

Underpotential deposition of cadmium onto Cu(111) and Cu(110) from chloride containing solutions

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Underpotential deposition (UPD) of Cd onto the (111) and (110) faces of copper in chloride containing electrolyte has been investigated by cyclic voltammetry and the potentiostatic pulse technique. It was shown that the UPD of Cd onto the (111) face of copper is characterized by two pairs of peaks, one pair corresponding to the formation of the $(\sqrt{19} \times \sqrt{19})R23.4^\circ$ structure of Cd and the other one, taking place close to the reversible potential of Cd deposition, corresponding to the alloying of Cu with Cd. Deposition of $(\sqrt{19} \times \sqrt{19})R23.4^\circ$ structure of Cd was found to take place by the mechanism of replacement of the adsorbed structure of chloride, without chloride desorption (the chloride stays adsorbed on top of the Cd layer). Similar behaviour was found for the (110) face of copper, with more pronounced alloying which provokes an irreversible change of the original (110) surface of copper.

Keywords: Cu(111), Cu(110), $(\sqrt{19} \times \sqrt{19})R23.4^\circ$ structure of Cd, alloying.

INTRODUCTION

Although underpotential deposition (UPD) of different metals onto Ag, Pt and Au single crystal surfaces has been widely investigated,¹ a limited number of fundamental studies of UPD has been performed onto Cu single crystal surfaces,^{2–6} all of them examining the UPD of lead. On the other hand, chloride adsorption onto copper single crystals has been extensively examined by cyclic voltammetry, *ex situ* LEED and AES techniques,^{7–11} as well as *in situ* by the STM technique.^{12–14} In the papers of Brisard *et al.*^{5,6} it was shown that the presence of chloride ions in the supporting electrolyte (0.01 M HClO₄) has a strong effect on the potential region where deposition/stripping of a Pb monolayer occurs, as well as on the reversibility of this reaction.

UPD of cadmium onto Cu(111) has been the subject of only two papers. Ge and Gewirth¹⁵ investigated the UPD of Cd onto Cu(111) in perchlorate medium by AFM

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and cyclic voltammetry. They found that UPD of Cd takes place in the potential region between 0.0 V and -0.2 V vs. SHE and that Cd forms $(\sqrt{4} \times \sqrt{4})$ structure with atomic spacing 0.343 nm, while overpotential deposition (OPD) of Cd commences at about -0.4 V vs. SHE with the resulting crystalline structure being Cd(0001) hcp.

Stuhlmann *et al.*¹⁶ investigated UPD of Cd onto Cu(111) in pure chloride containing solution (0.01 M HCl with addition of 0.0001 M or 0.001 M CdCl₂) by cyclic voltammetry and UHV based spectroscopies. By LEED, they detected an UPD layer of Cd of the structure $(\sqrt{19} \times \sqrt{19})R23.4^\circ$ with a coverage of 9/19 monolayers ($\theta = 0.474$) with respect to Cu(111) and a Cd–Cd distance within the layer of 0.371 nm, which is much larger than in bulk Cd but close to that of CdCl₂ (0.384 nm), suggesting that the adsorbed chloride may stabilize the structure. According to their low energy scattering spectrum, a Cd layer is sandwiched between a Cl layer and the Cu substrate. They also detected the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure at more positive potentials than the potential of Cd UPD, which was ascribed to the layer of adsorbed chloride atoms. The authors claim that Cl is completely discharged on the clean Cu(111) surface as well as on the Cd covered surface and that the adsorbed Cl does not contribute to the charge transfer during the formation of the Cd layer.

In this paper an attempt was made to investigate the UPD of Cd onto Cu(111) and Cu(110) in pure chloride solution of higher concentrations of cadmium ions. It was shown that on the (111) face of copper this process is characterized by two pairs of sharp peaks, one taking place at the potential of chloride adsorption/desorption and the other one at a potential close to the reversible potential of bulk deposition of Cd. On the (110) face of copper, the UPD of Cd is characterized by three pairs of peaks.

EXPERIMENTAL

All experiments were carried out in a two-compartment electrochemical cell at 25 \pm 1 $^\circ$ C in an atmosphere of purified nitrogen. The single crystal electrodes ($d = 2.54$ cm) were sealed in epoxy resin (resin EPON 828 + hardener TETA) in such a way that only the (111), or (110) disc surface was exposed to the solution. The surface area of the electrode exposed to the electrolyte was 5.05 cm². The counter electrode was a platinum sheet which was placed parallel to the working electrode. The reference electrode was a saturated calomel electrode (SCE), or Cd wire (99.999%) immersed in the solution of Cd²⁺ ions, which was placed in a separate compartment and connected to the working compartment by means of a Luggin capillary. The potential values are referenced to SCE or to the Cd²⁺/Cd electrode. All solutions were made from supra pure (99.999%) chemicals (Aldrich) and EASY pure UV water (Barnstead).

Copper single crystals (Monocrystals Comp.) were mechanically polished on fine grade emery papers (1200, 2400 and 4000) with subsequent polishing on polishing clothes impregnated with a suspension of polishing alumina with particles dimension of 1 μ m, 0.3 μ m and 0.05 μ m. After chemical polishing, the copper single crystals were electrochemically polished in a solution of 85% phosphoric acid at a constant voltage of 1.7 V (vs. Pt counter electrode) until the current density dropped to a value of about 18 mA cm⁻². The electrode was then thoroughly rinsed with pure water (Barnstead-EASY pure UV) and transferred to the electrochemical cell.

