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The Kinetics of Indium Electroreduction from Chloride Solutions

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Abstract—The electroreduction of indium on indium electrode (99.98%) in perchlorate-containing chloride electrolytes is studied by the methods of linear sweep and cyclic voltammetry, impedance spectroscopy, and chronoamperometry. The indium electroreduction is limited by diffusion, the reaction rate constant is 1.3×10^{-4} cm/s at the indium salt concentration of 0.1 M. The values of the apparent rate constant for the charge transfer stage found by linear sweep and cyclic voltammetry and also by impedance spectroscopy are 2.37×10^{-3}, 3.62×10^{-3}, 3.06×10^{-3} cm/s, respectively. The values of diffusion coefficient of indium(III) ions calculated according to the Cottrell equation based on chronoamperametric measurements and from the Warburg impedance found by impedance spectroscopy are in good agreement. The presence of the Gerischer impedance is stated, which suggests that a homogeneous reaction of formation of indium chloride complexes proceeds and its mechanism is chemical-electrochemical.

Keywords: indium, electroreduction, mass transfer, charge transfer, diffusion coefficient, rate constant, voltammetry, impedance

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INTRODUCTION

The methods of electrochemical refining of metal indium are very promising, especially at the deep cleaning from microimpurities. For synthesizing high-purity indium by electrochemical methods, the processes of discharge-ionization of indium and admixture metals should be studied in detail. The quality of cathodic deposits and the economy factors of electrochemical cleaning of metals depend on the nature of support and electrolyte and also on the electrolysis conditions. There are several publications associated with studying indium electrodeposition on various electrodes in chloride and perchlorate electrolytes [1–7]. In our previous studies [8, 9] we considered the electrochemical behavior of indium on solid electrodes in chloride electrolytes with high conductivity which provided the reversible discharge of indium ions on platinum electrode and their quasi-reversible discharge on titanium electrode.

To avoid the formation of hydro complexes, the electroreduction of indium was carried out at pH ≈ 1.5. In this case, in addition to discharge of metal ions, hydrogen ions can be discharged [10]. The exchange current of discharge of H^+ ions on indium electrode equal to 8×10^{-12} A/cm^2 [11] points to the sufficiently high overpotential of hydrogen evolution on this electrode which induces no considerable changes in the electrolyte pH in the near-electrode layer and allows neglecting the formation of hydroxohalide complexes.

The present study is aimed at determination of kinetics characteristics of this process by the methods of linear sweep (LSV) and cyclic (CV) voltammetry, electrochemical impedance spectroscopy (EIS), and chronoamperometry (CA). Among the goals of this study is elucidation of the limiting stage of this process in the aim of optimizing the conditions of indium electrodeposition.

EXPERIMENTAL

The electroreduction of indium was studied by the methods of cyclic voltammetry, chronoamperometry, and electrochemical impedance spectroscopy in a thermally controlled three-electrode electrochemical cell with the use of potentiostat-galvanostat Autolab PGSTAT 302N (Metrohm Autolab, Netherlands).

The working electrode represented an indium electrode made of In-2 indium bullion (99.98%) with the surface of 0.159 cm^2. The counter electrode represented a platinum plate with the surface of 12.960 cm^2, the reference electrode was silver-chloride (Ag/AgCl) electrode (E = 0.197 V vs. standard hydrogen electrode).

All experiments were carried out at the temperature of 25 ± 0.1°C. Perchlorate-containing chloride solutions with the composition of 0.025; 0.05; 0.1 M $In(ClO_4)_3$ + 2.0 M NaCl (pH 1.5) were prepared from 1.0 M indium perchlorate with using of 2.0 M sodium chloride as a supporting electrolyte. The solution of $In(ClO_4)_3$ was prepared by reacting metal indium In-2 (99.98%) with 60% perchloric acid solution (Sigma Aldrich, 99.99%). The basic supporting electrolyte was sodium chloride solution prepared from triply crystallized reagent-pure salt (99.9%). The solution pH (1.5–1.6) was attained by adding perchloric acid. Before each measurement, the indium electrode was mechanically trimmed with micron abrasive paper and then thoroughly washed with twice distilled water. To assess reproducibility of results, each measurement was repeated no less than 3 times.

Impedance was measured in the frequency range from 100 kHz to 0.1 Hz in the potentiostatic mode at the potential ±10 mV from E_{eq}. Chronopotentiometric measurements were carried out at the potential of –0.9 V vs. Ag/AgCl electrode. Cyclic voltammograms were recorded in the potential interval from –0.5 to –1.0 V. The potential sweep rate was varied in the interval from 5 to 160 mV/s.

