



Investigation of the electroreduction of silver sulfite complexes by means of electrochemical FFT impedance spectroscopy

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ABSTRACT

The electroreduction kinetics of silver sulfite complexes was investigated by electrochemical fast Fourier transform (FFT) impedance spectroscopy (0.061–1500 Hz). The time dependences of the real and imaginary components of impedance were determined in a solution containing 0.05 M Ag(I) and 1 M Na₂SO₃. The mean duration of silver ad-atom diffusion on the surface to the nearest crystallization centre was calculated: during the first 210 s of contact with the electrolyte, these values increase from 0.66 up to 1.77 s; thereafter, this variation stabilizes and the mean duration of silver ad-atom diffusion reaches an almost constant value (1.56 s).

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1. Introduction

Usually silver deposits for practical purposes are obtained from extremely toxic cyanide-based solutions [1]. Considerable attention has been paid in the literature to the process of silver electrodeposition from cyanide electrolytes [2,3] and till today this process is widely used in different fields of industry and science [4–14]. There are many publications dedicated to the application and mechanism of silver electroreduction from cyanide baths. However, the important problem, especially, of the cyanide toxicity is not solved yet. A great number of cyanide-free solutions [15–17] have been proposed in order to avoid the necessity to use some amount of hazardous materials during the preparation of silver electroplating baths. Unfortunately, silver deposits obtained using these electrolytes were rather of lesser quality than those obtained with traditional cyanide electrolytes. One of the most promising methods to solve this problem could be the application of the electroreduction process of silver sulfite complexes. The main problem with sulfite systems is the oxidation of sulfite ions by air oxygen and the low working densities of the cathodic current. These limitations can be avoided easily using the inert atmosphere by also increasing the temperature and stirring the electrolyte. Replacing the cyanide-based silver plating solutions with silver sulfite electrolytes could be particularly important in not only solving the problems of toxicity but also exploiting these electrolytes in the field of innovative technologies. Nowadays, it is very important to choose electrolytes that can be used to obtain silver deposits ideally suitable for

deep-etch X-ray lithography. Such silver electrolytes could be used in a relatively new technique known as LIGA (German: lithographic, galvanofarming, abformung; lithography, electroplating and micromoulding) [18–20] and could be successfully applied for silver deposition for micro-electro-mechanical systems (MEMSs). In that case the most important properties of electroplating baths are the throwing power of the electrolytes and high aspect ratio of microstructures. The properties mentioned above have determined successful application of gold sulfite electrolytes [21] instead of cyanide electrolytes in the microtechniques. Concerning silver sulfite electrolytes, it is known [22] that those electrolytes enable us to get silver deposits with good crystallinity. Furthermore, it was emphasized [22] that the throwing power of silver sulfite electrolytes is exceptionally good. Recently, sulfite-based solutions for electrochemical deposition of silver were proposed by Cojocar et al. [23]. Authors have noted that silver nanoparticles were deposited with high nucleation density and uniform size distribution [23]. Due to the fact that silver deposits obtained from silver sulfite electrolytes are of high quality, these electrolytes have great potential application in novel and innovative technologies. Consequently, investigations of the kinetics of silver sulfite complexes electroreduction became very important from the practical point of view.

In order to investigate the process of silver electrodeposition from sulfite solutions, the methods of rotating disk electrode (RDE) voltammetry, chronopotentiometry (CP) and electrochemical impedance spectroscopy (EIS) were used [24]. It was determined [24] that electrochemical reaction of silver sulfite complexes is hindered by a slow stage of silver ad-atom crystallization at equilibrium conditions. Furthermore, the longer the immersion time of silver electrode in the solution is, the more significant is the