Cyclic voltammetry experiments were performed using a universal programmer PAR M-175, a potentiostat PAR M-173 and an X–Y recorder (Houston Instrument 2000R). Potentiostatic j – t transients were recorded on a digital oscilloscope (Nicolet 4094 A) and transferred to the X–Y recorder.

RESULTS

To avoid IR drop effects, a solution of 0.1 M NaCl + 0.001 M HCl, of pH 3 was used as the supporting electrolyte in all measurements. Two concentrations of CdCl₂ were investigated. In the case of the low concentration (0.005 M), CdCl₂ was added to a solution of 0.1 M NaCl + 0.001 M HCl after the voltammogram of Cu(111) has been recorded in the supporting electrolyte. In this case the potential was referenced to SCE. For the high concentration of CdCl₂ (0.1 M), the solution was made as a mixture of 0.1 M NaCl + 0.001 M HCl + 0.1 M CdCl₂, Cd wire (99.999 %) was used as the reference electrode and, accordingly, the potential was referenced to the reversible potential of Cd in 0.1 M CdCl₂ solution (Cd²⁺/Cd). In this solution, the potential of the Cd wire was -0.704 V vs. SCE.

(111) Face of copper

Cyclic voltammograms of Cu(111) recorded in the supporting electrolyte at three different sweep rates are shown in Fig. 1a. As can be seen a sharp anodic peak appears on all three voltammograms, indicating chloride ions adsorption, while in the cathodic going direction one shoulder and one broad peak represent the desorption of chloride ions and the hydrogen evolution reaction.⁷⁻¹⁴ These voltammograms are in good agreement with the results of other authors.⁷⁻¹⁴

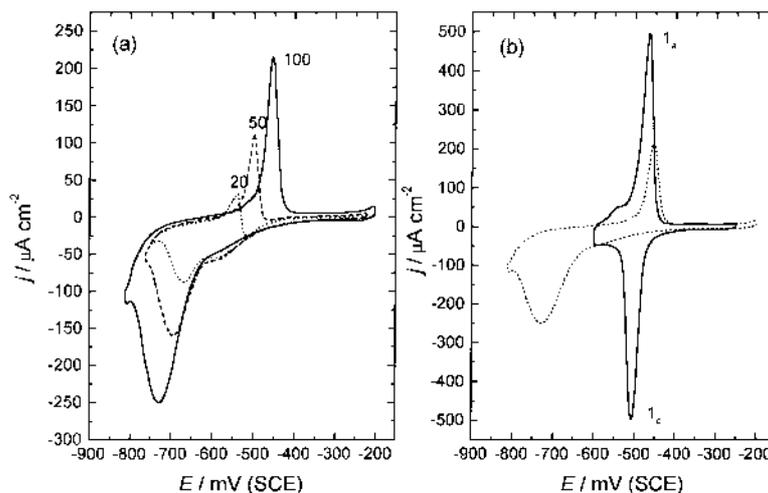


Fig. 1. (a) Cyclic voltammograms recorded at different sweep rates (marked in the figure in mV s^{-1}) onto the (111) face of copper in a solution of 0.1 M NaCl + 0.001 M HCl. (b) Cyclic voltammograms recorded at sweep rate of 100 mV s^{-1} onto the (111) copper in a solution of 0.1 M NaCl + 0.001 M HCl (dotted line) and in a solution of 0.1 M NaCl + 0.001 M HCl + 0.005 M CdCl₂.

After addition of 0.005 M CdCl₂ to the supporting electrolyte, the voltammogram shown in Fig. 1b (full line) was obtained. Well defined sharp peaks (1_c and 1_a) of the UPD of Cd onto Cu(111) at about -500 mV vs. SCE appear on the voltammogram. At a sweep rate of 100 mV s^{-1} , these peaks look like a single voltammetric peak, but they are actually composed of two peaks, as was shown for high CdCl₂ concentration.

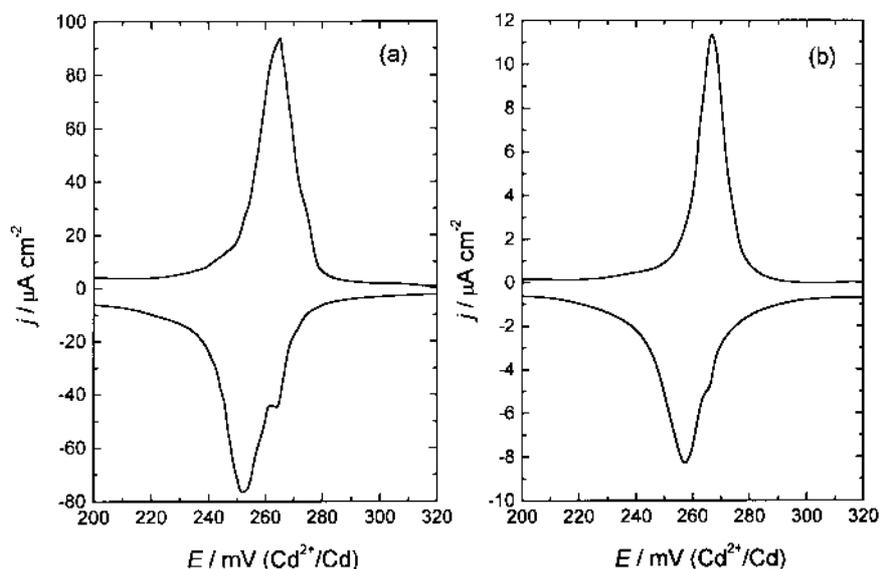


Fig. 2. Cyclic voltammograms recorded at a sweep rate of 10 mV s^{-1} (a) and 1 mV s^{-1} (b) onto the (111) face of copper in a solution of $0.1 \text{ M NaCl} + 0.001 \text{ M HCl} + 0.1 \text{ M CdCl}_2$.