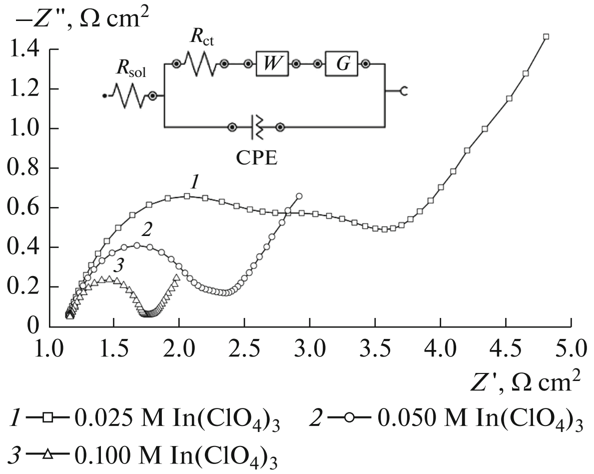

Fig. 1. Experimental impedance diagrams at 25°C on In electrode in 2.0 M NaCl solution with different content of $In(ClO_4)_3$. Insert: equivalent circuit of electrochemical cell.

RESULTS AND DISCUSSION

Charge Transfer Stage

In studying the stage of transfer of the electrochemical-reaction charge, pulse potentiostatic and galvanostatic techniques and relaxation methods are used most often. The polarization measurements are accompanied by an electrochemical reaction which proceeds in the mixed kinetics mode; hence, this requires elimination of diffusion limitations. The method of impedance spectroscopy allows finding the exchange current density (i_0) without introducing any corrections for concentration polarization [12–15]. At low overpotentials, the dependences between the exchange current density i_0 and the resistance of the charge-transfer stage (R_{ct}) can be expressed as follows [16]:

$$R_{ct} = \frac{RT}{nFi_0}, \tag{1}$$

where n is the number of electrons involved in the electrode process, R is the gas constant, T is the absolute temperature (K), F is the Faraday constant (96485 C/mol).

From the results of impedance measurements, it is evident (Fig. 1) that in the high-frequency range from 100 kHz to 49.4 Hz, this dependence represents a semicircumference, while in the low-frequency range from 5.2 to 0.1 Hz, a linear dependence corresponding to the Warburg impedance can be seen.

The found impedance diagrams can be adequately approximated by calculations (Fig. 2a) according to the equivalent circuit that corresponds to the charge transfer at high frequencies and to the homogeneous chemical reaction and mass transfer at low frequencies. The latter circuit contains the electric-double-layer capacitance ($C_{EDL} - \mathrm{CPE}$), the solution resistance (R_{sol}), the charge-transfer resistance (R_{ct}), the Gerischer impedance (G), and the Warburg impedance (W) (Fig. 1, insert).

The poor correlation between Nyquist diagrams experimental and calculated according to the Randles–Ershler circuit (Fig. 2a, curve *3*), points to inadequacy of this equivalent circuit in describing the indium electroreduction process. The appearance of the second semicircumference in Fig. 2a in the frequency range of 49.4–5.2 Hz is associated with the presence of the Gerischer impedance corresponding to realization of the chemical-electrochemical mechanism of indium electroreduction [17]. There is direct correlation between the Gerischer impedance values and the concentration of indium ions in solution. As the concentration of the potential-determining ion increases from 0.025 to 0.1 M, the Gerischer impedance decreases from 26.2 to 1.2 Ω, respectively. The possibility of reduction of indium ions from negatively charged complex species $[InCl_4]^-$ as a result of formation of ion pairs [18] with supporting electrolyte cations was studied by substituting potassium chloride for sodium chloride (Fig. 2b). The close values of charge-transfer resistance (2.16 Ω cm^2 for NaCl and 2.05 Ω cm^2 for KCl) and exchange current density (2.73 × 10^{-3} A/cm^2 for NaCl and 2.6 × 10^{-3} A/cm^2 for KCl) at electroreduction of indium from NaCl and KCl solutions suggest that these species are uninvolved in this process; probably, it is the discharge of cation-active complex species that takes place.

