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Adsorption of iodide anions onto Ag(111)

ABSTRACT

In this work, adsorption process of iodide anions onto Ag(111) was investigated using cyclic voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS) and differential capacitance (C_{diff} vs. ω) measurements. Fitting of experimental results was performed by using commercial program for fitting defined by Gamry Instruments Inc. in EIS 300 software, as well as by equation for C_{diff} vs. ω dependence defined in previous investigations for anion adsorption, containing Constant Phase Element – corresponding to the double layer capacitance (CPE_{dl}) connected in parallel with adsorption capacitance (C_{ad}) and adsorption resistance (R_{ad}). Although the C_{diff} vs. ω dependences were obtained from the EIS measurements, significant difference in parameters for anion adsorption obtained by both procedures indicated that the analysis of C_{diff} vs. ω dependence is more reliable.

Keywords: Ag(111), iodide adsorption, adsorption mechanism, EIS, C_{diff} vs. ω dependence.

1. INTRODUCTION

Iodide anions adsorption/desorption processes on silver single crystal surfaces have been investigated by C_{diff} vs. E , CV and surface analytical techniques [1-8]. CVs were characterized by the presence of a broad peak at more negative potentials and a sharp peak at less negative potentials, with a broad peak corresponding to the formation of randomly distributed ad-layer at potentials negative of -0.8 V vs. Ag/AgCl and its transformation into a $(\sqrt{3} \times \sqrt{3})R30^\circ$ ordered structure between -0.8 and -0.4 V vs. Ag/AgCl and a sharp peak detected at potentials slightly positive of -0.4 V vs. Ag/AgCl corresponding to compression of $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure into (8×8) iodide structure [1,2].

In situ STM and *ex situ* LEED studies of Yamada et al. [3] confirmed continuous compression of the iodide ad-lattice from square $(\sqrt{3} \times \sqrt{3})R30^\circ$, via $(\sqrt{3} \times \sqrt{3})R\beta^\circ$ ($q \approx 1$, $0 \leq \beta \leq 30$), to $(\sqrt{3} \times \sqrt{3})R30^\circ$ at potentials between -1.2 V and -0.8 V. At potentials more positive than sharp peak $(\sqrt{3} \times \sqrt{3})R(30^\circ + \alpha^\circ)$ has been detected [3].

Although the structure of the adsorbed iodide ad-layers has been extensively studied, practically no attempt was made to analyze the mechanism of iodide adsorption and define the equivalent circuit for such process. In previous works [9-12] chloride and bromide anions adsorption onto Ag single crystals, as well as hydroxide anions adsorption onto Cu single crystals has been analyzed by predicting equivalent circuit for anion adsorption. Equivalent circuit was composed of C_{dl} connected in parallel with C_{ad} and R_{cl} [9,10], as well as of CPE_{dl} connected in parallel with C_{ad} and R_{ad} [11,12]. It has been shown that such equivalent circuits could be used for fitting experimental results by the analysis of C_{diff} vs. ω dependences.

1.1. Differential capacitance for different cases of anion adsorption

C_{diff} vs. E dependences were introduced in electrochemistry with the beginning of double layer structure investigations as a suitable technique for determining the double layer capacitance (C_{dl}) on both, liquid (mercury) and solid metal electrodes [13,14]. This technique was very convenient for determining the potential of zero charge, E_{pzc} on solid electrodes as a minimum on C_{diff} vs. E curves [13-15]. Since the minimum existed only in the presence of a diffuse part of the double layer [16,17], these experiments were performed in dilute

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solutions of the concentrations lower than 10^{-2} M, usually of the order of 10^{-3} M [18,19]. In all these experiments ohmic resistance had to be compensated in order to obtain the real value of C_{dl} . In such a case the value of C_{diff} was equal to the value of C_{dl} and was independent of frequency. Accordingly measurement at one frequency was sufficient to determine the value of the double layer capacitance.