The fine structure of these peaks can only be detected at sweep rates lower than 20 mV s^{-1} . Cyclic voltammograms recorded in a solution of $0.1 \text{ M CdCl}_2 + 0.1 \text{ M NaCl} + 0.001 \text{ M HCl}$ at a sweep rate of 10 mV s^{-1} (a) and 1 mV s^{-1} (b), shown in Fig. 2, clearly indicates the presence of two peaks in the cathodic branch of the voltammogram, most probably corresponding to two processes taking place simultaneously. The charge under the cathodic (as well as under the anodic) peak recorded at a sweep rate of 10 mV s^{-1} amounts to about 220 C cm^{-2} .

By using a computer program (PeakFit) for fitting experimentally recorded voltammograms it is possible to obtain much better insight into the processes taking place under the cathodic (i_c) and anodic (i_a) peaks. The results of such analysis are shown in Fig. 3. As can be seen in Fig. 3a, the best fitting of the cathodic peak was obtained with three peaks, two of them being very sharp, while the best fitting of the anodic peak is obtained using two sharp peaks (Fig. 3b). Hence, neither the cathodic nor the anodic peak is a simple voltammetric peak, indicating the simultaneous occurrence of two or more processes.

In the presence of 0.005 M CdCl_2 in the supporting electrolyte, the peak of hydrogen evolution is suppressed and at about -720 mV vs. SCE another pair of peaks appears on the voltammogram, as can be seen in Fig. 4a. Because of the commencement of bulk Cd deposition, these peaks cannot be resolved at sweep rates higher than 5 mV s^{-1} , but they are clearly seen on the voltammogram recorded at 1 mV s^{-1} (see Fig. 4a). It is interesting to note that the charges under the anodic and cathodic part of this voltammogram amounts to about 500 C cm^{-2} and 560 C cm^{-2} , respectively, which are higher than the charge needed for a Cd monolayer deposition ($Q_{\text{mon}} = 412 \text{ C cm}^{-2}$).

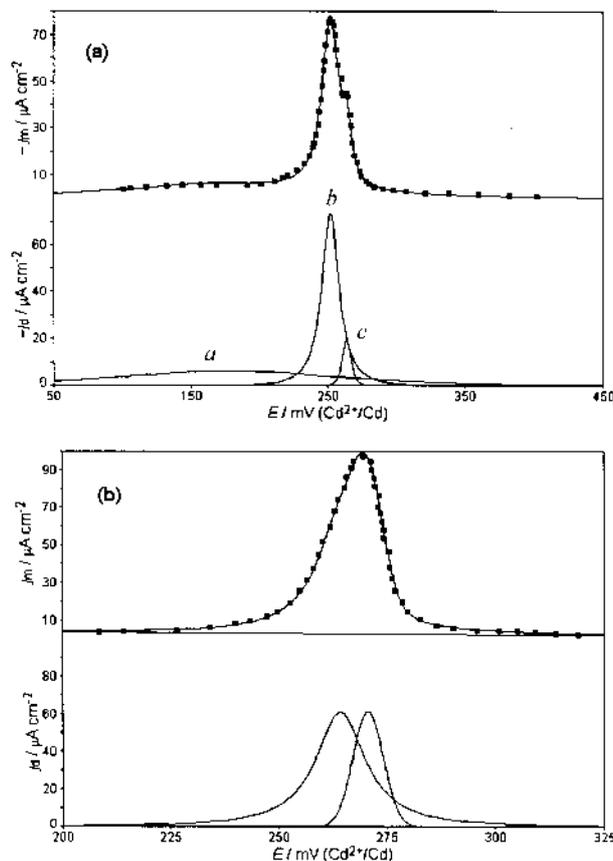


Fig. 3. Results of the deconvolution of the experimentally recorded cathodic (a) and anodic (b) peak recorded on the (111) face of copper at a sweep rate of 10 mV s^{-1} in a solution of $0.1 \text{ M NaCl} + 0.001 \text{ M HCl} + 0.1 \text{ M CdCl}_2$. The experimental points are presented by squares ($j_m - E$ dependence), the fitted curve is presented by the full line on the same dependence, while the deconvoluted peaks are marked with a , b and c and presented by $j_d - E$ dependence.