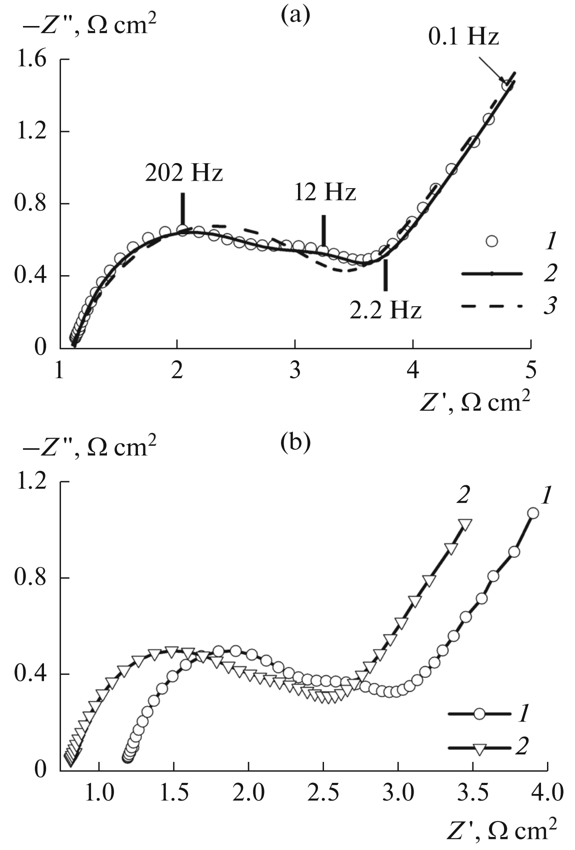

Fig. 2. (a) Nyquist diagrams of indium electroreduction at 25°C on In electrode in 0.025 M $In(ClO_4)_3$ + 2.0 M NaCl solution: (*1*) experimental, (*2*) calculated with regard to Gerischer impedance, (*3*) calculated with disregard to Gerischer impedance (Randles–Ershler circuit); (b) experimental impedance diagrams at 25°C on In electrode. Supporting electrolyte: (*1*) 2.0 M NaCl; (*2*) 2.0 M KCl + 0.025 M $In(ClO_4)_3$.

Based on these data, the resistance of charge-transfer stage was calculated which allowed calculating the exchange current according to Eq. (1) [16] (Table 1).

Table 1. Polarization resistance (R_p), solution resistance (R_{sol}), charge-transfer resistance (R_{ct}), and exchange current density (i_0) at the reduction of In^{3+} on indium electrode in 2.0 M sodium chloride solution with different contents of $In(ClO_4)_3$

$c_{In^{3+}}$, M	EIS			
	R_p, Ω cm^2	R_{sol}, Ω cm^2	R_{ct}, Ω cm^2	i_0, mA/cm^2
0.025	3.34	1.18	2.16	2.73
0.050	2.27	1.14	1.13	7.57
0.100	1.75	1.15	0.60	14.26

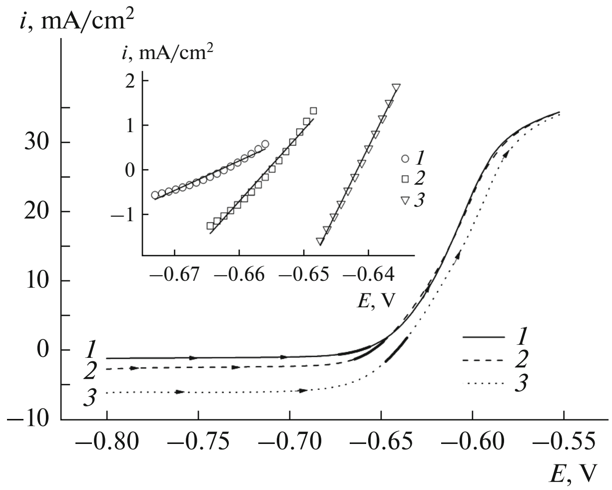

Fig. 3. Polarization curves of indium discharge-ionization on indium electrode at 25°C, v = 5 mV/s in 2.0 M NaCl solution with different content of $In(ClO_4)_3$: (*1*) 0.025 M; (*2*) 0.050 M; (*3*) 0.100 M. Insert: linear segment, region of low overpotentials.

The increase in the concentration of potential-determining ion leads to the regular increase in the exchange current and the decrease in the charge-transfer resistance.