With introduction of single crystal surfaces, this technique in combination with CV, has frequently been used for determining E_{pzc} as well as adsorption behavior of different anions. Typical frequencies for these measurements varied between 10 Hz and 20 Hz [19], while the sweep rate used was usually 5 - 10 mV s⁻¹. For interpretation of the obtained results concerning adsorption of anions it was assumed that the "specific adsorption" of anions does not involve the charge transfer between the electrode surface and adsorbed anions.

About 25 years ago the equivalent circuit composed of C_{dl} connected in parallel with the charge transfer resistance (R_{ct}) and C_{ad} was used for the first time for the analysis of adsorption of fluoride, sulfate, acetate and chloride anions onto silver single crystals [9,10]. The same equivalent circuit, with adsorption resistance (R_{ad}) instead of R_{ct} has later been used for the analysis of OH⁻ species adsorption onto Cu(111) from fluoride or sulfate containing solutions of different pH [20].

Z. Kerner et al. [21] demonstrated that the frequency dependence of capacitance on solid electrodes was due to the atomic scale inhomogeneities rather than due to the geometry aspect of roughness. They criticized old physical theories used for explaining capacitance dispersion as a function of surface roughness [22,23] and pointed out physico-chemical approach of T. Pajkossy [24,25], claiming that the origin of the capacitance dispersion can be allocated in the double layer and that it can be attributed to the presence of atomic scale inhomogeneities – "disorder" of the electrode surface, together with the presence of some kinetic process, most probably with the "specific adsorption" of anions [21].

Introduction of *in situ* techniques (STM and surface X-ray scattering) in the investigation of the structure of adsorbed anions onto single crystal faces provided significant contribution to the understanding of the process of anion adsorption [26-30], showing that in the case of chloride and bromide anions adsorption onto Au single crystals incommensurate, hexagonal-close-packed mono-

layers, compressing uniformly with increasing potential were formed [29-31]. The ad-atom spacing of these compressed structures was found to approach van der Waals diameter, indicating at least partial discharge of anions [29-31]. *In situ* X-ray absorption fine structure (XAFS) studies of bromide adsorption onto Ag(111) revealed the formation of AgBr(111) monolayer with the Br-Ag bond distance of 2.72 ± 0.05 Å, indicating complete charge transfer between bromide anions and Ag(111) surface [32].

In this paper the dependence of C_{diff} vs. ω for different cases of simple and complex anion adsorption processes for ideal, homogeneous and "real surfaces" (introducing CPE instead of C_{dl} [33-35]) have been analyzed. Two cases were considered: 1) double layer capacitance represented by a parallel plate condenser (assuming ideal, homogeneous surface) and 2) double layer capacitance represented by a CPE (assuming nonhomogeneous charge distribution at the surface).

1.2. Ideal, homogeneous surface

Equivalent circuit for ideal double layer behavior of the electrode impedance is presented by ohmic resistance R_{Ω} and double layer capacitance C_{dl} connected in series. Differential capacitance is by definition imaginary component of electrode admittance over frequency and for such equivalent circuit is given by the equation:

$$C_{diff} = \frac{Y''}{\omega} = \frac{C_{dl}}{1 + \omega^2 C_{dl}^2 R_{\Omega}^2} \quad (1)$$

In most cases $1 \gg \omega^2 C_{dl}^2 R_{\Omega}^2$ and accordingly $C_{diff} \approx C_{dl}$. On the other hand in dilute solutions with high value of R_{Ω} the value of C_{diff} could be influenced by the R_{Ω} , as shown in equation (1). Hence, imaginary component of electrode admittance should be corrected for R_{Ω} in order to obtain the real value of C_{dl} . This could be done either by compensating R_{Ω} during differential capacitance measurements (using IR compensation technique on the potentiostat), or by subtracting it from the real component of electrode impedance, $Z'_{corr} = Z' - R_{\Omega}$ and calculating Y'_{corr} by following equation (R_{Ω} - determined from the high frequency intercept of impedance diagrams, or by some other technique):

$$Y'' = \frac{Z''}{(Z'_{corr})^2 + (Z'')^2} \quad (2)$$

Hence, by using Y'_{corr} for determining C_{diff} ($Y'_{corr}/\omega = C_{diff}$) it is possible to obtain the real value of differential capacitance.

