place on the electrodeposited Cd layer.

Similar behaviour was found in the case of labelled sulfate species (see below).

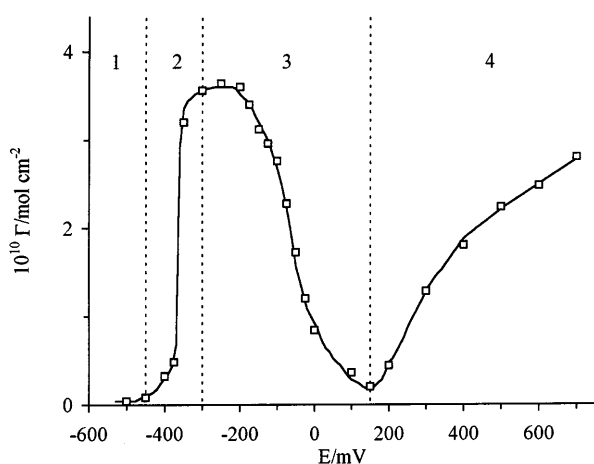


Fig. 1 Potential dependence of the adsorption of Cl^- ions ($c = 2 \times 10^{-3} \text{ mol dm}^{-3}$) in the presence of Cd^{2+} ions ($8 \times 10^{-3} \text{ mol dm}^{-3}$) in $1 \text{ mol dm}^{-3} \text{ HClO}_4$ supporting electrolyte

A study of the open circuit behaviour of the system (i.e. the spontaneous corrosion of the electrodeposited layer) gives an insight into the factors determining the observations presented above. Figure 2 shows the potential versus time curve obtained following an electrodeposition at -600 mV and thereafter opening the electric circuit. Three well-defined sections can be distinguished on the curve presented in Fig. 2. The first section corresponds to the dissolution of the bulk metal deposit, indicating the mixed potential of the two processes involved in the corrosion. The almost constant potential value characterising this section could not be very far from the equilibrium Cd/Cd^{2+} potential owing to the high hydrogen overpotential on Cd. The second section, as will be shown and discussed in detail, reflects the behaviour of an Au/Cd alloy formed in the course of the deposition of Cd. In the potential range corresponding to the third section, Cd should be present in the form of adatoms.

The polarisation behaviour of the system in the potential ranges discussed above is shown in Fig. 3. Evidently, no real steady state polarisation curves can be taken in the first two potential sections owing to the dissolution of bulk deposit (section 1) and alloy (section 2). Nevertheless, for short periods both anodic and cathodic branches can be observed. In the anodic branches the negative current corresponding to the discharge of protons is overcompensated by the dissolution of Cd. In the region of upd (section 3), only the formation of H_2 could be the main process at negative potentials.

No adsorption of anions takes place on the bulk Cd deposit and following a switch from a potential value where bulk deposition of Cd^{2+} takes place to the open circuit potential (i.e. interrupting the electric circuit), no change in the low anion adsorption value can be observed. Polarising the electrode in small potential steps starting from the open circuit potential, the results reflected by Fig. 4 are obtained. In Fig. 4 the current and radiation intensity values are plotted against time, fol-

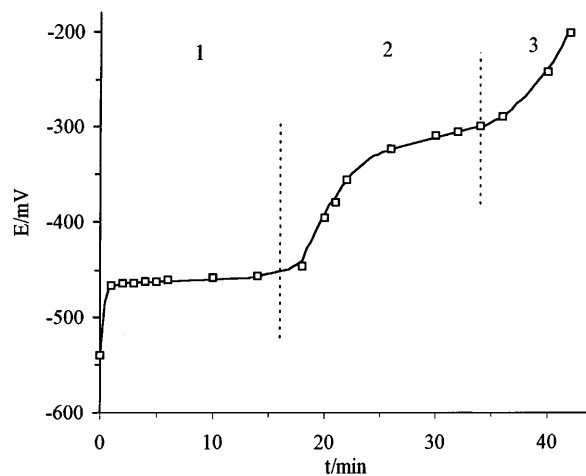


Fig. 2 The potential vs. time curve following the electrodeposition of Cd at -600 mV and thereafter opening the electric circuit (data as in Fig. 1)