According to the slow discharge theory, the dependence between the exchange current density and the concentration of the oxidized form of indium is described by the following equation [17]:

$$\log i_0 = \log(nFk^{\exp}) + (1-\alpha)\log c_{In^{3+}}, \qquad (2)$$

where i_0 is the exchange current density (A/cm^2), $k^{\exp}$ is the rate constant for the charge transfer stage (cm/s), α is the electron transfer coefficient, $c_{In^{3+}}$ is the concentration of In^{3+} ions in solution volume (mol/cm^3).

The rate constant of charge-transfer $k^{\exp}$·calculated from the $\log i_0 - \log c_{In^{3+}}$ dependence (Eq. (2)) is 3.06×10^{-3} cm/s and ignores the effects of the charged interface structure and the specific adsorption of Cl^- anions on the indium electrode surface.

To confirm the accuracy of the value of rate constant for the charge-transfer stage calculated based on results of impedance measurements, we studied indium electrodeposition on indium electrode by the LSV (Fig. 3) and CV methods.

For calculating the polarization resistance, we used the low overpotential region in which the current density depends linearly on the potential (insert to Fig. 3). Table 2 shows the calculated values of polarization resistance and exchange current found by LSV and EIS methods. Comparing these results shows that LSV gives the higher values than EIS. This is explained by impossibility of compensating the mass-transfer con-

Table 2. Values of polarization resistance, exchange current density, and diffusion resistance, found for different concentrations of indium ions by the EIS and LSV methods

$c_{\mathrm{In}^{3+}}$, M	EIS		LSV				
					with regard to R_d		
	R_p, Ω cm^2	i_0, mA/cm^2	R_p^1, Ω cm^2	i_0, mA/cm^2	R_p, Ω cm^2	i_0, mA/cm^2	R_d, Ω cm^2
0.025	4.12	2.73	14.18	0.66	4.31	2.69	10.00
0.050	2.27	7.57	5.73	1.87	2.32	11.72	4.01
0.100	1.75	14.26	3.28	4.00	1.66	30.57	2.00

tribution when using the linear voltammetry technique where measurements are carried out under conditions of nonstationary diffusion and also by the absence of strict linearity of segments used in calculations, which leads to overrated slope values. The use of the LSV method for studying the charge-transfer stage of electrode processes is correct only for reactions with the low heterogeneous rate constant. The rate constant for charge transfer at the reduction of In^{3+} ions on indium electrode which we found from impedance data points to the substantial contribution of mass transfer and requires introducing corrections for concentration polarization.

If assume that the total polarization resistance (R_p^1) additively combines the solution resistance (R_sol), the charge-transfer resistance (R_ct), and the mass transfer resistance (diffusion resistance) (R_d)

$$R_\mathrm{p}^1 = R_\mathrm{sol} + R_\mathrm{ct} + R_\mathrm{d} = R_\mathrm{p} + \frac{RT}{nF\left|i_\mathrm{lim}\right|},$$

then taking into account the diffusion resistance becomes possible provided the limiting diffusion current (i_lim) is known. Based on chronoamperograms, we found i_lim values which allowed the polarization resistance to be calculated with regard to the diffusion resistance (Table 2).

According to table, the polarization resistance values found by two methods are close to one another. The rate constant for charge transfer stage k^exp found from the results of linear sweep voltammetry (Eq. (2)) is 2.37×10^{-3} cm/s and well agrees with the constant obtained based on EIS method (Fig. 4).

For studying the discharge of indium ions, we measured cyclic voltammograms (Fig. 5). The increase in the potential sweep rate from 5 to 160 mV/s shifts the peak of indium reduction by 98 mV. Furthermore, its shift strongly increases at high polarization rates.

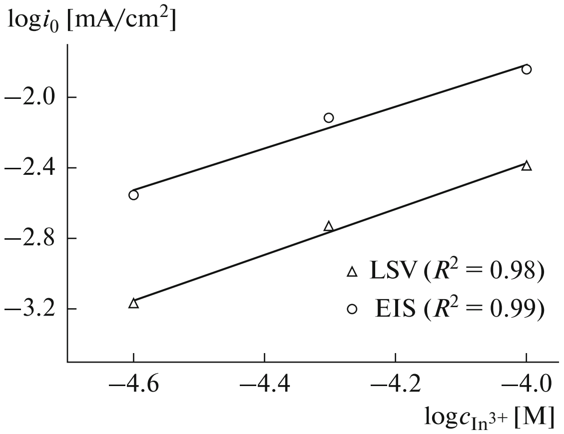

Fig. 4. Logarithmic dependence of exchange current density on In^{3+} salt concentration in 2.0 M NaCl solution. R^2—correlation factor.