In the presence of specific adsorption presented by the R_{ad} and C_{ad} connected in series, C_{diff} (corrected for R_{Ω}) should depend on frequency [9-12]. The simplest case of specific adsorption at "real electrode surface" is usually represented by the equivalent circuit shown in Figure 1, where the R_{ad} and C_{ad} connected in series are placed in parallel with the CPE_{dl} (representing double layer capacitance of "real electrode surface").

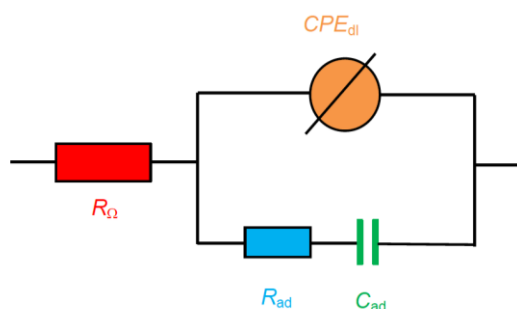


Figure 1. Equivalent circuit for anion adsorption

1.3. Real surface

Taking into account that even single crystal faces contain significant number of monoatomic terraces and cannot be considered as ideal (homogeneous) surface, introduction of CPE defined as $CPE = Z_{dl}(j\omega)^{-\alpha}$ [33-35] is mandatory.

For the case of simple anion adsorption, presented by the equivalent circuit shown in Figure 1, differential capacitance as a function of frequency (using the definition given in equation (2)) is defined by the following equation:

$$C_{diff} = C_{dl}\omega^{\alpha-1} \sin\left(\frac{\alpha\pi}{2}\right) + \frac{C_{ad}}{1 + \omega^2 C_{ad}^2 R_{ad}^2} \quad (3)$$

Hence, by plotting C_{diff} vs. ω dependences obtained for constant potential from EIS measurements it is possible to fit these dependences by the equation (3) and obtain the values of C_{dl} , α , R_{ad} and C_{ad} .

It is also possible to obtain these parameters by fitting EIS measurements with the commercial software, either by using Bode diagrams, or Z' vs. ω and $-Z''$ vs. ω dependences.

2. EXPERIMENTAL

All experiments were carried out in a two-compartment electrochemical cell at 25 ± 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 cm². The counter electrode (CE) was a Pt sheet and was placed

parallel to the working electrode. The reference electrode (RE) was a saturated silver chloride electrode (Ag/AgCl). The RE was placed in a separate compartment and connected to the working compartment by means of a Luggin capillary. Solution of 0.1 M NaI was made from supra pure (99.999% – Aldrich) chemicals and extra pure UV water (Smart2PureUV, TKA).

The single crystals were prepared by a mechanical polishing procedure followed by chemical polishing in the solution containing NaCN and H₂O₂ as explained in previous paper [36]. 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 (PHE 200 and EIS 300 software -Gamry Instruments Inc.). EIS measurements were performed at constant potentials, in the frequencies range from 5000 Hz to 10 Hz, with the RMS amplitude of 10 mV and 10 points per decade.

3. RESULTS AND DISCUSSION

3.1. Iodide adsorption/desorption in 0.1 M NaI

CVs recorded at the sweep rates of 100 mV s⁻¹ and 50 mV s⁻¹ in 0.1 M NaI are presented in Figure 2. The process of iodide adsorption/desorption is characterized by one pair of broad peaks, composed of several small, sharp peaks in the negative potential region (from ~ -0.8 to ~ -1.2 V) [37] and one pair of sharp peaks at less negative potentials (around -0.36 V). The sudden increase of cathodic current density corresponding to the hydrogen evolution was recorded immediately after the cathodic limit on the presented CVs.

