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Mechanism of underpotential deposition of cadmium onto Ag(111) surface from sulfate containing solution

ABSTRACT

In this work the mechanism of underpotential deposition (UPD) of Cd onto Ag(111) surface from sulfate containing solution has been investigated using cyclic voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS). The CVs of Cd UPD were characterized by the presence of 3 cathodic peaks: Peak 3 corresponding to the formation of ordered ad-layer of Cd with the structure $(\sqrt{3}x\sqrt{3})R30^o$*; Peak 2 corresponding most probably to the formation of a monolayer od Cd, with the possibility of the beginning of surface alloying of Ag and Cd; Peak 1 corresponding to the surface alloying of Ag and Cd. Peak 3 has been corrected for a base line, deconvoluted and analyzed by using Frumkin adsorption isotherm. Peaks (A,B) obtained by deconvoluetion were characterized by negative values of interaction parameter f, more negative than -4, indicating phase transition during the formation of this ordered structure. Z' vs.* ω *and -Z'' vs.* ω *dependences obtained in the potential range of peak 3 by the EIS measurements in the frequency range 10 kHz – 0.1 Hz were analyzed by two equivalent circuits: (a) one containing adsorption capacitance (*C_{ad}*) as parallel plate condenser and another one (b) with adsorption capacitance being expressed as a Constant Phase Element (*CPE_{ad}*). It was shown that the equivalent circuit (b) is more suitable for real interpretation of adsorption parameters* C_{dl},C_{ad} *and* R_{ad}*. It is important to note that this is the first time in the literature that such approach has been applied for analyzing the process of UPD.*

Keywords*: Ag(111), adsorption of Cd, phase transition of Cd ad-layer, EIS,* C_{dl}*,* C_{ad} *and* R_{ad} *determination.*

1. INTRODUCTION

The theoretical background for the process of UPD of metals on foreign substrates was given by Gerischer et al. [1] in 1974. With introduction of single crystal electrodes in electrochemical investigations this phenomenon attracted great attention. In the chapters of D.M. Kolb [2] and R.R. Adžić [3] thorough review of all investigated UPD systems has been presented. Among other systems the UPD behavior of lead and thallium onto silver single crystal substrates has been extensively examined [4–19]. Unfortunately there are only few papers concerning the UPD of Cd onto silver single crystals [16-19]. In most of these papers particular attention has been given to the process of UPD alloying of Ag with Cd in the UPD region [16,17,19]. H. Bort et al. [16] investigated UPD alloy formation in the systems Ag(111) / Cd^{2+} and Ag(100)/Cd^{2+} from sulfate containing solution. Well-defined three peaks for Cd UPD were detected onto Ag(111) surface. The UPD of Cd (first peak) commenced at a potential of about 0.3 V vs. Cd^{2+}/Cd (reversible potential for Cd electrodeposition) being characterized by one broad and one sharp peak, corresponding to the formation of a $(\sqrt{3}x\sqrt{3})R30°$ structure of adsorbed Cd. A second cathodic peak at about 0.07 V vs. Cd^{2+}/Cd has been ascribed to a monolayer formation of Cd, while a third cathodic peak has been ascribed to the formation of a second monolayer of Cd. In the potential region slightly more negative than the reversible potential of Cd electrodeposition Ag-Cd alloy formation has been detected. The time dependence of the Ag-Cd alloy formation process was described by a parabolic rate law, with the rate constant being a function of both, potential and temperature.

The influence of different anions (sulfate, perchlorate and citrate) on theUPD of Cd onto Ag single crystal was also investigated [18]. It was

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confirmed that both, CV and C_{diff} vs. E curves change in the presence of different anions. V.D. Jović et al. [19] investigated Ag-Cd alloy formation in the UPD potential region in the systems Ag(111)/Cd^{2+} from chloride containing solution. Concerning the kinetics of surface alloying of Ag with Cd similar conclusions as in Ref. [16] were presented, except the fact that two sharp cathodic peaks on the CV at potentials close to the reversible potential of Cd correspond to alloying of Ag with Cd. It was also stated that chloride ad-atoms, which are adsorbed on the silver substrate when UPD of Cd starts, do not desorb. They become replaced by Cd ad-atoms and remain adsorbed and on top of a Cd layer. Adsorption of $(\sqrt{3}\,x\sqrt{3})R30°$ structure of Cd was analyzed by Frumkin adsorption isotherm showing negative values of interaction parameter f for all deconvoluted peaks (attraction between adsorbed Cd ad-atoms) and for certain peaks phase transformation of adsorbed Cd layer (values of interaction parameter f more negative than -4) has been observed [19], indicating formation of ordered ad-atoms structure.

Hence, in all investigated solutions two processes took place simultaneously: adsorption/ desorption of anions and adsorption/desorption of cations (UPD). In order to electrodeposit certain ordered structure of metals (cf. Cd, Pb, Tl, Cu, Pd) in the UPD region, already adsorbed anions should be removed from the surface. These anions should probably remain adsorbed on the rest of the single crystal surface and on top of adsorbed layer of metals, or interact with the adsorbed metal structures forming well-ordered surface compounds. In situ techniques, such as STM and surface X-ray scattering should be excellent tool for investigations of possible formation of surface compounds. Unfortunately these techniques were mainly used for the anion adsorption investigation [20-26]. There is only one paper analyzing formation of surface compounds in the system Au(111)-Tl-Br using in situ X-ray diffraction technique [27]. It was shown that close-packed rotated hexagonal Br monolayers starts to disorder at the potentials where Tl starts to co-adsorb forming $TlBr_2$ surface compound in 3$TlBr_2$-$(\sqrt{13}x\sqrt{13})$ phase and TlBr surface compound in (2TlBr-$(3x\sqrt{3})$ phase at more negative potentials.