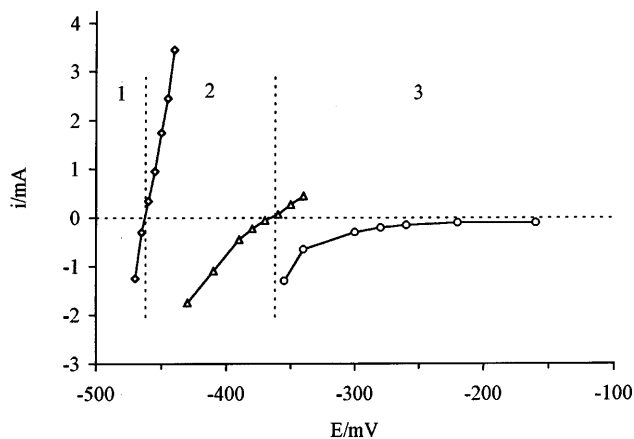


Fig. 3 Polarization behaviour of the Au/Cd system in the bulk electrodeposition region (1), the alloy formation region (2) and the upd region (3); detailed explanation in the text

lowing potential switches in the presence of labelled sulfate ions. It may be seen from this figure that despite the anodic dissolution of the Cd layer, no significant change in the anion adsorption takes place. The extent of the anion adsorption remains at a constant low level over a wide potential range, as shown by Fig. 4. This potential range corresponds to that considered as the "alloy formation region". Under potentiostatic control negative current flows, there is no bulk Cd on the surface. Attaining a certain potential value the appearance of a transient positive current and a continuous increase in the anion adsorption can be observed for a long period of time, as shown by Fig. 5. The apparent Γ values are reported owing to the possible changes in the real surface area (see below).

Data presented in Fig. 5 clearly demonstrate a slow transformation, indicating the slow oxidation of a spe-

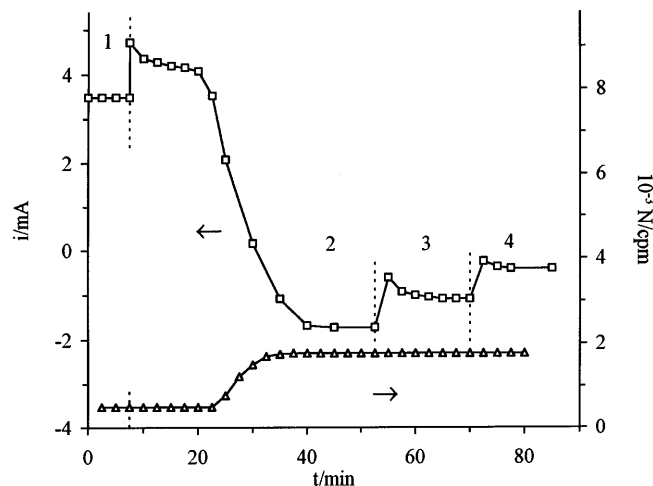


Fig. 4 Simultaneous measurement of current and radiation intensity following potential switches in the presence of labelled sulfate ions in the potential range where the dissolution of bulk Cd deposit takes place ($c_{H_2SO_4} = 2 \times 10^{-4}$, $c_{Cd} = 1 \times 10^{-2}$ mol dm⁻³ in 1 mol dm⁻³ HClO₄): (1) -440; (2) -430; (3) -410; (4) -390 mV