In the solution containing a much higher concentration of CdCl_2 (0.1 M), the peaks appearing at potential close to the reversible potential of Cd deposition are much bigger at the same sweep rate of 1 mV s^{-1} , as can be seen in Fig. 4b. As in the previous case, these peaks can only be detected at sweep rates lower than 5 mV s^{-1} . Since in this case a Cd wire was used as the reference electrode, it can be seen that a second cathodic UPD peak (2_c) appears at a potential of about $5 \text{ mV vs. Cd}^{2+}/\text{Cd}$, while the OPD process (peak 3_c) starts immediately after reaching the reversible potential of Cd deposition. The anodic peak of bulk dissolution of Cd (3_a), appearing at about $2 \text{ mV vs. Cd}^{2+}/\text{Cd}$, is very sharp, while the second anodic UPD peak (peak 2_a – corresponding to the dissolution of Cd deposited under the cathodic peak 2_c) appears at about $25 \text{ mV vs. Cd}^{2+}/\text{Cd}$. Hence, it is obvious that just before the commencement of the OPD of Cd, the appearance of a second pair of UPD peaks (2_c and 2_a) characterizes the process of UPD of Cd onto Cu(111). In this case the anodic and cathodic charge under the voltammogram are also higher than the charge needed for the deposition of a Cd monolayer, amounting to 591 C cm^{-2} and 1500 C cm^{-2} , respectively.

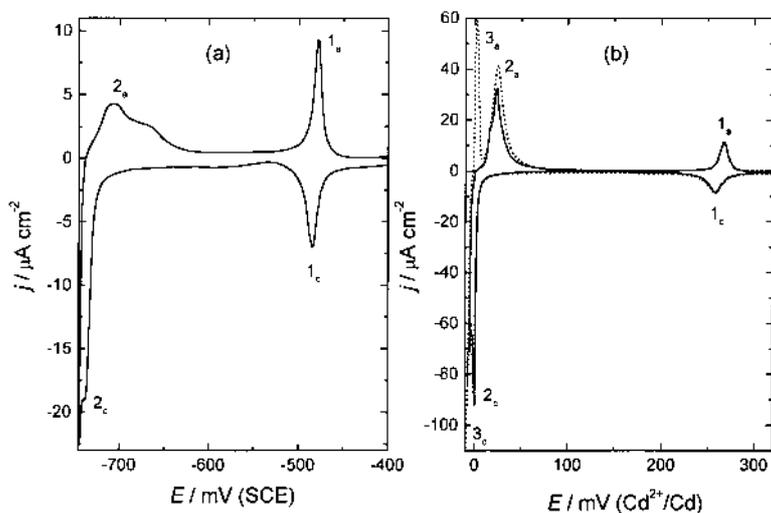


Fig. 4. Cyclic voltammograms recorded at a sweep rate of 10 mV s^{-1} onto the (111) face of copper in a solution of $0.1 \text{ M NaCl} + 0.001 \text{ M HCl} + 0.005 \text{ M CdCl}_2$ (a) and $0.1 \text{ M NaCl} + 0.001 \text{ M HCl} + 0.01 \text{ M CdCl}_2$ (b).

Since the second UPD peak can be detected only at sweep rates lower than 5 mV s^{-1} and this peak cannot be resolved from the increase in the cathodic current corresponding to the OPD of Cd at a sweep rate of 10 mV s^{-1} , a holding experiment at the commencement of this process (potential of $E_h = 0 \text{ mV vs. Cd}^{2+}/\text{Cd}$) was performed (at the potential of $0 \text{ mV vs. Cd}^{2+}/\text{Cd}$, the cathodic current density recorded at 10 mV s^{-1} just starts to increase and there is no corresponding anodic peak on the voltammogram re-

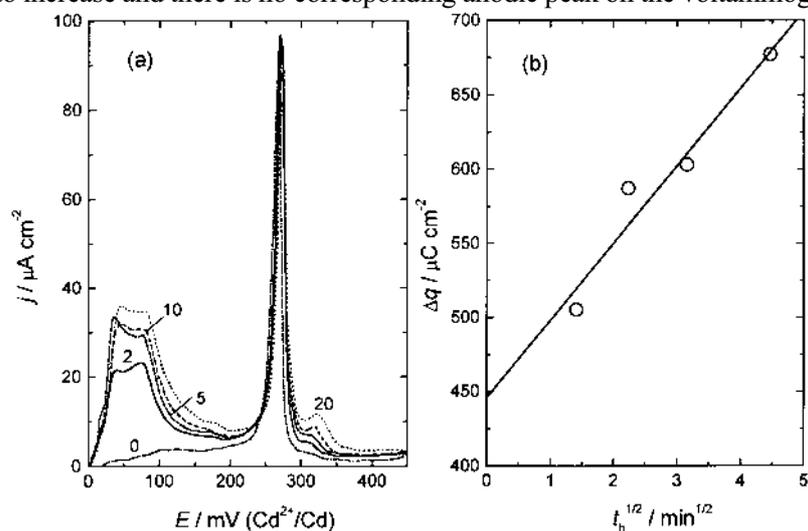


Fig. 5. (a) Anodic voltammograms recorded at a sweep rate of 10 mV s^{-1} after holding the (111) face of copper at a potential of $E_h = 0 \text{ mV vs. Cd}^{2+}/\text{Cd}$ for different times (marked in the Figure in minutes) in a solution of $0.1 \text{ M NaCl} + 0.001 \text{ M HCl} + 0.1 \text{ M CdCl}_2$. (b) Corresponding $q - t_h^{1/2}$ dependences.