It is interesting to note that mainly CV and potential pulse electrochemical techniques were used for the investigation of UPD of different metals onto different single crystal surfaces. There was no attempt to predict equivalent circuit for adsorption/desorption process of cations in the case of UPD and perform EIS measurements in order to determine the mechanism of metal cations adsorption. Equivalent circuit composed of constant phase element (CPE_{dl}) instead of double layer capacitance (C_{dl}) connected in parallel with adsorption capacitance (C_{ad}) and adsorption resistance (R_{ad}) was used for analyzing anions adsorption only. Fitting of experimental results in these cases produced good results [28-31].

In this paper particular attention has been given to the analysis of the mechanism of Cd adsorption onto Ag(111) surface from sulfate containing solution using EIS measurements in the potential region of ordered $(\sqrt{3}\,x\sqrt{3})R30°$ structure formation. Two equivalent circuits were used for fitting EIS results in order to obtain adsorption parameters C_{dl}, C_{ad} and R_{ad}.

2. EXPERIMENTAL

All experiments were carried out in a two–compartment electrochemical cell at 25 $\pm$ 1 °C. The single crystal electrode (Monocrystals Company, d = 0.9 cm) was sealed in epoxy resin in such a way that only the (111) disc surface was exposed to the solution. The surface area of the electrode exposed to the electrolyte was 0.636 cm^2. The counter electrode (CE) was a Pt sheet and was placed parallel to the working electrode. The reference electrode (RE) was Cd wire (99.999 %) placed in the 0.1 M $CdSO_4$ + 0.1 M Na_2SO_4 solution (Cd^{2+}/Cd). The RE was placed in a separate compartment and connected to the working compartment by means of a Luggin capillary. Solutions of 0.1 M $CdSO_4$ and 0.1 M Na_2SO_4 were made from supra pure (99.999% – Aldrich) chemicals and extra pure UV water (Smart 2 Pure UV, TKA).

The single crystals were prepared by a mechanical polishing procedure followed by chemical polishing in the solution containing NaCN and H_2O_2 as explained in a previous paper [14]. Before each experiment, the electrolyte was purged with high purity nitrogen (99.999%) for 45 min., while a nitrogen atmosphere was maintained over the solution during the experiment to prevent contamination with oxygen.

All experiments were performed using potentiostat Reference 600 and PHE 200 and EIS 300 software (Gamry Instruments Inc.). EIS measurements were performed at constant potentials, in the frequency range from 10 kHz to 0.1 Hz, with the root mean square (RMS) amplitude of 10 mV and 10 points per decade. Two sets of measurements were performed: (1) For obtaining differential capacitance vs. potential (C_{diff} vs. E) curves in the range of 0.04 V to 0.38 V, C_{diff} was calculated from the relation $C_{diff} = Y''/\omega = \{Z''/[(Z' - R_s)^2 + (Z'')^2]/\omega\}$ (see Refs. [28-31]) for several frequencies (0.1, 1.0, 10, 100 and 1000 Hz); (2) In

order to plot C_{dl} vs. E, C_{ad} vs. E and R_{ad} vs. E curves potentials in the range of 0.14 V to 0.38 V were applied and EIS results were fitted using two equivalent circuits presented in Figure 1 (a) and (b). For the equivalent circuit (a) C_{diff} was calculated for each applied potential from the relation presented earlier [32], while for the equivalent circuit (b) the values for C_{dl}*, C_{ad}*, R_{ad}, α_{dl} and α_{ad} were obtained by fitting EIS results using commercial software (EIS 300, Gamry Instruments Inc.). Parameters C_{dl}* and C_{ad}* represent constants of *CPE* with the dimensions F cm^{-2} s$^{\alpha}$.

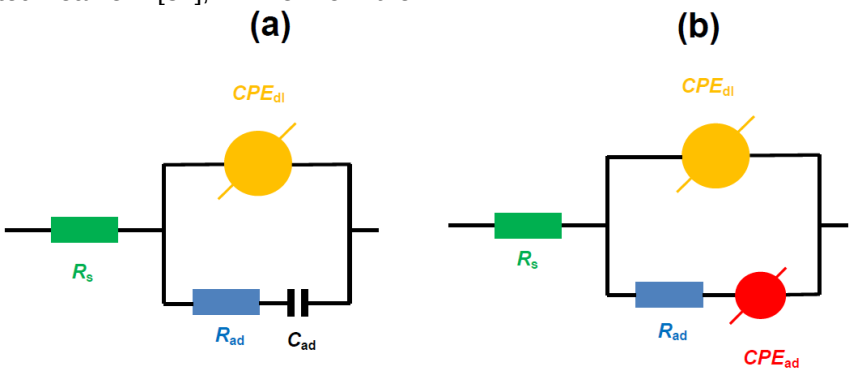


Figure 1. Equivalent circuits for fitting EIS results

3. RESULTS AND DISCUSSION

3.1. Analysis of cyclic voltammetry (CV) results

The CV for UPD of Cd onto Ag(111) surface, recorded in sulfate containing solution is presented in Figure 2(a). The UPD of Cd is characterized by the presence of 3 peaks: Peak 3 corresponding to the formation of $(\sqrt{3}\,x\sqrt{3})R30°$ ordered structure; Peak 2 corresponding most probably to the formation of a monolayer of Cd with the possibility of the beginning of surface alloying of Ag and Cd (as was the case in chloride containing solution [19]); Peak 1 corresponding to the surface alloying of Ag and Cd. As stated in section 1 during the adsorption of metal cations already adsorbed anions should be removed from the electrode surface and replaced with the adsorbed metal cations. As shown in Figure 2(b) CVs of sulfate anions adsorption/desorption and Cd^{2+} adsorption/ desorption are placed in the same potential region (the CV for sulfate adsorption is taken from [33]).