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influence of the crystallization stage on the silver electroreduction [24]. In order to investigate exactly the stage of a slow crystallization the electrochemical fast Fourier transform (FFT) impedance spectroscopy [25,26] seems to be the most suitable method, because this method enables us (i) to ensure equilibrium potential conditions and (ii) to reduce as much as possible the time needed for determination of electrochemical impedance spectrum. Both (i) and (ii) are very important for avoiding changes of the parameters of electrochemical reaction emergent due to time dependent surface processes, i.e. recrystallization of the metal phase, adsorption or desorption of sulfite ions etc. Above-mentioned processes change both the electrical double layer capacitance and the parameters of investigated electrochemical system. Meanwhile, while analysing impedance spectra, all elements in the model of electrochemical equivalent circuit are treated as constants. If the measurements of impedance spectrum take too long, the components in the equivalent circuit can be determined incorrect. Moreover, not only the values of the equivalent circuit components can be determined with significant errors but the model of investigated system itself can change. Thus, one can conclude that the method of FFT impedance spectroscopy is very useful for investigating so complicated a process as electroreduction of silver sulfite complexes. Furthermore, this method is irreplaceable in investigating the changes of metal ad-atoms surface diffusion.

The aim of this work was to investigate the kinetics of silver electrocrystallization from the sulfite solutions analysing the impedance spectra measured by means of FFT impedance spectrometry. Performing the measurements in galvanostatical conditions (at zero direct current) we were able to investigate a slow stage of silver crystallization, i.e. to calculate (i) the values of components of the equivalent circuit which represent the investigated electrochemical system and (ii) the dependences of the mean duration of silver ad-atom surface diffusion on the immersion time of silver electrode in the solution of sulfite complexes.

2. Experimental

The solutions prepared were based on distilled water and p.a. quality Na_2SO_3 and Ag_2SO_4 . The electrolytes were prepared freshly before every new experimental series, in order to avoid the sulfite ion oxidation by air oxygen. All experiments were performed at 20°C temperature.

The EIS measurements were performed using an ordinary three-electrode cell. The working electrode was a platinum wire of 0.5 mm in diameter and 1.08 cm in length. Working surface of the Pt electrode was treated with alcoholic solution of NaOH, then this electrode was mechanically polished using a series of aluminium powders (1.0–0.15 μm). Care was taken during the polishing to wash the electrode properly before changing the Al_2O_3 powders and especially before mounting it into the cell. Working Pt electrode after such preparations was coated (10 μm) with silver galvanostatically (3 mA cm^{-2}) in a sulfite-based electrolyte (2 M Na_2SO_3 and 0.3 M AgNO_3) before each measurement. The surface area of the working electrode was 0.17 cm^2 . The counter electrode was made of an Ag spiral of 40 cm^2 . The reference electrode was a saturated Ag/AgCl, KCl electrode, placed as close as possible to the working electrode by means of a Luggin capillary. Throughout this work the potential of the working electrode is referred to the normal hydrogen electrode (NHE).

In this investigation all impedance spectra were recorded galvanostatically at controlled zero direct current using a fast Fourier transform (FFT) impedance spectrometer [25,26]. The amplitude of the perturbation current was chosen in such a way that the response voltage would not exceed 5–10 mV. The obtained impedance spectra were validated by comparing the power spec-

tra of perturbation and response as described in Ref. [27]. First of all, FFT impedance spectrometer differs from conventional devices of this type by the way how investigated system is perturbed. In FFT impedance spectrometry, system is perturbed not by the consequently applied sine waves of different frequencies, but by the superposition of 50 sine waves with properly chosen frequencies. All frequencies are multiples of the lowest one, and they increase linearly in logarithmic scale. Such method enables us to reduce the duration of determining impedance spectrum, depending on frequency range, 5–20 times (when compared with conventional equipment). The overall measurement time in FFT impedance spectroscopy is limited only by the lowest frequency in the spectrum and by the data transfer to the computer. It should be noted that significant distortions of response signal emerge during the first period of oscillation of lowest frequency. It happens due to additional harmonic oscillations [27]. Usually, the bigger is the capacitance of electrode, the larger these distortions are. Because of the above-mentioned reasons, only response obtained during the second oscillation of lowest frequency was used for calculations. Thus, the measurement time of the electrochemical impedance spectrum depends on the used lowest frequency only: measurement time in the frequency range 1.5–50,000 Hz continues for 1.3 s, while measurement time in the frequency range 0.003–100 Hz takes 11 min. In these experiments we have attempted to choose the lowest frequency satisfying following requirements: it must be low enough to get as much as possible data, and also it has to ensure minimal distortions of response signal.