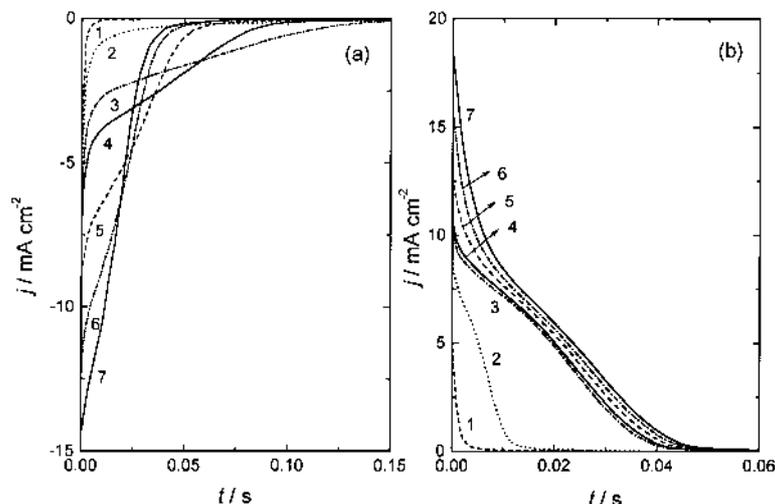


Fig. 6. Cathodic potentiostatic $j-t$ transients recorded onto the (1110 face of copper in a solution of 0.1 M NaCl + 0.001 M HCl + 0.1 M CdCl₂ by pulsing from $E_{in} = 400$ mV vs. Cd²⁺/Cd to the following potentials (given in mV vs. Cd²⁺/Cd): 1.300; 2.260; 3.220; 4.200; 5.150; 6.100; 7.50. (b) Anodic $j-t$ transients recorded by pulsing back to E_{in} .

corded by repetitive cycling – see voltammogram marked with 0 in Fig. 5a). The results of such an experiment are shown in Fig. 5. As can be seen in Fig. 5a, the shape of the voltammogram changes with holding time, *i.e.*, anodic peaks recorded in the potential region between 0 mV and 100 mV vs. Cd²⁺/Cd, as well as a small peak appearing at a potential of about 325 mV vs. Cd²⁺/Cd, increase with time of holding the electrode at $E_h = 0$ mV vs. Cd²⁺/Cd. The linear $q-t_h^{1/2}$ dependence shown in Fig. 5b indicates the occurrence of solid state diffusion and alloying of Cu with Cd.¹⁷⁻²¹

The results of potentiostatic pulse experiments, performed in the potential region positive to peak 2_c are shown in Fig. 6. As can be seen, cathodic and anodic $j-t$ transients typical for UPD are obtained.²² By integration of the charge under the cathodic $j-t$ transients, the Q_m-E dependence, shown in Fig 7a is obtained. Assuming that the charge recorded in the potential region between 400 mV and 300 mV vs. Cd²⁺/Cd corresponds to the double layer charge, it is possible to correct the measured charge (Q_m) for the double layer charge (Q_{dl}) in order to obtain the charge needed for the UPD process (Q_{UPD}). As can be seen on the $Q_{UPD}-E$ curve a sharp increase in charge (from 5 C cm⁻² to 180 C cm⁻²) is recorded in the potential region between 280 mV and 240 mV vs. Cd²⁺/Cd. As can be seen in Fig. 7b, an almost identical $Q_{UPD}-E$ dependence is obtained by integration of anodic $j-t$ transients.

(110) Face of copper

As in the case of Cu(111), the fine structure of the UPD process can only be detected at sweep rates lower than 20 mV s⁻¹. The voltammograms recorded in a solution of 0.1 M CdCl₂ + 0.1 M NaCl + 0.001 M HCl at a sweep rate of 5 mV s⁻¹ (a) and 10 mV s⁻¹ (b) are shown in Fig. 8. As can be seen, the cathodic and anodic parts of the voltammograms differ

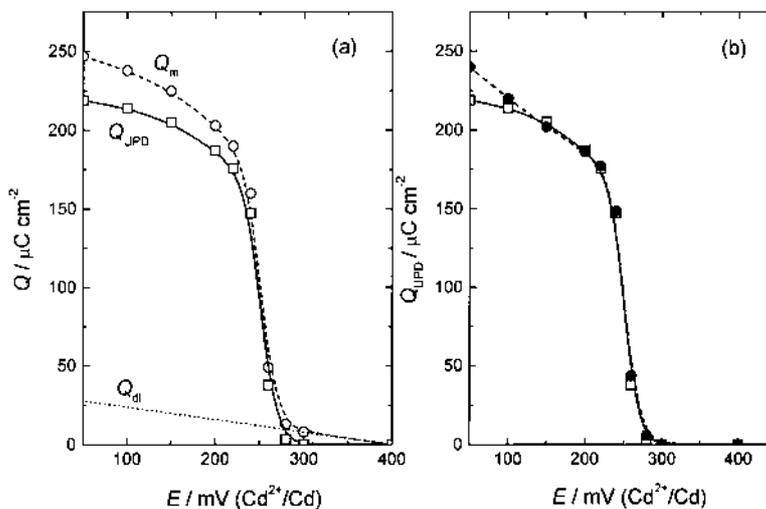


Fig. 7. (a) Q - E dependences obtained by the integration of the cathodic j - t transients shown in Fig. 6. (b) Cathodic (full line - \square) and anodic (dashed line - \bullet) QUPD - E dependences obtained by integration of the cathodic and anodic j - t transients shown in Fig. 6.

significantly in the potential region of the first pair of peaks (1_c , $1_c'$ and 1_a , $1_a'$). It is interesting to note that the anodic and cathodic charges recorded for peaks 1 and 2 amount to 520 C cm^{-2} and 694 C cm^{-2} , respectively, indicating that more than a monolayer of Cd had already been deposited at the potential of 100 mV vs. Cd^{2+}/Cd . Hence, peak 3_c can be ascribed to the process of surface alloying of Cu with Cd.