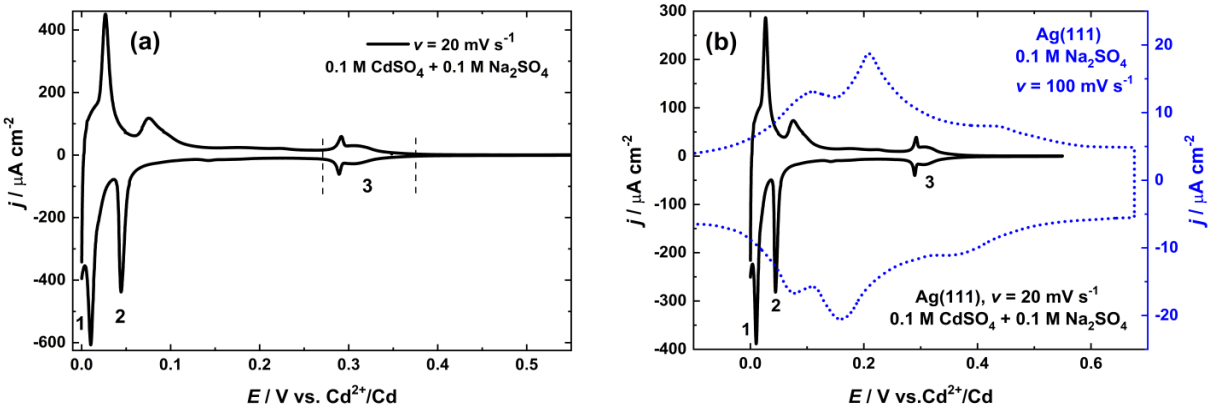


Figure 2. (a) The CV for UPD of Cd onto Ag(111), sweep rate of 20 mV s^{-1}, solution 0.1 M $CdSO_4$ + 0.1 M Na_2SO_4. (b) The CV of Cd UPD and the CV of sulfate adsorption/desorption onto Ag(111)

First, the base line was created and subtracted from the experimentally obtained CV in the range of peak 3 (Figure 2(a)). After that peak 3 was deconvoluted by Multiple Peak Fit function in Origin 21. Results of deconvolution are presented in Figure 3(a). Deconvolution of peak 3 produced two peaks, A and B. The next step was transformation of peaks A, B into potential vs. coverage functions (E vs. θ) and finally obtained E vs. θ dependences were fitted with the Frumkin adsorption isotherm presented in the following form [19]:

$$E = \frac{RT}{F}\left[ln\left(\frac{\theta}{1-\theta}\right) + f\theta - ln(K^{o}_{ads,\,\theta\rightarrow 0}c_o)\right] \quad (1)$$

where θ is coverage, f is interaction parameter, c_o is bulk concentration of Cd ions and K_{ads}^{o} is

adsorption constant.

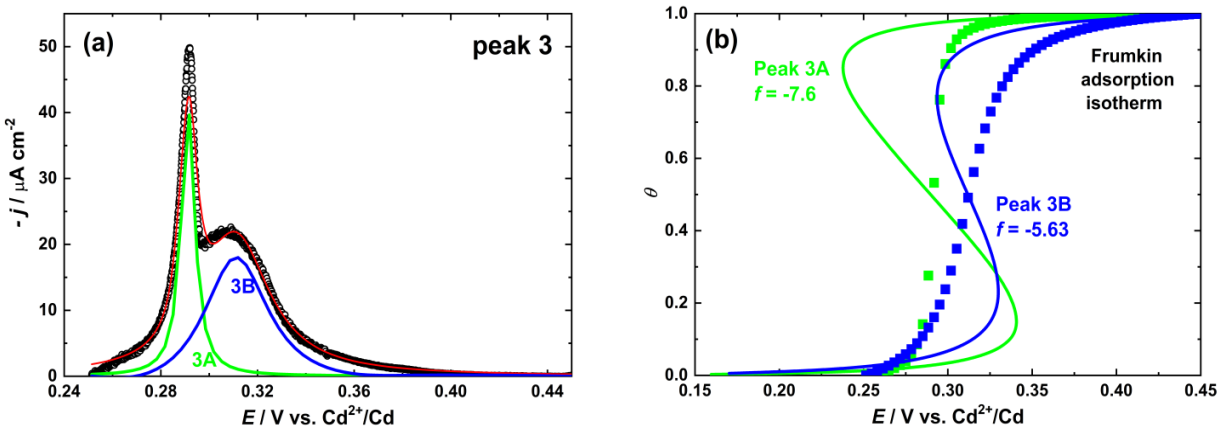


Figure 3. (a) Results of the deconvolutionof peak 3. (b) Results of fitting experimental θ vs. E curves (symbols) using Frumkin adsorption isotherm (lines)