3. Results and discussion

In order to analyse the measured impedance spectra and even to extract kinetic data, first of all we have tested the validation of measured impedance data by comparing the spectra of perturbation current and response voltage. By the use of extremely selective analyser of alternating current spectra we have highlighted all frequencies emerged in response, not only those used in the perturbation of the investigated system. If very fast changes of system parameters occur in electrochemical system, additional lines in impedance spectrum appear. It was checked how obtained frequencies of response correspond to frequencies of perturbing signal. As distortions of only frequencies of response impedance spectrum can be treated, which are multiples to frequencies used in perturbing signal, frequencies caused by power source (50, 100, 150 Hz, etc.) were not taken into consideration. As one can see from the results obtained (Fig. 1), it would be incorrect to analyse spectrum which begins at 0.00305 Hz, because of a lot of lateral frequency lines visible on it. In this paper experimental EIS measurements were carried out at least two times. First of all impedance was determined at 0.00305 Hz; and later the lowest frequency was increased up to values at which distortions were minimal (see Fig. 1). Since probability of nonlinearities increases with decreased alternating current frequency, experimentally FFT electrochemical impedance spectra were determined in the frequency range from 0.061–1500 Hz in solution containing 0.05 M Ag (I) and 1 M Na_2SO_3 (Fig. 2). Equilibrium potential of the electrode in solution of such composition is $E_{\text{H}} \cong 0.24\text{ V}$. It took 30 s to determine one impedance spectrum in the chosen range of frequencies.

While investigating electrode processes by means of the EIS method, behaviour of electrochemical system usually is represented by an equivalent circuit composed of different components. The component of the double layer capacitance may be useful only in the case to represent the system with homogeneous electrode surface. The surfaces of solid electrodes mostly are not enough equipotential, i.e. electrolyte resistance of the each microscopic surface area is different. Consequently, infinity of $R_i C_i$ parallel ele-

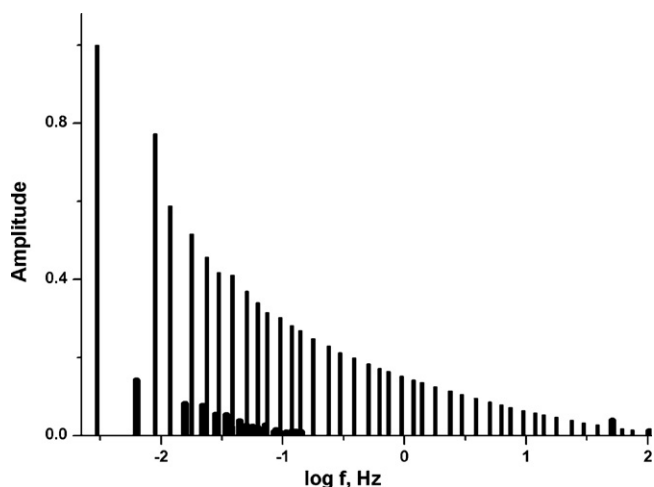


Fig. 1. Frequency distribution of FFT impedance response (potential) lines. Narrow lines correspond to frequencies of perturbation and wide lines to additional frequencies of response emerging due to nonlinearity of system.

ments should be introduced into equivalent circuit instead of the component of double layer capacitance. The input of R_iC_i elements to the total impedance mathematically is simulated as the constant phase element (CPE) whose impedance can be defined as [28]:

$$Z_{\text{CPE}} = A^{-1}(j\omega)^{-n} \quad (1)$$

where A is the proportion factor of the constant phase element; its physical meaning corresponds to the average double layer capacitance; n is the exponential number which shows the impedance phase shift. When the electrode surface is homogenous, i.e. $n = 1$, Eq. (1) transforms into the simple double layer capacitor impedance equation:

$$Z_{\text{CPE}} = (C_D j\omega)^{-1} \quad (2)$$

The deviation of exponential number n from unit usually is small even for a rough metal surface and its range is within 0.9–1. However, deviations of n may increase drastically when the metal surface is covered with a low conductivity layer [28], for example, the oxide layer etc. While analysing the impedance spectra determined in the solution of silver sulfite complexes it was found that the exponential number n is very close to unit ($0.9 \leq n \leq 1$). According to Eqs. (1) and (2), CPE in the equivalent circuit representing