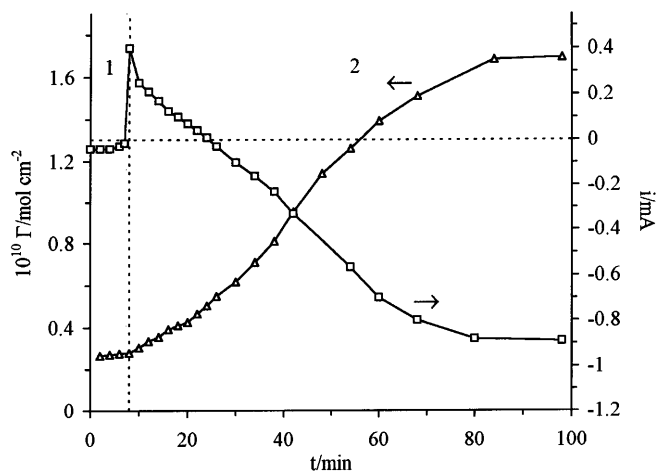


Fig. 5 Current vs. time and apparent adsorption (Γ referred to the original real surface area) vs. time curves in the course of dissolution of Cd/Au alloy following a potential switch from -365 to -360 mV (data as in Fig. 4)

cies. We have no other choice as to assume the oxidation of Cd dissolved in gold, i.e. the dissolution of the Cd component of the Cd/Au alloy formed during the electrodeposition of Cd²⁺ ions. The attainment of the steady state requires a very long time (more than an hour in the present case). This very fact seems to be in agreement with the assumption of alloy formation, as in this case the slow transport of Cd atoms from the bulk alloy phase to the surface of the electrode could be the rate determining step in the overall oxidation process [5]. If the dissolution of the alloy is completed there is no change in the extent of anion adsorption shifting the potentials by 100–150 mV to more positive values. This situation corresponds to the maximum coverage with respect to Cd adatoms. A decrease in anion adsorption takes place only at potentials where the upd of Cd follows the well-known patterns.

The alloy formation and thereafter its dissolution lead to a significant roughening of the gold surface, reflected by an increase in the count rate corresponding to the anion adsorption. Figure 6 shows the increase in the count rate in the case of labelled chloride ions at potentials where the formation of adatoms can be neglected. The roughening was clearly demonstrated by the changes in the oxide layer reduction charge data (see Experimental).

Competitive adsorption between Cl⁻ and HSO₄⁻ ions

It has been shown in a previous communication that the relative adsorption strength of chloride and sulfate ions is different on a Pt electrode and on Zn adatoms covering a Pt support [10]. In contrast to the general rule that the adsorption strength of chloride ions on noble metals is significantly higher than that of sulfate ions, the opposite was found for surfaces covered with Zn adatoms. A similar behaviour was found for the Cd-Au couple. It is well known that chloride ions present in very low

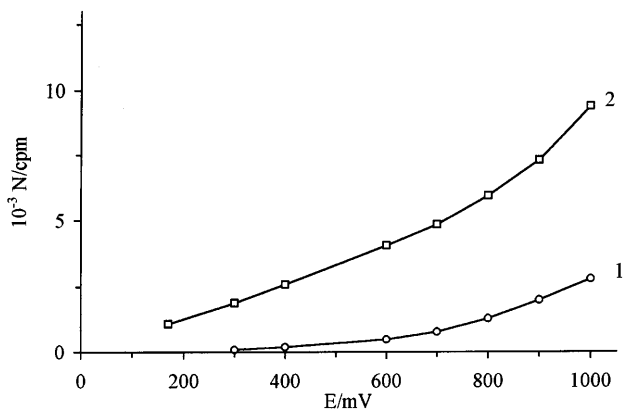


Fig. 6 Radiation intensity measured on the gold surface before (1) and after (2) alloy formation in the presence of labelled Cl^- species (data as in Fig. 1)