Results of fitting *E* vs. θ curves (presented as θ vs. *E* dependences) by Frumkin adsorption isotherm for peak 3 is shown in Figure 3(b). The parameter *f* in the Frumkin adsorption isotherm could be either positive or negative. If there is no attraction between adsorbed species *f* is positive, if the attraction between adsorbed species exists, parameter *f* is negative. If the value of *f* is more negative than -4, this is an indication of strong attraction between adsorbed species and the formation of ordered structure of cations (or anions) on the electrode surface. If this is happening Frumkin adsorption isotherm is characterized by the S-shape (Fig. 15 of Ref. [14]), as it was the case for Cd adsorption onto Ag(111) in the potential region of peak 3A and 3B. After subtracting background curve from the experimental *j* vs. *E* curve and deconvolution of obtained dependence using Lorentzian function peaks 3A and 3B were obtained (Fig. 3(a). When these peaks were transferred into θ vs. *E* dependences Origin program offered dependences presented with points in Fig. 3(b). Why these dependences do not coincide with the fitting results at low coverage (using Frumkin adsorption isotherm) is not known, although they start from zero value. On the other side, at high coverage these curves are seen to coincide.

3.2. Differential capacitance vs. potential curves (C_{diff} vs. E)

C_{diff} vs. *E* curves, obtained by the procedure (1) (see section 2) for frequencies 0.1, 1.0, 10, 100 and 1000 Hz are presented in Figure 4.

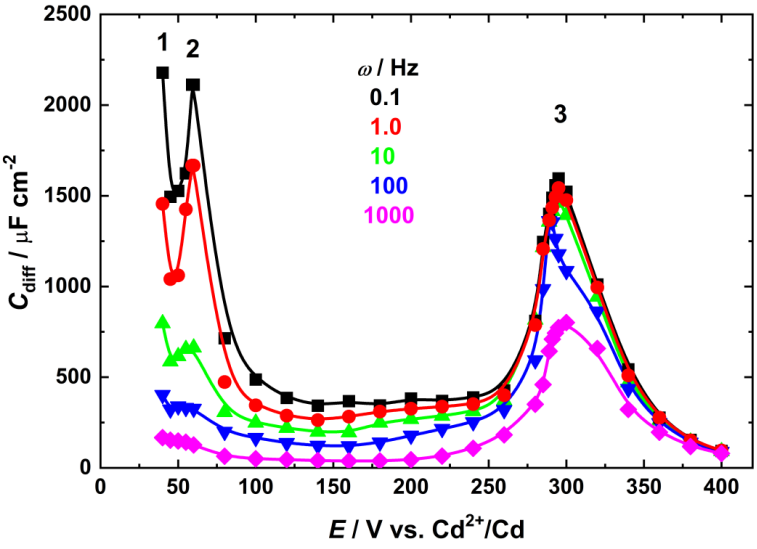


Figure 4. C_{diff} vs. E curves, obtained by the procedure (1) (section (2) for frequencies 0.1 Hz, 1.0 Hz, 10 Hz, 100 Hz and 1000 Hz

It is obvious that the shapes of C_{diff} vs. E curves recorded for frequencies 0.1 and 1.0 Hz are very similar to the shape of cathodic part of the CV presented in Figure 2(a). At higher frequencies the peaks on the C_{diff} vs. E curves become smaller and not well defined, indicating that these dependences cannot be used for the analysis of the UPD process, as was also the case with the adsorption/desorption of anions [28-31].

In order to apply procedure (2) (section 2) using equivalent circuit (a) and obtain good fits for C_{diff} vs. ω dependences the frequency range had to be reduced to 1 kHz – 7 Hz. Although this analysis was limited to the potential range from 0.14 V to 0.38 V vs. Cd^{2+}/Cd (since it was shown in previous papers [16-19] that surface alloying of Cd with Ag might occur even under the peak 2), and fitting results for C_{diff} vs. ω dependences were very good (as seen in Figure 5 (a-d)), such approach cannot be considered as relevant due to low frequency range applied.

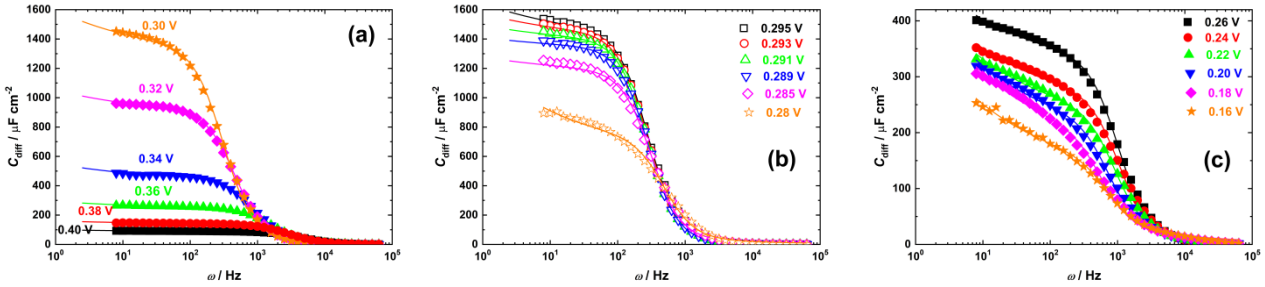


Figure 5. C_{diff} vs. ω curves for each applied potential (designated in the Figure). Experimental points are presented with symbols, while fitting curves are presented with the lines

3.3. Fitting with the equivalent circuit (b)

As can be seen in Figure 1(b) adsorption capacitance was represented by the Constant Phase Element (CPE_{ad}), introducing one more parameter – surface heterogeneity factor α_{ad}. In the case that such assumption was not realistic and that equivalent circuit (a) should be used, fitting of the EIS results would produce constant value of α_{ad} = 1. Since fitting procedure using commercial software produced α_{ad}< 1 (except for potentials around the sharp peak 3 – phase transition) equivalent circuit (b) was considered as relevant for representing adsorption of Cd onto Ag(111).