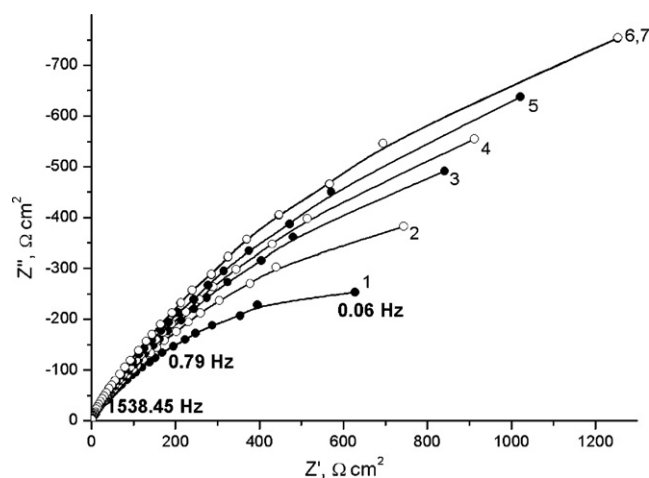


Fig. 2. Electrochemical FFT impedance spectra. Solution composition: 0.05 M Ag (1), 1 M Na₂SO₃. Time passed after immersing Ag electrode into the solution: (1) 30 s, (2) 60 s, (3) 120 s, 5–450 s, (6) 1770 s and (7) 1800 s.

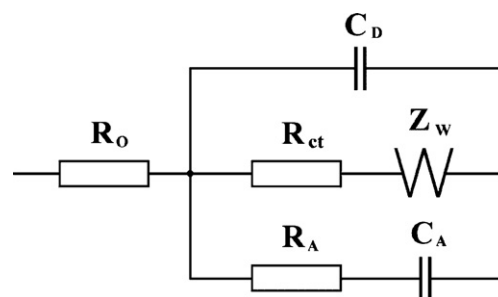


Fig. 3. Equivalent circuit representing adsorption and charge transfer on the surface of the electrode. (R_0) uncompensated resistance of electrolyte, (C_D) electrical double layer capacitance, (R_{ct}) charge transfer resistance, (Z_w) diffusion impedance, (R_A) and (C_A) adsorption resistance and capacitance.

our investigated electrochemical process turns to conventional component of double layer capacitance. Thus, we could simplify the analysis of obtained data, i.e. to analyse the experimentally determined impedance spectra of electroreduction of silver sulfite complexes using a typical equivalent circuit (Fig. 3), which was composed of uncompensated electrolyte resistance R_0 , electrical double layer capacitance C_D , charge transfer resistance R_{ct} , diffusion impedance Z_w which represents the influence of surface diffusion of silver ad-atoms appearing due to electrocrystallization of metal [29], and from adsorption branch of adsorption resistance R_A and adsorption capacitance C_A . By means of the computer program “Zview” we have got satisfactory coincidence of experimental data with results calculated using equivalent circuit representing the investigated process. Discrepancies were observed in the low frequency range only (below 1.5 Hz). By further analysing the experimentally determined impedance spectra we have attempted to estimate changes of both real and imaginary impedance components vs time. It was determined that the absolutely time-independent component of the equivalent circuit was the uncompensated electrolyte resistance R_0 and its values were about $0.25 \pm 0.02 \Omega \text{ cm}^2$. The obtained variation of the values R_{ct} and C_D is presented in Fig. 4. It is seen (Fig. 4) that both charge transfer resistance and double layer capacitance increase slightly during the first 100 s: R_{ct} increases from 6 to $10.7 \Omega \text{ cm}^2$, and C_D grows from 320 to $420 \mu\text{F cm}^{-2}$. Thereafter, the values of components R_{ct} and C_D decrease gradually to their initial values. The time dependences of the components of adsorption branch R_A and C_A , are given in Fig. 5. As shown in Fig. 5, both adsorption resistance