concentration displace sulfate ions adsorbed on Au, i.e. no adsorption of the latter species can be observed in the presence of the former ones [1]. In contrast to this, no significant change in the adsorption of labelled sulfate ions induced by Cd adatoms can be achieved by addition of Cl^- ions to the solution phase in a concentration commensurable or less than that of sulfate ions. This observation allows us to use the “simultaneous double labelling” for the investigation of the sorption phenomena in the Cd/Au system. This procedure consists of the simultaneous use of ^{36}Cl -labelled chloride ions and ^{35}S -labelled sulfate ions. Figure 7 shows the result of the “double labelling”. In the present case, only the count rates were plotted against the potential as the specific activity of the two labelled species is different, ignoring the different counting efficiencies owing to the different radiation energies and other factors. Despite this problem it follows from Fig. 7 that at potentials where no adatoms are on the surface, Cl^- ions displace completely the sulfate species. (The count rate versus potential curve is characteristic for Cl^- even in the presence of labelled sulfate.) In contrast to this, the opposite phenomenon can be observed at low potentials in the presence of adatoms. Despite the presence of Cl^- ions the count rate potential curve practically coincides with that obtained for sulfate species in the absence of Cl^- ions, proving that Cl^- ions are not able to displace sulfate species adsorbed on adatoms. This means that in the presence of a small amount of Cl^- ions the induced adsorption of sulfate ions can be measured without the interference of the adsorption of the sulfate ions taking place on free Au sites. This observation could be of some importance for further studies.

Conclusions

The experimental results presented above confirm the idea that the study of induced specific adsorption of anions may contribute to the better understanding of phenomena occurring at electrodes and it can be used as

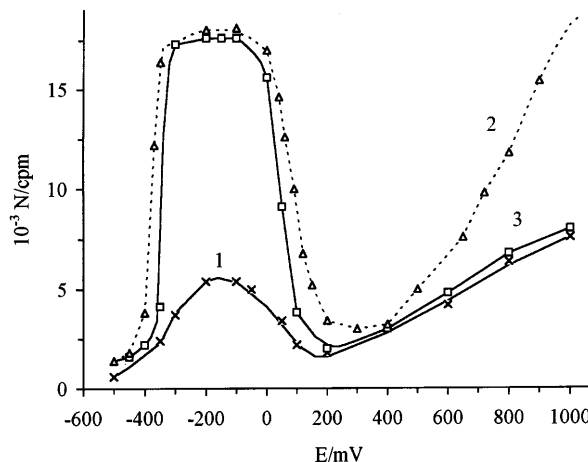


Fig. 7 Count rate vs. potential curves in the case of double labelling (simultaneous presence of labelled Cl^- and HSO_4^- ions) (curve 3). Curve 1: labelled Cl^- ions alone. Curve 2: labelled HSO_4^- species alone. $c_{\text{Cl}^-} = 2 \times 10^{-5} \text{ mol dm}^{-3}$, $c_{\text{H}_2\text{SO}_4} = 1 \times 10^{-4} \text{ mol dm}^{-3}$, $c_{\text{Cd}^{2+}} = 1 \times 10^{-2} \text{ mol dm}^{-3}$ in $1 \text{ mol dm}^{-3} \text{ HClO}_4$

a tool for the investigation of processes taking place in the course of bulk and underpotential depositions, and even induced anion adsorption furnishes some information on alloy formation.

It is important to emphasise that the phenomenon observed should be ascribed to specific interactions alone. Owing to the presence of the great excess of ClO_4^- ions, the role of electrostatic forces in the enhancement of the adsorption of Cl^- and HSO_4^- (SO_4^{2-}) species could be only of minor importance. The data obtained attest that there is a specific interaction of anions with Cd adatoms and with the surface of Cd/Au alloy while no significant adsorption occurs at potentials where the bulk deposition of Cd takes place. An interesting feature is the observation that the adsorption strength of sulfate species on Cd adatoms is higher than that of Cl^- ions, in contrast to the rule for “pure” gold and other noble metals.

Acknowledgements Financial support from the Hungarian Scientific Research Fund is acknowledged (OTKA Grant T 023056).

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