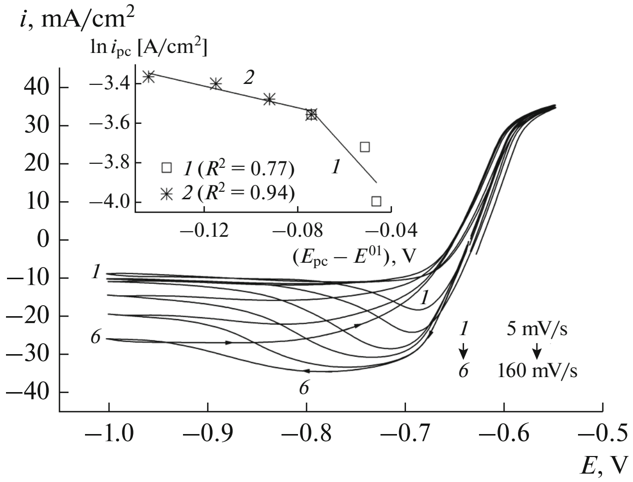

Fig. 5. Cyclic voltammograms of indium at 25°C on indium electrode in 0.1 M $\mathrm{In(ClO_4)_3}$ + 2.0 M NaCl solution at different polarization rates. Insert: dependence of $\ln i_\mathrm{pc}$ on $\left(E_\mathrm{pc} - E^{01}\right)$ at different potential sweep rates: (*1*) low (5–20 mV/s), (*2*) high (20–160 mV/s).

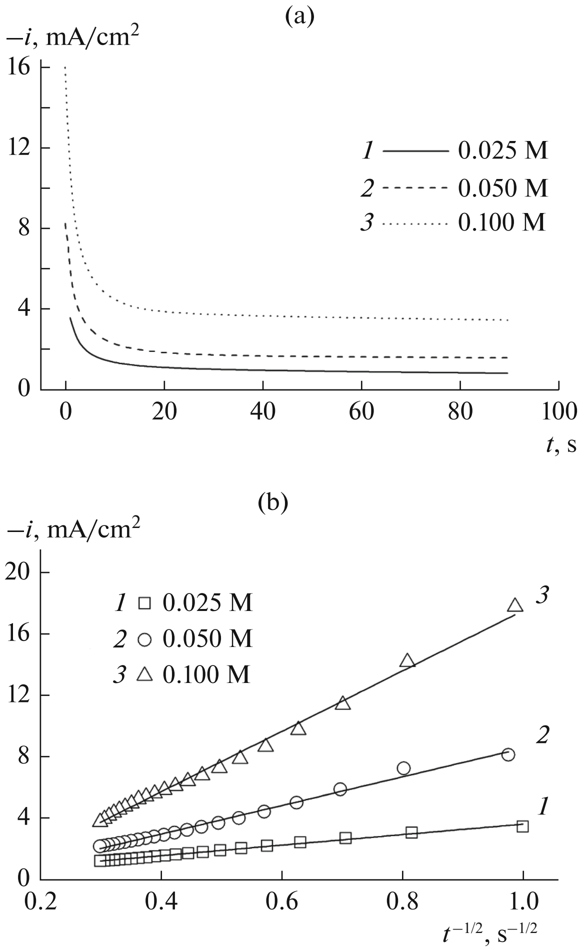

Fig. 6. (a) Chronoamperograms of indium electrodeposition at 25°C on indium electrode from 2.0 M NaCl solution with different content of $In(ClO_4)_3$ at $E = -0.9$ V; (b) i_c–$t^{-1/2}$ dependence.

If the shift of cathodic-peak potential from the formal electrode potential and the current of this peak depend on the potential sweep rate, then the $\ln j_{pc}$–$\left(E_{pc} - E^{01}\right)$ dependence is described as follows [19, 20]:

$$\ln i_{pc} = \ln(0.227 nFc_{In^{3+}}k^{exp}) - \frac{\alpha nF}{RT}(E_{pc} - E^{01}), \quad (3)$$

where E_{pc} is the cathodic-peak potential (V), E^{01} is the formal electrode potential (V), i_{pc} is the cathodic-peak current density (A/cm^2).