By integrating the total surface under the cathodic and anodic parts of the CVs shown in Figure 2 corresponding charges were obtained, with the maximum anodic charge (Q_a) of ~ 90 μ C cm⁻² and the maximum cathodic charge (Q_c) of ~ 97 μ C cm⁻². Taking into account that the theoretical charge (assuming complete charge transfer) for the ($\sqrt{3} \times \sqrt{3}$)R30° iodide ad-layer amounts to 74 μ C cm⁻², it appeared that this ad-layer is formed under the broad peak [1-8,37].

3.2. The use of commercial program for fitting the EIS results

In order to obtain data for the mechanism of iodide anions adsorption EIS measurements were performed at constant potentials in the range of potentials presented in Figure 2.

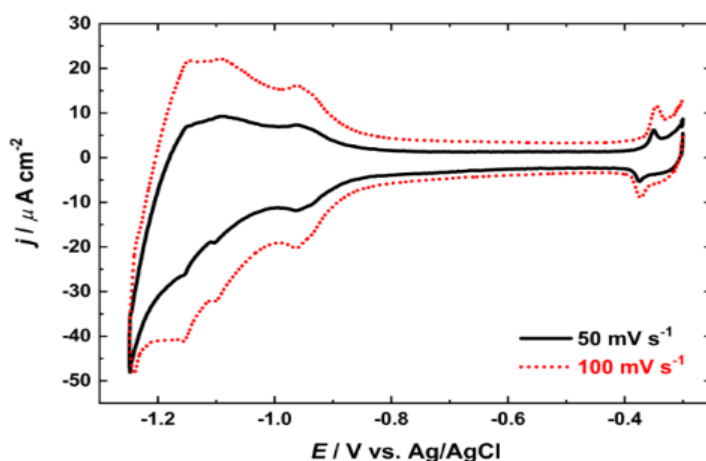


Figure 2. CVs recorded at 100 mV s^{-1} and 50 mV s^{-1} for the process of adsorption/desorption of iodide anions onto Ag(111) in 0.1 M NaI

Since there are three different regions, measurements in the region of broad peak (between -0.9 V and -1.2 V) were taken at 50 mV difference, in the double layer region (between -0.8 V and -0.4 V) at 100 mV difference, while in the region of sharp peak (between -0.4 V and -0.32 V) at 20 mV difference. Since Z' vs. ω and $-Z''$ vs. ω dependences were necessary for calculating C_{diff} (equation (2)) these dependences were plotted and

fitted. Typical examples of Z' vs. ω and $-Z''$ vs. ω dependences fitted with the commercial program, recorded in the region of broad ($E = -1.0 \text{ V}$) and the region of the flat portion of the CV (just before a sharp peak, $E = -0.4 \text{ V}$), are presented in Figure 3. Fitting lines are seen not to deviate from experimental points, indicating precise fitting procedure.

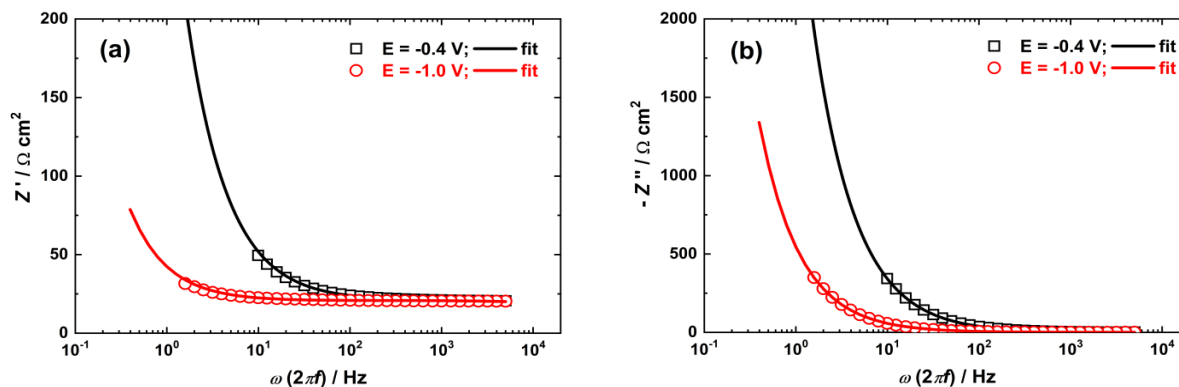


Figure 3. Z' vs. ω (a) and $-Z''$ vs. ω (b) dependences fitted with the commercial program, recorded in the different potential regions of the CV