Hence, Z' vs. ω and $-Z''$ vs. ω dependences were fitted with the commercial software using equivalent circuit (b) and the results for certain potentials (designated in the figure) are presented in Figure 6. It is obvious that very good fits were obtained in the whole range of frequencies (10 kHz to 0.1 Hz).

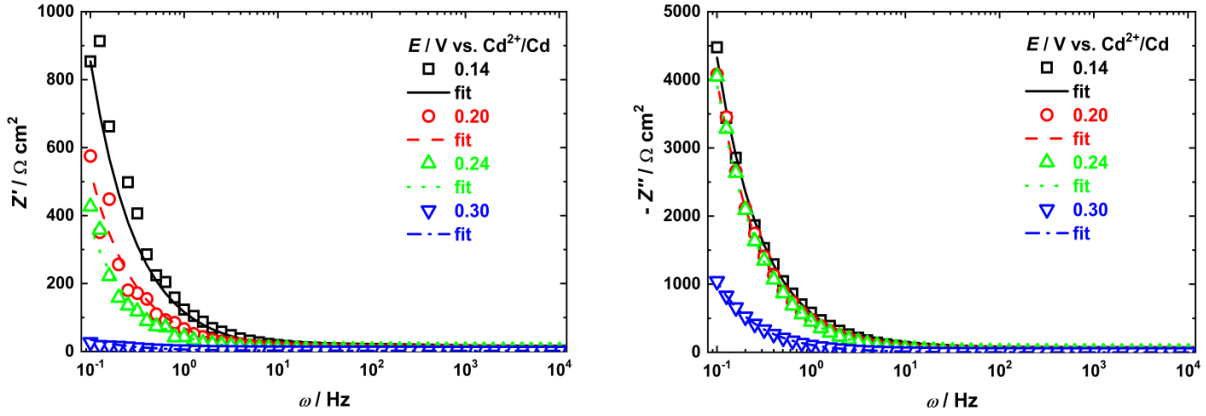


Figure 6. Z' vs. ω and $-Z''$ vs. ω dependences fitted using commercial software and equivalent circuit (b). Experimental points are presented with symbols, while fitting curves are presented with the lines Potentials are designated in the figure

Fitting procedure at each applied potential provided values for C_{dl}*, C_{ad}*, R_{ad}, α_{ad} and α_{dl}. Corresponding dependences C_{dl}* vs. E, C_{ad} vs. E, α_{ad} vs. E, R_{ad} vs. E and α_{dl} vs. E are presented in Figure

7.