Figure 5 (insert) shows the dependence of logarithm of peak's current density on peaks's potential shift $\left(E_{pc} - E^{01}\right)$. For the low polarization rate of 5 and 10 mV/s, the shift of cathodic peak potential from the formal value is 46 and 51 mV, respectively. As the sweep rate increases, the shift $\left(E_{pc} - E^{01}\right)$ strongly increases to become 144 mV for the sweep rate of 160 mV/s.

According to Fig. 5 (insert), this dependence is linear ($R^2 = 0.94$) in the interval of potential sweep rate from 20 to 160 mV/s and described by Eq. (3), which allowed the rate constant of charge transfer stage to be calculated to be 3.62×10^{-3} cm/s. The deviation from linearity at low sweep rates is explained by the contribution of diffusion overpotential.

The experimental values charge-transfer rate constant found by the aforementioned methods are 3.06×10^{-3} (EIS); 2.37×10^{-3} (LSV); 3.62×10^{-3} cm/s (CV). Comparing the results of studying the charge transfer stage of indium reduction on indium electrode by the aforementioned methods showed their good agreement.

It is generally assumed that indium electroreduction proceeds in several stages with the limiting state $In^{3+} + e = In^{2+}$ [17]. Indium compounds with the lower degrees of oxidation are unstable and tend to disproportionation reactions [21]. It is shown that stability of In^+ ions in solution depends on the content of trivalent indium, temperature, and solution pH. It is only with the increase in these parameters in concentrated solutions of alkali and alkali-earth metals in which the water activity decreases and also in salt melts that the In^+ content is observed to increase [22]. For low concentrations of In^+ ions in solution, the successive discharge becomes the most probable. The effects of disproportionation can occur only at very high concentrations of intermediate species, which is possible only at the anodic dissolution of indium [23]. According to aforesaid, the total number of electrons involved in indium reduction on indium electrode is three.

Mass Transfer Stage

The chronoamperometric technique makes it possible to find the kinetic mode of the process in the system studied, calculate the diffusion coefficients and the effective mass-transfer constant [24]. For determining the diffusion coefficients and the mass transfer constant, we measured chronoamperograms of indium reduction from chloride electrolytes at the varied concentration of indium salt (Fig. 6a).

For this reaction to proceed completely during chronoamperometric measurements, we applied potential of −0.9 V on the electrode. In this case, for studying the mass-transfer stage, the Cottrell equation can be used which expresses the dependence of the current density on the time for the case of nonstationary diffusion [25]:

$$i_c(t) = i_d(t) = -nFc_{In^{3+}}\sqrt{\frac{D_{In^{3+}}}{\pi t}}, \quad (4)$$

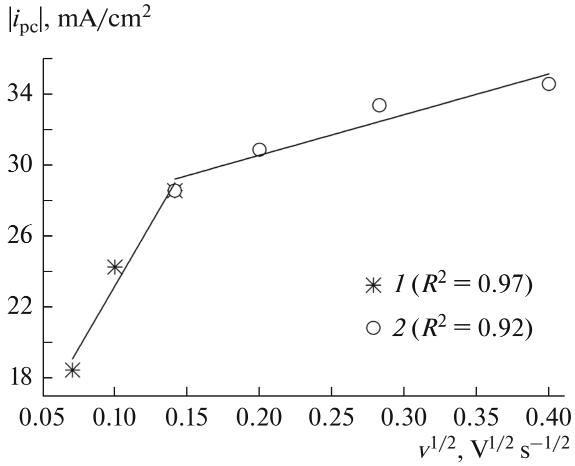

Fig. 7. Dependence of cathodic-peak current density on square root of potential sweep rate in 2.0 M NaCl solution containing 0.1 M $In(ClO_4)_3$: (*1*) at low (5–20 mV/s) and (*2*) high (20–160 mV/s) polarization rates.

where $D_{In^{3+}}$ is the diffusion coefficient (cm^2/s), t is the time (s).

The diffusion coefficient of the electroactive substance can be found based on chronoamperametric data from the slope of the line $i_c(t) = f\left(1/t^{1/2}\right)$ (Fig. 6b).

To determine the diffusion coefficient of In^{3+} ions during their reduction, the CV and EIS methods can also be used. Based on CV data, the dependence of the cathodic current density on square root of the potential sweep rate was determined (Fig. 7). For the low polarization rate, this dependence is described by the Randles–Ševćik equation; at the high polarization rate it is described by the Delahay equation [26], the $D_{In^{3+}}$ values found from the slope of aforementioned dependences are 1.0 × 10^{-6} and 0.81 × 10^{-6} cm^2/s, respectively.