Unfortunately, one result could not be fitted (EIS at $E = -1.2 \text{ V}$) with the commercial program, actually some of the parameter values for C_{dl} , α , C_{ad} and R_{ad} were unrealistic. The results for C_{dl} vs. E , C_{ad} vs. E and R_{ad} vs. E obtained by fitting procedure are presented in Figure 4(a,b,c) respectively. It is obvious that, although fitting procedure gave high precision (in all cases so called "goodness of fit" was lower than 1×10^{-4} corresponding to the deviation lower than 1 %),

obtained results seem to be unrealistic. Generally, extremely high values for C_{ad} and R_{ad} at potentials more negative than -0.8 V are unexpected. Concerning R_{ad} it should be stated that this resistance represents a sum of two resistances: $R_{\text{ad}}^{\text{mt}}$ – corresponding to the adsorption of anions at the edge of monoatomic terraces and defects on the surface and $R_{\text{ad}}^{\text{os}}$ – corresponding to the adsorption of anions at the flat part of monoatomic terraces, representing adsorption resistance for the formation of ordered structures. Unfortunately,

these two resistances cannot be separated and determined independently, at least not by using equivalent circuit shown in Figure 1. With the use of different equivalent circuit, as shown in Ref. [38], it is possible to separate and determine these two

resistances, but the problem arises in the physical meaning of such equivalent circuit.

The value of α was found to vary between 0.8 and 0.9.

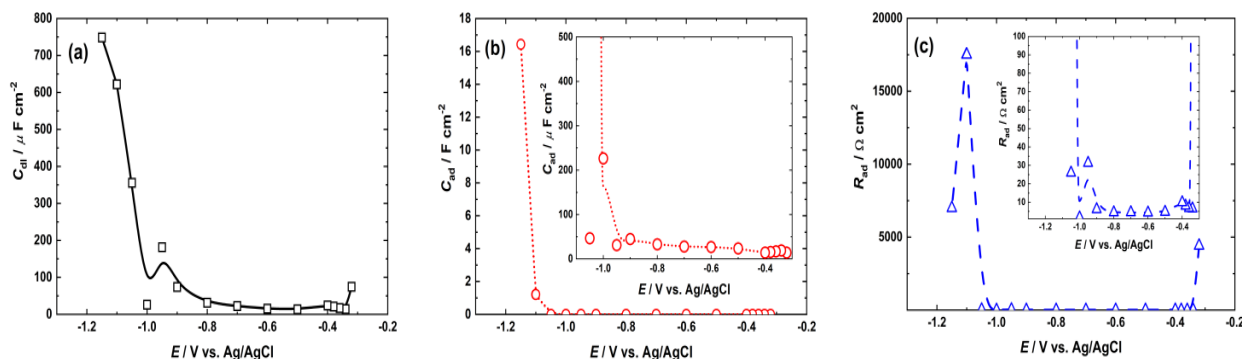


Figure 4. (a) C_{dl} vs. E , (b) C_{ad} vs. E and (c) R_{ad} vs. E dependences obtained by using commercial program for fitting experimental results. In the inset of (b) and (c) are presented C_{ad} vs. E and R_{ad} vs. E dependences at higher sensitivities of C_{ad} and R_{ad}

3.3. The use of equation (3) for fitting C_{diff} vs. ω dependences

As already stated Z' vs. ω and $-Z''$ vs. ω dependences for each applied potential were used to calculate C_{diff} vs. ω dependences. Obtained C_{diff} vs. ω dependences were plotted and fitted by

equation (3) using non-linear curve fitting in Origin program. Experimental points and fitted curves for each applied potential are presented in Figure 5. As can be seen all fits are excellent. The values of parameters C_{dl} , C_{ad} and R_{ad} obtained by fitting procedure are presented in Figure 6(a,b).