To confirm this statement, a holding experiment was performed at the potential of

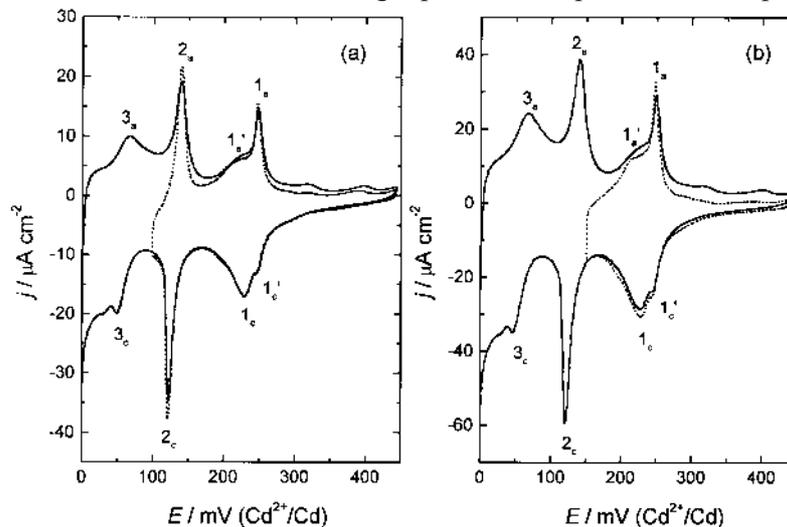


Fig. 8. Cyclic voltammograms recorded at a sweep rate of 5 mV s^{-1} (a) and 10 mV s^{-1} (b) onto the (110) face of copper in a solution of $0.1 \text{ M NaCl} + 0.001 \text{ M HCl} + 0.01 \text{ M CdCl}_2$.

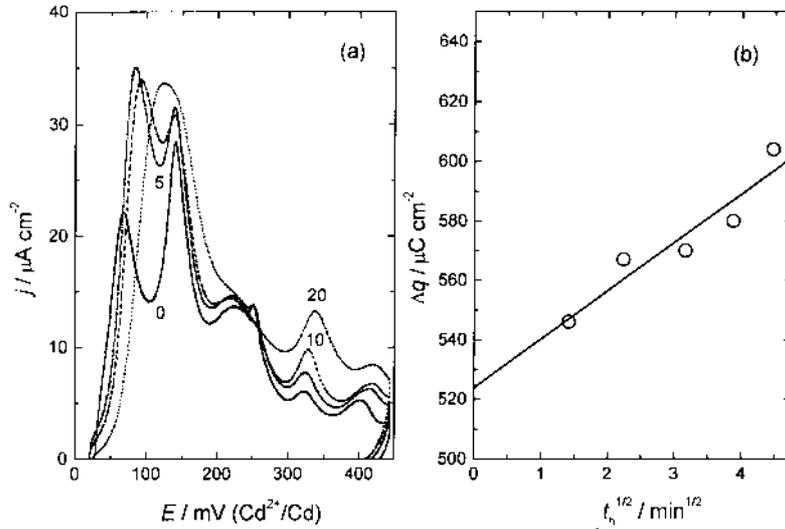


Fig. 9. (a) Anodic voltammograms recorded at a sweep rate of 10 mV s^{-1} after holding the (110) face of copper at a potential of $E_h = 20 \text{ mV vs. Cd}^{2+}/\text{Cd}$ for different times (marked in the Figure in minutes) in a solution of $0.1 \text{ M NaCl} + 0.001 \text{ M HCl} + 0.1 \text{ M CdCl}_2$. (b) Corresponding $q - t_h^{1/2}$ dependences.

$20 \text{ mV vs. Cd}^{2+}/\text{Cd}$. The obtained results are shown in Fig. 9. As can be seen almost all the anodic peaks increase with holding time (Fig. 9a). A linear $q - t_h^{1/2}$ dependence shown in Fig. 9b indicates, as in the case of Cu (111), the occurrence of solid state diffusion and alloying of Cu with Cd.¹⁷⁻²¹

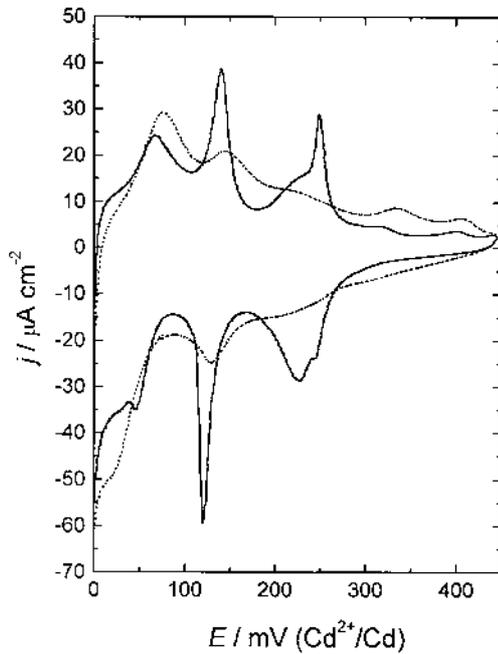


Fig. 10. Cyclic voltammograms recorded at a sweep rate of 10 mV s^{-1} onto the (110) face of copper in a solution of $0.1 \text{ M NaCl} + 0.001 \text{ M HCl} + 0.1 \text{ M CdCl}_2$ before (full line) and after alloying of Cu(110) with Cd (dotted line).