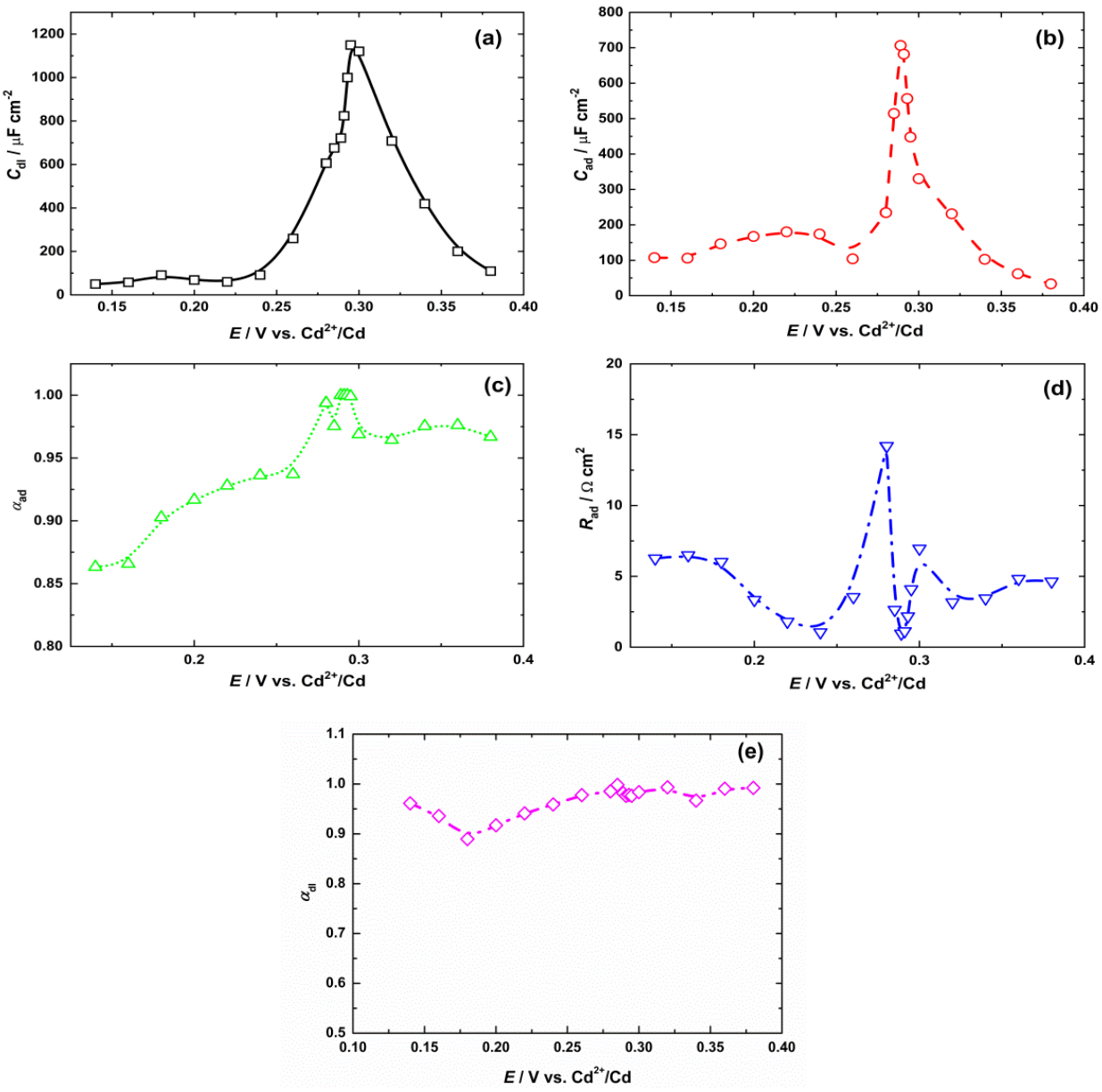


Figure 7. (a) C_{dl}(C_{dl}) vs. E, (b) C_{ad} vs. E, (c) α_{ad} vs. E, (d) R_{ad} vs. E, (e) α_{dl} vs. E dependences*

As stated in a previous publication [32], by using commercial software for fitting EIS results the real value of capacitance (C_{dl} or C_{ad}) could only be obtained for parallel or serial connection of *CPE* and resistance (R) (equations (7) and (8) [32]). Considering equivalent circuit (b) CPE_{dl} is in parallel connection with R_{ad}, while CPE_{ad} is in serial connection with R_{ad}. If the physical meaning of these parameters is neglected, both, C_{dl} and C_{ad} could be obtained using equations for parallel or serial connection of *CPE* and *R* by above mentioned equations. In this case it is logical to assume that serial connection between R_{ad} and CPE_{ad} has a physical meaning, representing mechanism of Cd adsorption.The real value of C_{ad} was obtained from the equation

$$C_{ad} = \left[C_{ad}^{*} R_{ad}^{(1-\alpha_{ad})}\right]^{\frac{1}{\alpha_{ad}}} \qquad (2)$$

Corresponding C_{ad} vs. *E*curve, presented in Figure 7(b) is characterized by the shape similar to the shape of CV with the maximum of about 710 μF cm^{-2} being positioned exactly at the potential of sharp peak on the CV. The charge under this

dependence was found to be only 43 μC cm^{-2}, indicating only partial charge transfer between Cd and Ag(111).

C_{dl}* vs. *E*curve (Figure 7(a)) is similar to C_{ad} vs. *E* curve (Figure 7(b)) with the maximum of about 1180 μF cm^{-2} at the potential of sharp peak on the CV. Considering α_{dl} vs. *E* curve (Figure 7(e)), with α_{dl} being close to 1, it could be assumed that C_{dl}* vs. *E* is almost identical to the C_{dl} vs. *E* dependence.

As it could be expected R_{ad} vs. *E* curve is characterized by the minimum at the potential of maximum on the C_{ad} vs. *E* curve.

4. CONCLUSIONS

1. The process of Cd UPD onto Ag(111) is characterized by the presence of 3 cathodic peaks on the CV: peak 3 corresponding to the formation of ordered ad-layer of Cd with the structure $(\sqrt{3}x\sqrt{3})R30^o$; peak 2 corresponding most probably to the formation of a monolayer od Cd with the possibility of the beginning of surface alloying of Ag and Cd; peak 1 corresponding to the surface alloying of Ag and Cd.
2. Analysis of peak 3 by Frumkin adsorption isotherm confirmed strong lateral interaction between adsorbed Cd ad-atoms and the presence of phase transition of adsorbed layer.
3. By fitting experimentally obtained *Z'* vs. ω and -*Z''* vs. ω dependences using commercial software and equivalent circuit (b), the dependences C_{dl}* vs. *E*, C_{ad} vs. *E*, α_{ad} vs. *E*, R_{ad} vs. *E* and α_{dl} vs. *E* were obtained.
4. The charge under the C_{ad} vs. *E* curve for the formation of ordered structure $(\sqrt{3}x\sqrt{3})R30^o$ confirmed partial charge transfer between Cd and Ag(111) by using both fitting procedures.
5. The use of equivalent circuit (b) is more appropriate for describing adsorption of Cd onto Ag(111).
6. This is the first attempt in the literature that fitting of EIS results has been applied to the analysis of the process of UPD.

5. REFERENCES

[1] H. Gerischer, D.M. Kolb, M. Przasnyski (1974) Chemisorption of metal atoms on metal surfaces in correlation to work function differences, Surf. Sci., 43, 662-666. https://doi.org/10.1016/0039-6028(74)90286-6

[2] D.M. Kolb, Physical and electrochemical properties of metal monolayers on metallic substrates, in: H. Gerischer, C.W. Tobias (Eds.), Advances in Electrochemistry and Electrochemical Engineering, vol. 11, Wiley-Intersience, New York,1978, pp. 125-271.