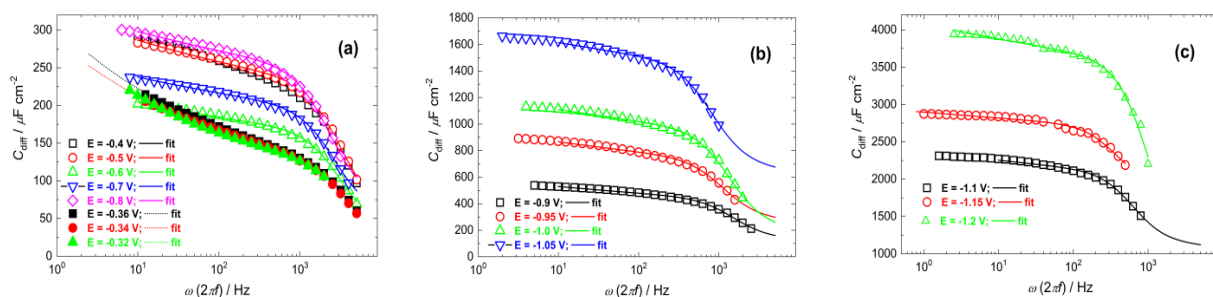


Figure 5. C_{diff} vs. ω dependences recorded for each applied potential (designated in the figure) are presented with points, while fitting results are presented with lines.

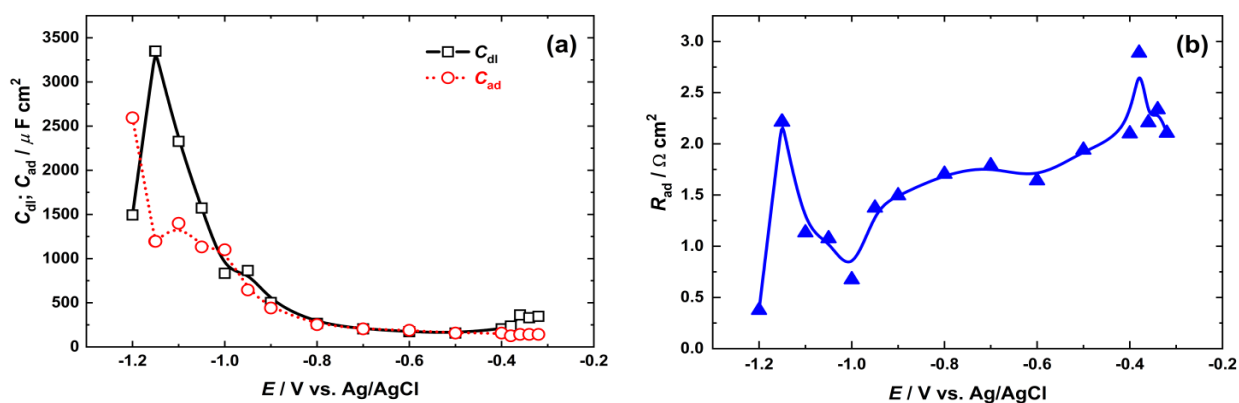


Figure 6. (a) C_{dl} vs. E , C_{ad} vs. E and (b) R_{ad} vs. E dependences obtained by fitting C_{diff} vs. ω dependences

Presented results seem more realistic, being in accordance with the CVs. The values of C_{dl} and C_{ad} are quite high in the region of iodide adsorption, while in the region of final phase transformation [37] (between -0.4 V and -0.32 V) C_{ad} is practically constant indicating that there is no additional adsorption of iodide anions during the final phase transformation (compression of $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure into (8×8) iodide structure[1,2]).