The voltammograms recorded in a solution of 0.1 M CdCl₂ + 0.1 M NaCl + 0.001 M HCl at a sweep rate of 10 mV s⁻¹ before (full line) and after performing the holding experiment (dotted line) are shown in Fig. 10. As can be seen the (110) face of copper is irreversibly changed after alloying with Cd.

DISCUSSION

(111) Face of copper

Since there is only one paper concerning Cd UPD in chloride containing solution,¹⁶ our results can only be compared with the results presented in this paper. According to the results of Stuhlmann *et al.*¹⁶ UPD of Cd is characterized by the presence of only one peak of a complex nature, recorded in the potential region between -0.8 V and -0.85 V vs. saturated sulphate electrode (SSE) (for CdCl₂ concentration of 0.001 M), while the cyclic voltammogram of the same process in a solution of 0.0001 M CdCl₂ is characterized by one spike at about -0.82 V vs. SSE and a broad peak situated between -0.82 V and -0.90 V vs. SSE (Figs. 1 and 2 of Ref. 16). It is quite interesting that for a solution of 0.0001 M CdCl₂ the XPS intensity for Cd starts to increase sharply at about -0.85 V vs. SSE, in the region of the broad peak on the voltammogram (Fig. 2 of Ref. 16), while the intensity for Cl also slightly increases in the potential region between -0.85 V and -1.15 V vs. SSE. Although the authors did not explain this voltammogram, it seems that the spike appearing at the potential of about -0.82 V vs. SSE is not connected with the process of Cd UPD and might be the consequence of a phase transformation of ordered ($\sqrt{3} \times \sqrt{3}$)R30° chloride structure into a randomly adsorbed layer of chloride as the first step in the process of UPD of Cd, since it is hard to believe that the formation of some ordered structure (such as structure ($\sqrt{19} \times \sqrt{19}$)R23.4° found for Cd) can start with a spike, which is characteristic of a phase transformation process, on the cyclic voltammograms. It is also interesting to note that, although ordered ($\sqrt{3} \times \sqrt{3}$)R30° chloride structure has been evidenced by LEED and STM on Cu(111) in pure chloride solution,⁷⁻¹⁴ the voltammogram of its formation is not characterized by the presence of a spike neither in the cathodic nor anodic region.⁷⁻¹⁴ Under the second, broad peak, (Fig. 1c of Ref. 16), on commencement of UPD of Cd the randomly adsorbed chloride layer is replaced with ordered Cd structure ($\sqrt{19} \times \sqrt{19}$)R23.4°, while the chlorides do not desorb but remain adsorbed on top of the Cd layer. According to the change of XPS intensity with potential for chloride (slight increase in the potential region between -0.85 V and -1.15 V vs. SSE) it seems that during the formation of the ($\sqrt{19} \times \sqrt{19}$)R23.4° structure of Cd, additional chloride ions adsorb on top of the Cd layer.

Concerning the appearance of peak 1 there is relatively good agreement between the results presented in our paper with those published by Stuhlmann *et al.*¹⁶ It can be seen that at low¹⁶ and high (our paper) concentration of cadmium ions this peak is composed of at least two peaks, indicating the simultaneous occurrence of two processes. Taking into account the charge under this peak and $Q_{\text{UPD}}-E$ dependence (Fig. 7), it is obvious that the Cd structure detected by Stuhlmann *et al.*¹⁶ is formed and that the desorption of the complete ordered ($\sqrt{3} \times \sqrt{3}$)R30° chloride structure does not occur. The contribution of chloride

desorption is very small and can be attributed to a phase transformation of this ordered structure into a randomly adsorbed one, while the corresponding peak should be peak *a*, obtained by the deconvolution of peak 1_c and presented in Fig. 3a. By transforming peak *a* into a $-E$ dependence and fitting this dependence by Frumkin adsorption isotherm, the interaction factor $f_a = -6.64 \pm 0.42$ is obtained, indicating strong attraction between the adsorbed atoms, as is to be expected for an ordered 2D structure (in this case $(\sqrt{3} \times \sqrt{3})R30^\circ$ chloride structure). Once this structure is transformed into randomly adsorbed chloride, cadmium starts to replace chloride atoms forming the $(\sqrt{19} \times \sqrt{19})R23.4^\circ$ structure of Cd, the process being characterized by peak *b* (Fig. 3a), while the chloride remains adsorbed on top of this Cd structure. By fitting peak *b* in the same way as peak *a*, the interaction factor $f_b = -3.76 \pm 0.07$ is obtained, again indicating strong attraction between the adsorbed atoms. It is interesting to note that different results are obtained by the deconvolution of the anodic peak 1_a , as can be seen in Fig. 3b. The best fit of the experimentally recorded peak 1_a are obtained by two peaks, *a* and *b*. Again, by fitting these peaks with Frumkin adsorption isotherm, the interaction factor $f_a = -6.61 \pm 0.43$ (in this case the phase transformation of the randomly adsorbed chloride layer into the $(\sqrt{3} \times \sqrt{3})R30^\circ$ chloride structure) and $f_b = -4.41 \pm 0.18$, desorption of the $(\sqrt{19} \times \sqrt{19})R23.4^\circ$ structure of Cd. As can be seen, the values of the anodic and cathodic f_a parameters are almost identical, while the f_b parameters differ, which is most probably the consequence of the different number of peaks resulting from the deconvolution procedure. The additional peak *c* obtained by deconvolution of the experimentally recorded cathodic peak (Fig. 4a) might represent a contribution of the hydrogen evolution reaction, which is assumed to occur during desorption of chloride anions.⁷⁻¹⁴