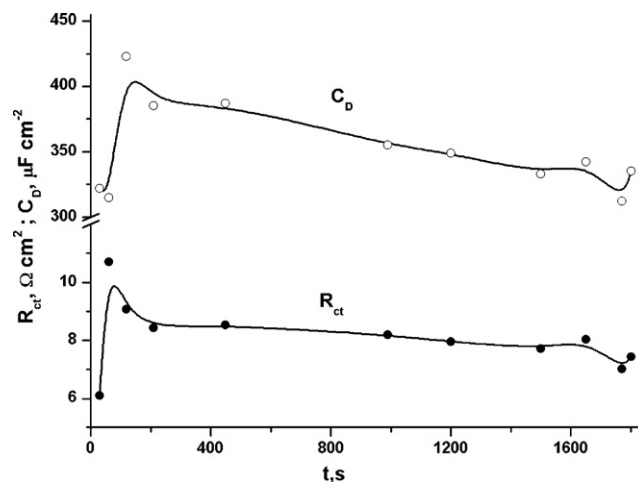


Fig. 4. Dependencies of the electrical double layer capacitance (C_D) and charge transfer resistance (R_{ct}) on the time, determined analysing the FFT impedance spectra (from Fig. 2).

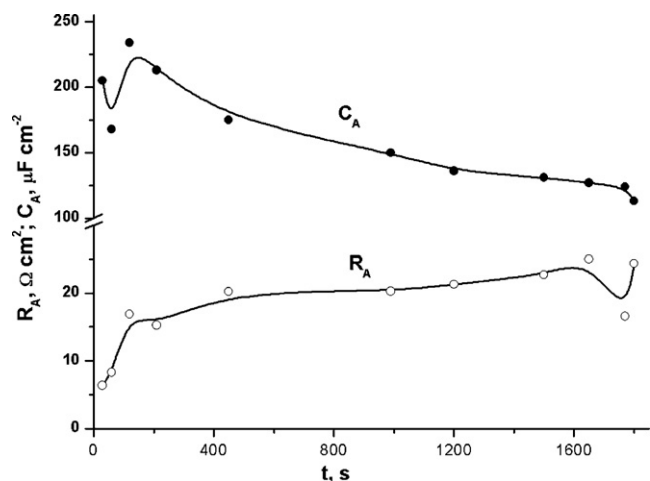


Fig. 5. Dependencies of the adsorption capacitance (C_A) and adsorption resistance (R_A) on the time, determined analysing the FFT impedance spectra (from Fig. 2).

and adsorption capacitance increase during the first 120 s, then C_A values start to decrease marginally and R_A increases, respectively. It was interesting to observe the change of the coefficient B , which represents a slow electrocrystallization of silver ad-atoms. Sotnikov et al. [29] have reported a model describing the surface diffusion impedance by surface diffusion resistance and capacitance connected in parallels. Both the components depend on the alternating current frequency as this is the case with the Warburg impedance. In our analysis we have chosen a simplified approach, taking into account that the non-dimensional alternating current frequency term of the mathematical expressions given in Ref. [29] becomes sufficiently large for higher frequencies. As a result, the surface diffusion impedance becomes qualitatively similar to the conventional Warburg impedance, with a coefficient B characterizing the surface diffusion of ad-atoms instead of the Warburg constant for the case of three-dimensional diffusion:

$$Z' = -Z'' = \frac{B}{\sqrt{\omega}} \quad (3)$$

As one can see in Fig. 6, in the electrochemical system of silver sulfite complexes the coefficient B increased up to $2500 \Omega \text{ cm}^2 \text{ s}^{-1/2}$ during the first 60 s. Thereafter, the change of coefficient B is not consistent, but it is obvious that the values of this coefficient are big rather than small ($>2000 \Omega \text{ cm}^2 \text{ s}^{-1/2}$). This could be explained unambiguously by a slow stage of silver electrocrystallization.