It should be stated that although commercial fits are precise, the values of R_{ad} and C_{ad} are practically quite insensitive to a fitting procedure. This software is giving fitted results and possible error in their determination. One, actually the worse example, of the table with fitting results is presented in Table 1. Goodness of fit of $16.08e^{-6}$ is quite satisfactory, but the errors for R_{ad} and C_{ad} are unacceptable.

Table 1. Probably the worse example for presented results in commercial fitting program

Parameter	Value	$\pm$ Error	Dimensions
R_s	31.00	1.186	ohm
Y_{dl}	$34.06e^{-6}$	$12.79e^{-6}$	$S \cdot s^\alpha$
α_{dl}	$939.8e^{-3}$	$36.47e^{-3}$	
C_{ad}	$20.77e^{-6}$	$13.78e^{-6}$	F
R_{ad}	6.965	5.404	ohm
Goodness of Fit	$16.08e^{-6}$		
-0.8V.DTA			

Another factor that could influence the precision of fitting with the commercial program might be the number of points, actually the range of frequencies used for the EIS measurements. Frequencies from 5000 Hz to 10 Hz are satisfactory for C_{diff} vs. ω dependences, but it seems that for fitting with the commercial program it is necessary to extend the frequency range from 100 kHz to 0.01 Hz and probably extend the number of points per decade to 20?

With a present knowledge of fitting procedure in the commercial EIS 300 software it is not possible to make any reasonable explanation for the difference in the fitting results, but it could be stated that the use of equation (3) for fitting C_{diff} vs. ω dependences is much more realistic.

4. CONCLUSIONS

The CVs of the process of iodide anions adsorption onto Ag(111) are characterized by three potential regions: from -1.2 V to -0.8 V (broad peaks) adsorption/desorption of randomly distributed iodide anions with a formation of

ordered structure $(\sqrt{3} \times \sqrt{3})R30^\circ$ at about -0.8 V; double layer region from -0.8 V to -0.4 V (flat CVs); further compression of $(\sqrt{3} \times \sqrt{3})R30^\circ$ into (8×8) ad-layer of iodide expressed by the sharp peaks between -0.4 V and -0.32 V.

Extremely high values of C_{dl} and C_{ad} in the region of adsorption/desorption peaks, their constant values in the double layer region and constant value of C_{ad} in the region of phase transformation (compression into (8×8) iodide ad-layer) are in accordance with the CVs.

Finally, it was shown that fitting of C_{diff} vs. ω dependences using equation (3) produces more realistic results for C_{dl} vs. E , C_{ad} vs. E and R_{ad} vs. E dependences than the use of commercial fitting procedure.

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IZVOD

ADSORPCIJA ANJONA JODIDA NA Ag(111)

U ovom radu, proces adsorpcije jodidnih anjona na Ag(111) je ispitan korišćenjem ciklične voltametrije (CV), elektrohemijske impedansne spektroskopije (EIS) i merenja diferencijalnog kapaciteta (C_{diff} vs. ω). Fitovanje eksperimentalnih rezultata je izvršeno korišćenjem komercijalnog programa za fitovanje definisanog od strane Gamry Instruments Inc. u EIS 300 softveru, kao i jednačinom za zavisnost C_{diff} vs. ω definisanu u prethodnim istraživanjima za adsorpciju anjona, koja sadrži element konstantne faze – koji odgovara dvoslojnom kapacitetu (CPEdl) povezanom paralelno sa adsorpcionim kapacitetom (C_{ad}) i adsorpcionim otporom (R_{ad}). Iako su zavisnosti C_{diff} vs. ω dobijene iz EIS merenja, značajna razlika u parametrima za adsorpciju anjona dobijenim oba postupka ukazala je da je analiza zavisnosti C_{diff} vs. ω pouzdanija.

Ključne reči: Ag(111), adsorpcija jodida, mehanizam adsorpcije, EIS, zavisnost C_{diff} vs. ω .

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