The main difference between our results and results of Stuhlmann *et al.*¹⁶ is the appearance of a second pair of peaks, 2_c and 2_a , close to the reversible potential of Cd deposition, as seen in Fig. 4. Although there is an indication of the appearance of a second pair of peaks in the paper of Stuhlmann *et al.*¹⁶ (Fig. 2 of Ref. 16), the authors paid no attention to these peaks. As can be seen in Fig. 4, with increasing concentration of cadmium ions these peaks become sharper and the charge under the peaks increases. It is also important to note that the process taking place under these peaks is slow and these peaks can be detected only at very low sweep rates ($< 5 \text{ mV s}^{-1}$). Since the corresponding anodic charge for the whole voltammogram exceeds the charge (about 500 C cm^{-2} for 0.005 M CdCl_2 and 591 C cm^{-2} 0.1 M CdCl_2) needed for the deposition of a Cd monolayer ($Q_{\text{mon}} = 412 \text{ C cm}^{-2}$), it is obvious that these peaks represent the process of alloying of Cu with Cd. This is confirmed by the results presented in Fig. 5. The linear $q - t_h^{1/2}$ dependence shown in Fig. 5b is typical for solid state diffusion and alloying of Cu with Cd.¹⁷⁻²¹

(110) Face of copper

The results obtained on the (110) face of copper cannot be compared to any other results, since there are no data in the literature about UPD of Cd onto this surface. From the voltammograms shown in Fig. 8 it seems that an ordered, open structure Cd layer is adsorbed under peaks $1_c'$ and 1_c and desorbed under peaks $1_a'$ and 1_a . Again, as in the case of the (111) face of copper, these peaks are significantly different (dashed line in

Fig. 8b). This difference is most probably the consequence of the same factors as were assumed for the (111) face of copper. The sharp peaks 2_c and 2_a might represent phase transformation of this open structure into a monolayer of Cd, but the charge under the voltammogram recorded at the cathodic potential limit of 100 mV vs. Cd^{2+}/Cd (dashed line in Fig. 8a) is significantly higher than that needed for a full monolayer of Cd. Such a behaviour could be the consequence of two processes: alloying of Cu with Cd might commence already at the potential of these two peaks, or a significant amount of additional chloride ions is adsorbed on top of the Cd monolayer. This statement needs to be confirmed by additional holding experiments performed at the potential of peak 2_c . This is going to be the subject of further investigations. Alloying of Cu with Cd is confirmed for the peak 3_c in Fig. 9 by the well defined linear dependence $q - t_h^{1/2}$, typical for solid state diffusion and alloying.¹⁷⁻²¹ For a more open surface, as is the (110) face compared to the (111) face, more pronounced alloying might be expected, as is the case, since the original (110) surface is destroyed after alloying of Cu with Cd (Fig. 10).

CONCLUSIONS

Considering the presented results, it can be concluded that in chloride containing electrolyte UPD of Cd onto the (111) face of copper is characterized by two pairs of peaks, one pair corresponding to the formation of the $(\sqrt{19} \times \sqrt{19})R23.4^\circ$ structure of Cd and the other one, taking place close to the reversible potential of Cd deposition, corresponding to alloying of Cu with Cd. Deposition of the $(\sqrt{19} \times \sqrt{19})R23.4^\circ$ structure of Cd occurs by replacement of the adsorbed structure of chloride, without chloride desorption (the chloride stays adsorbed on top of the Cd layer). A similar behaviour was found for the (110) face of copper, with more pronounced alloying which provokes irreversible changes of the original (110) surface of copper.

ИЗВОД

ТАЛОЖЕЊЕ КАДМИЈУМА ИЗ РАСТВОРА ХЛОРИДА НА $\text{Cu}(111)$ И $\text{Cu}(110)$ ПРИ ПОТЕНЦИЈАЛИМА ПОЗИТИВНИЈИМ ОД РАВНОТЕЖНОГ

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Методама цикличне волтаметрије и потенциостатског пулса испитиван је процес таложења кадмијума из раствора хлорида на монокристалима бакра оријентација (111) и (110) при потенцијалима позитивнијим од равнотежног. Показано је да се на оба монокристала прво формира уређена, али не густо пакована структура адсорбованог кадмијума. На основу количине наелектрисања испод цикличног волтамограма и потенциостатских $j-t$ одговора установљено је да се на $\text{Cu}(111)$ формира структура типа $(\sqrt{19} \times \sqrt{19})R23.4^\circ$, која је детектована у раду Stuhlmann *et al.*¹⁶ помоћу LEED технике и да се ова структура таложи на тај начин што се слој адсорбованих хлорида истискује са површине $\text{Cu}(111)$. При томе се хлориди не десорбују, већ остају адсорбовани на слоју адсорбованог кадмијума. При негативнијим потенцијалима, близу равнотежног потенцијала таложења кадмијума, на оба монокристала долази до леги-

рања бакра са кадмијумом, при чему је овај процес израженији на Cu(110) и изазива трајну деформацију оригиналне површине монокристала бакра.

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