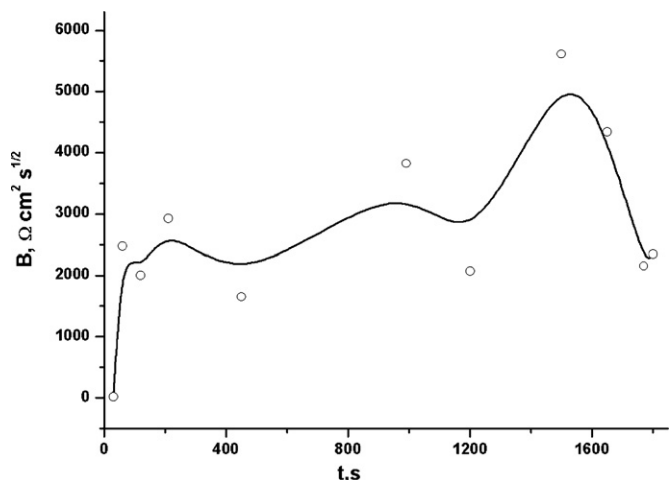


Fig. 6. Dependence of the silver electroreduction representing coefficient B on the time, determined analysing the FFT impedance spectra (from Fig. 2).

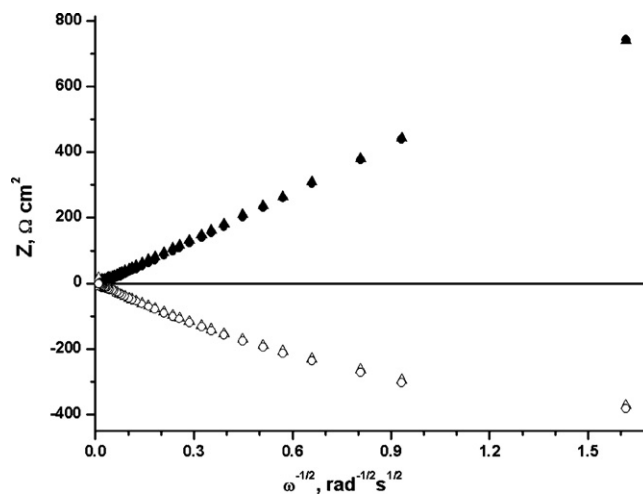


Fig. 7. Frequency dependence of the real (filled symbols) and imaginary (hollow symbols) components of impedance. (Circles) experimental data, (from Fig. 2, curve 2), (triangles) calculated impedance of silver electrocrystallization.

For further analysis, the input of the components R_0 , R_{ct} , C_D , R_A and C_A to both real and imaginary components of impedance was deducted. After such calculations, only impedance of “pure” crystallization should remain in the spectra. In Fig. 7 it is shown that the calculated impedance spectrum of surface diffusion of silver ad-atoms (Fig. 7, triangles) is in good coincidence with the experimentally obtained impedance spectrum (Fig. 7, circles) in all frequency ranges. The values of both real and imaginary components of impedance are similar in a high frequency range, whereas the values of real component increase much more with decreasing of alternating current frequency. The same good coincidences between experimental and calculated data were observed in all impedance spectra (q. v. Fig. 2). These results suggest that the impedance spectra of silver sulfite complexes determined at equilibrium conditions correspond to those of “pure” crystallization; thus, experimental data can be analysed according to surface diffusion impedance model presented in Ref. [29]. According to this model it is possible to compare the theoretical dependence of the ratio of surface diffusion impedance components on the non-dimensional frequency $1/b$ with the dependence of silver sulfite complexes impedance components on the alternating current frequency $\omega^{-1/2}$. Suffice to choose non-dimensional frequency $1/b$ with regard to the really used frequency $\omega^{-1/2}$ (Fig. 8). The results presented in Fig. 8 enables us to use Eq. (4) proposed in Ref. [29] and calculate the mean duration of silver ad-atoms diffusion on the surface, τ :

$$b = r \sqrt{\frac{\omega}{D}}; \quad \frac{1}{1.1b} = \omega^{-1/2}; \quad \tau = \frac{r^2}{D} = 0.83 \text{ s} \quad (4)$$

Accordingly, the mean durations of silver ad-atoms diffusion on the surface were calculated from the impedance spectra determined after immersing silver electrode in the solution different times (Fig. 9). The obtained results have shown that the duration of surface diffusion of silver ad-atoms increases threefold in the first 210 s (from 0.66 to 1.77 s). Thereafter, this growth stops and after a longer time of silver electrode’s contact with electrolyte, the mean duration of silver ad-atom diffusion on the surface stabilizes and reaches the constant value, 1.56 s.