[3] R.R. Adžić, Electrocatalytic properties of the surfaces modified by foreign metal adatoms, in: H. Gerischer, C.W. Tobias (Eds.), Advances in Electrochemistry and Electrochemical Engineering, vol. 13, Wiley, New York, 1984, pp. 159-260.

[4] W.J. Lorenz, H.D. Herrman, H. Wütrich, F. Hilbert (1974) The Formation of Monolayer Metal Films on Electrodes, J. Electrochem. Soc., 121, 1167-1173. DOI 10.1149/1.2402005

[5] G. Staikov, K. Jüttner, W. J. Lorenz, E. Budevski (1978) Metallionen adsorption auf elektrolytisch gewachsenen (111) und (100) silberein kristallflächen, Electrochim. Acta, 23, 319-324. https://doi.org/10.1016/0013-4686(78)80068-1

[6] H. Siegenthaler, K. Jüttner, E. Schmidt, W.J. Lorenz (1978) Voltammetric investigation of thallium adsorption on silver single crystal electrodes, Electrochim. Acta, 23, 1009-1018. https://doi.org/10.1016/0013-4686(78)85007-5

[7] K. Jüttner, H. Siegenthaler (1978) Potentiostatic pulse experiments of thallium adsorption on Ag(111) single crystal surfaces, Electrochim. Acta, 23, 971-975. https://doi.org/10.1016/0013-4686(78)85001-4

[8] M. Klimmeck, K. Jüttner (1982) Impedance measurements of the underpotential deposition of Pb^{2+} and Tl^{+} on single crystal Ag surfaces, Electrochim. Acta, 27, 83-87. https://doi.org/10.1016/0013-4686(82)80064-9

[9] H. Bort, K. Jüttner, W.J. Lorenz (1978) Lead adsorption on silver single crystal surfaces, J. Electroanal. Chem., 90, 413-424. https://doi.org/10.1016/S0022-0728(78)80076-X

[10] K. Takayanagy, D.M. Kolb, K. Kambe, G. Lempfuhl (1980) Deposition of monolayer and bulk lead on Ag(111) studied in vacuum and in an electrochemical cell, Surf. Sci., 100, 407-422. https://doi.org/10.1016/0039-6028(80)90382-9

[11] A. Bewick, B. Thomas (1975) Optical and electrochemical studies of the underpotential deposition of metals Part I. Thallium deposition on single crystal silver electrodes, J. Electroanal. Chem., 60, 911-931. https://doi.org/10.1016/0368-1874(75)85166-5

[12] A. Bewick, B. Thomas (1977) Optical and electrochemical studies of the under-potential deposition of metals: Part III. Lead deposition on silver single crystals, J. Electroanal. Chem., 84, 127-140. https://doi.org/10.1016/S0022-0728(77)80235-0

[13] A. Bewick, B. Thomas (1977) Optical and electrochemical studies of the underpotential deposition of metals: Part II. Phase transitions and two-dimensional nucleation, J. Electroanal. Chem., 84, 329-337. https://doi.org/10.1016/S0022-0728(77)80299-4

[14] J.N. Jovićević, V.D. Jović, A.R. Despić (1984) The influence of adsorbing sustances on the lead UPD onto (111) oriented silver single crystal surface – I, Electrochim. Acta, 29, 1625-1638.

https://doi.org/10.1016/0013-4686(84)89002-7

[15] V.D. Jović, J.N. Jovićević, A.R. Despić (1985) The influence of adsorbing sustances on the lead UPD onto (111) oriented silver single crystal surface – II, Electrochim. Acta, 30, 1455-1464. https://doi.org/10.1016/0013-4686(85)80006-2

[16] H. Bort, K. Jüttner, W.J. Lorenz, G. Staikov (1983) Underpotential—overpotential transition phenomena in metal deposition processes, Electrochim. Acta, 28, 985-991. https://doi.org/10.1016/0013-4686(83)85176-7

[17] E. Schmidt, M. Christen, P. Beyeler (1973) Adsorption und legierungsbildung bei der Cd-abscheidung an silber, J. Electroanal. Chem., 42, 275-289. https://doi.org/10.1016/S0022-0728(73)80398-5

[18] V.D. Jović, B.M. Jović, A.R. Despić (1990) The influence of solution composition on lead, cadmium and thallium underpotential deposition on (111) oriented silver single crystal surfaces, J. Electroanal. Chem., 288, 229-243. https://doi.org/10.1016/0022-0728(90)80037-7

[19] V.D. Jović, B.M. Jović (2002) Underpotential deposition of cadmium onto (111) face of silver from chloride containing solution, Electrochim. Acta 47, 1777–1785. https://doi.org/10.1016/S0013-4686(02)00020-8

[20] G. Aloisi, A.M. Funtikov, T. Will (1994) Chloride adsorption on Ag(111) studied by in-situ scanning tunnelling microscopy, J. Electroanal. Chem., 370, 297-300. https://doi.org/10.1016/0022-0728(93)03140-K

[21] O. Magnussen, B.M. Ocko, R.R. Adžić, J.X. Wang (1995) X-ray diffraction studies of ordered chloride and bromide monolayers at the Au(111)-solution interface, Phys. Rev. B, 51, 5510-5518. https://doi.org/10.1103/PhysRevB.51.5510

[22] O. Magnussen, B.M. Ocko, J.X. Wang, R.R. Adžić (1996) In-Situ X-ray Diffraction and STM Studies of Bromide Adsorption on Au(111) Electrodes, J. Phys. Chem. B, 100, 5500-5508. https://doi.org/10.1021/jp953281j

[23] J.X. Wang, R.R. Adžić, B.M. Ocko, In Situ X-ray Scattering Studies of Electrosorption, in: A. Wieckowski (Ed.), Interfacial Electrochemistry: Accomplishments and Challenges, Marcel Dekker Inc., New York, 1999, pp. 175-185.