The electrode impedance at the low frequency of sinusoidal current (5.2–0.1 Hz) is characterized by diffusion impedance (Warburg impedance Z_w) which depends on concentration and diffusion coefficient of the potential-determining ion (Fig. 1). The absolute value of Warburg impedance is [17]

$$|Z_W| = \frac{1}{c_{In^{3+}}\sqrt{D_{In^{3+}}}}\frac{RT}{n^2F^2\sqrt{\omega}},$$

where Z_W is the Warburg impedance (Ω cm^2), ω is the angular frequency (rad/s).

Based on this equation, we plotted the $|Z_W| - \omega^{-1/2}$ dependences (Fig. 8) for different $c_{In^{3+}}$. From the slope of these dependences, we found the diffusion coefficient of In^{3+} (Table 3).

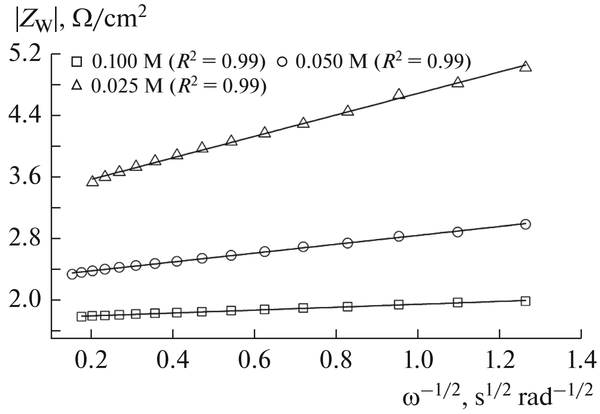

Fig. 8. Dependence of Warburg impedance of indium electrode on ac frequency under conditions of low polarization in 2.0 M NaCl solution containing different concentrations of $In(ClO_4)_3$.

Table 3 shows the values of diffusion coefficient of In^{3+} ions found by CA and EIS methods.

The absence of substantial difference in the values of diffusion coefficient of In^{3+} ions at their reduction confirms the reliability of obtained results. The small deviations in the diffusion coefficient values determined by CV methods for 0.1 M concentration do not cast any doubt on the results obtained.

For the case of limiting diffusion current (i_{lim}), Eq. (4) takes the following form (Fig. 6a) [11]:

$$i_{lim} = -nFc_{In^{3+}}\frac{D_{In^{3+}}}{\delta_{eff}} = -nFm_{eff}c_{In^{3+}}, \tag{5}$$

where δ_{eff} is the effective thickness of the diffusion layer (cm), m_{eff} is the effective mass-transfer constant (cm/s).

From Eq. (5), we calculated the effective rate constant for mass transfer of indium ions at different concentration of In^{3+} during electroreduction on indium electrode (Table 3).

Table 3. Diffusion coefficient of indium ions and effective mass-transfer constant for electroreduction of indium in 2.0 M NaCl solution

$c_{In^{3+}}$, M	$D_{In^{3+}}$, 10^{-6} cm^2/s		m_{eff}, 10^{-4} cm/s
	CA	EIS	CA
0.025	0.69	0.71	1.04
0.500	1.13	1.04	1.12
0.100	1.98	2.42	1.30

Comparison of the apparent charge-transfer rate constant (3.06×10^{-3} cm/s, EIS) and the effective rate constant for mass transfer of substance (1.3×10^{-4} cm/s, CA) suggests that electroreduction of indium proceeds in the diffusion mode.

CONCLUSIONS

Kinetic characteristics of electroreduction of In^{3+} ions on indium electrode in perchlorate-containing chloride electrolytes are determined by methods of linear sweep voltammetry, cyclic voltammetry, chronoamperometry, and impedance spectroscopy. The analysis of impedance data revealed the presence of the Gerischer impedance which points to the chemical-electrochemical mechanism of the process under study. It is found that the nature of cation has no effect on charge-transfer resistance and exchange current density. This suggests that indium electroreduction proceeds from cation-active chloride complexes.

The effective constant of mass transfer determined by chronoamperometric method is 1.3×10^{-4} cm/s. By comparing the rate constants for mass and charge transfer, the diffusion nature of the limiting stage of electroreduction of indium ions was revealed. The rate constant for the charge transfer stage calculated according to the slow discharge theory based on impedance data is 3.06×10^{-3} cm/s, which agrees with the results of voltammetric measurements.