Theoretically the rate of ad-atoms’ surface diffusion should be independent of the duration of electrode contact with solution. Differences observed probably are concerned with the change in the number of new crystallization centres on the surface. It is presumable that the increase of duration of silver ad-atoms surface diffusion is related to the decrease of concentration of crystalliza-

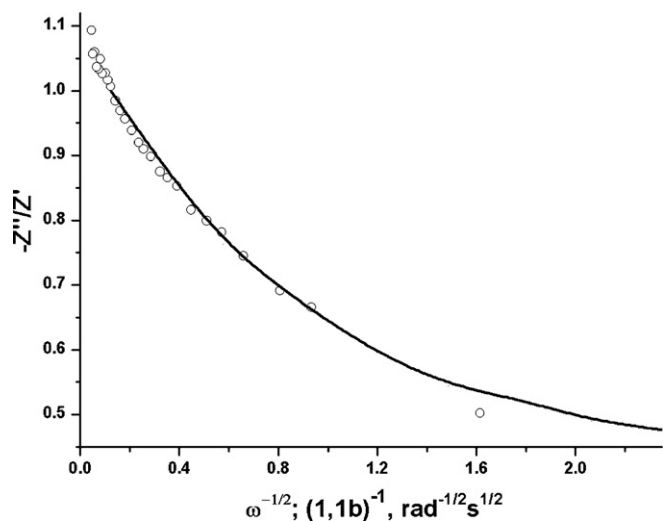


Fig. 8. Dependences of the ratio of real and imaginary impedance components on the frequencies: $\omega^{-1/2}$ (symbols) and $(1.1b)^{-1}$ (line). (Symbols) experimental data represented in Fig. 2, curve 2. (Line) theoretical dependence [29].

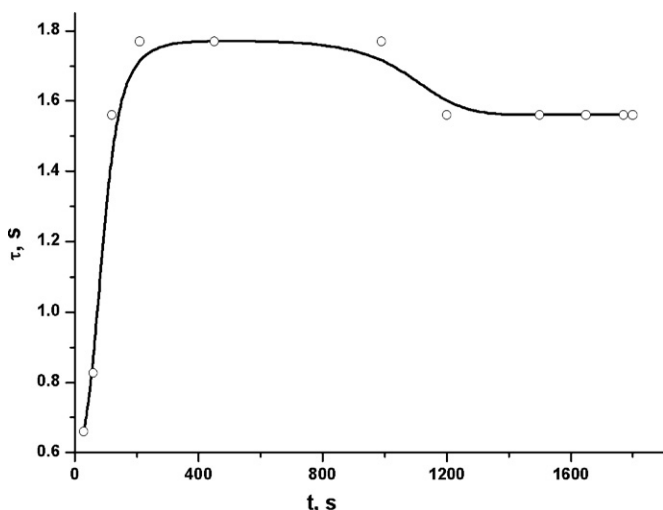


Fig. 9. Dependence of mean duration of silver ad-atoms surface diffusion on the time elapsed after immersing the Ag electrode into the electrolyte.

tion centres. Recurrence of the obtained data is not very good, and it may be related to the sensibility of investigated phenomena to pretreatment of electrode surface which can be poorly controlled. This can explain the poor recurrence of results in the present paper compared with those we have obtained and published earlier [24]. On the other hand, recurrences can be explained by differences in used electrodes and solutions. At least, it becomes more and more important to investigate the process of silver electrodeposition from sulfite electrolytes because of its potential application for non-toxic silver electroplating and for safer and cleaner technologies.

4. Conclusions

The kinetics of electroreduction of silver sulfite complexes has been investigated using the method of the electrochemical FFT impedance spectroscopy under galvanostatic conditions. Dependences of double layer capacitance (C_D), charge transfer resistance (R_{ct}), adsorption components (R_A and C_A) and coefficient B , which

characterizes the silver ad-atoms surface diffusion, on the time were determined. The calculated values of the mean duration of silver ad-atoms diffusion on the surface to the nearest crystallization centre show that initially, during the first 210 s of contact with the electrolyte, these values increase from 0.66 up to 1.77 s. Thereafter, this variation stabilizes and the mean duration of silver ad-atoms diffusion reaches an almost constant value (1.56 s).

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