[24] Th. Wandlowski, J.X. Wang, B.M. Ocko (2001) Adsorption of bromide at the Ag(100) electrode surface, J. Electroanal. Chem., 500, 418-434. https://doi.org/10.1016/S0022-0728(00)00380-6

[25] O. Endo, D. Matsumura, K. Kohdate, M. Kiguchi, T. Yokoyama, T. Ohta (2000) In-situ XAFS studies of Br adsorption on the silver(111) electrode, J. Electroanal. Chem., 494, 121-126. https://doi.org/10.1016/S0022-0728(00)00338-7

[26] Z. Shi, J. Lipkowski (1996) Chloride adsorption at the Au(111) electrode surface, J. Electroanal. Chem., 403, 225-239. https://doi.org/10.1016/0022-0728(95)04313-6

[27] J.X. Wang, I.K. Robinson, R.R. Adžić (1998) Formation of well-ordered surface compounds by coadsorption of thallium and bromide on the Au(111) electrode surface, Surf. Sci., 412/413, 374–383.

[28] V.D. Jović, B.M. Jović (2003) EIS and differential capacitance measurements onto single crystal faces in different solutions. Part I - Ag(111) in 0.01 M NaCl, J. Electroanal. Chem. 541, 1-11. https://doi.org/10.1016/S0022-0728(02)01309-8

[29] V.D. Jović, B.M. Jović (2003) EIS and differential capacitance measurements onto single crystal faces in different solutions. Part II - Cu(111) and Cu(100) in 0.1 M NaOH, J. Electroanal. Chem. 541, 13-21. https://doi.org/10.1016/S0022-0728(02)01310-4

[30] S. Härtinger, K. Doblhofer (1995) The electrochemical interface between copper (111) and aqueous electrolytes, J. Electroanal. Chem. 380, 185-191. https://doi.org/10.1016/0022-0728(94)03650-R

[31] V.D. Jović (2026) Adsorption of iodide anions onto Ag(111), Zastita Materijala, 67, 191-198. https://doi.org/10.62638/ZasMat1671

[32] V.D. Jović (2026) Determination of adsorption capacitance and adsorption resistance in the process of anions adsorption, Zastita Materijala, 67, 391-408. https://doi.org/1062638/ZasMat1744

[33] B.M. Jović, D.M. Dražić, V.D. Jović (1999) Mechanism and kinetics of the electrosorption of sulphate anions on the (111) face of silver, J. Serb. Chem. Soc., 64, 539-552. UDC 541.138/.183.5:546.57/548.21/

IZVOD

MEHANIZAM TALOŽENJA KADMIJUMA NA POVRŠINU Ag(111) PRI POTENCIJALIMA POZITIVNIJIM OD RAVNOTEŽNOG (UPD) IZ RASTVORA KOJI SADRŽI SULFATE

*U ovom radu ispitan je mehanizam taloženja kadmijuma (Cd) na površinu Ag(111) pri potencijalima pozitivnijim od ravnotežnog (UPD) iz rastvora koji sadrži sulfate, primenom ciklične voltametrije (CV) i elektrohemijske impedansne spektroskopije (EIS). Voltamperogrami (CV) procesa UPD kadmijuma karakterisani su prisustvom tri katodna pika: pik 3 odgovara formiranju uređenog adsorbovanog sloja Cd strukture (√3 x √3)R30°; pik 2 najverovatnije odgovara formiranju monosloja Cd, uz mogućnost početka površinskog legiranja Ag i Cd; pik 1 odgovara površinskom legiranju Ag i Cd. Pikovi 3 i 2 su korigovani u odnosu na baznu liniju, dekonvoluirani i analizirani pomoću Frumkinove (Frumkin) izoterme adsorpcije. Oba pika su karakterisana negativnim vrednostima parametra interakcije *f* (vrednostima manjim od -4), što ukazuje na fazni prelaz tokom formiranja ovih uređenih struktura. Zavisnosti Z' – ō i -Z'' – ō, dobijene u opsegu potencijala pika 3 merenjima pomoću EIS u opsegu frekvencija od 100 kHz do 0,1 Hz, analizirane su pomoću dva ekvivalentna kola: (a) jednog koje sadrži adsorpcionu kapacitivnost (Cad) predstavljenu kao kondenzator sa paralelnim pločama, i drugog (b) kod kojeg je adsorpciona kapacitivnost izražena kao element konstantne faze (CPEad). Pokazano je da je ekvivalentno kolo (b) pogodnije za realnu interpretaciju adsorpcionih parametara Cdl, Cad i Rad. Važno je napomenuti da je ovo prvi put u literaturi da je takav pristup primenjen za analizu procesa UPD.*

***Ključne reči**: Ag(111), adsorpcija Cd, fazna transformacija Cd adsorbovanog sloja, EIS, određivanje C_{dl}, C_{ad} i R_{ad}.*

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