The results obtained here can be used in simulation of the process of electrochemical refining of indium.

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REFERENCES

1. Te, P., YuYing, C., Sihzih, C., and Shuehlin, Y., In situ scanning tunneling microscopy of electrodeposition of indium on a copper thin film electrode predeposited on Pt(111) electrode, *J. Phys. Chem. C,* 2013, vol. 117, p. 26659. doi 10.1021/JP4095968
2. Yonghwa, C. and Chi-Woo, L., Nucleation process of indium on a copper electrode, *J. Electrochem. Sci. Technol.*, 2013, vol. 4, p. 93. doi 10.5229/JECST.2013.4.3.93
3. Munoz, A.G., Saidman, S.B., and Bessone, J.B., Electrodeposition of indium onto vitreous carbon from acid chloride solutions, *J. Electrochem. Soc.*, 1999, vol. 146, p. 2123. doi 10.1149/1.1391902
4. Saidman, S.B., García, S.G., and Bessone, J.B., Electrochemical behaviour of Al-In alloys in chloride solutions, *J. Appl. Electrochem.*, 1995, vol. 25, p. 252. doi 10.1007/BF00262964
5. Breslin, C.B. and Carroll, W.M., The activation of aluminium by indium ions in chloride, bromide and iodide solutions, *Corros. Sci.*, 1993, vol. 34, p. 327. doi 10.1016/0010-938X(93)90010-E
6. Saidman, S.B. and Bessone, J.B., Activation of aluminium by indium ions in chloride solutions, *Electrochim. Acta*, 1997, vol. 42, p. 413. doi 10.1016/S0013-4686(96)00236-8
7. Piercy, R. and Hampson, N.A., The indium electrode in chloride electrolytes, a kinetic study, *J. Electroanal. Chem*, 1975, vol. 59, p. 261. doi 10.1016/S0022-0728(75)80181-1
8. Rakhymbay, G.S., Nauryzbayev, M.K., Burkitbayeva, B.D., Argimbaeva, A.M., Jumanova, R., Kurbatov, P., Eyraud, M., Knauth, P., and Vacandio, F., Electrochemical deposition of indium: nucleation mode and diffusional limitation, *Russ. J. Electrochem.*, 2016, vol. 52, p. 99. doi 10.1134/S1023193516020087
9. Burkitbayeva, B.D., Argimbaeva, A.M., Rakhymbay, G.S., Beysenova, G.S., Avchukir, K., Kurbatov, A.P., and Nauryzbayev, M.K., A study of the electrochemical behavior of indium on a titanium electrode by cyclic voltammetry method, *Khim. Zh. Kazakhstana*, 2015, vol. 51, no. 3, p. 34.
10. Kozin, V.F., Sheka, I.A., and Belinskii, V.N., Studies of acidity of near-electrode layers at indium electrodeposition, *Ukr. Khim. Zh.*, 1983, vol. 49, no. 2, p. 148.
11. Damaskin, B.B., Petrii, O.A., and Tsirlina, G.A., *Elektrokhimiya (Electrochemistry)*, Moscow: Khimiya, KolosS, 2006.
12. Gonzalez-Buch, C., Herraiz-Cardona, I.M, Ortega, E., Mestre, S., and Perez-Herranz, V., Synthesis and characterization of Au-modified macroporous Ni electrocatalysts for alkaline water electrolysis, *Int. J. Hydrogen Energy*, 2016, vol. 41, p. 764. doi 10.1016/j.ijhydene.2015.10.142
13. Xu, C., Zhou, J., Zeng, M., Fu, X., Liu, X., and Li, J., Electrodeposition mechanism and characterization of Ni-Mo alloy and its electrocatalytic performance for hydrogen evolution, *Int. J. Hydrogen Energy*, 2016, vol. 41, p. 13341. doi 10.1016/j.ijhydene.2016.06.205
14. Jovic, B.M., Lacnjevac, U.C., Jovic, V.D., and Krstajic, N.V., Kinetics of the oxygen evolution reaction on NiSn electrodes in alkaline solutions, *J. Electroanal. Chem.*, 2015, vol. 754, p. 100. doi 10.1016/j.jelechem.2015.07.013
15. Pettit, C.M., Garland, J.E., Etukudo, N.R., Assiongbon, K.A., Emery, S.B., and Roy, D., Electrodeposition of indium on molybdenum studied with optical second harmonic generation and electrochemical impedance spectroscopy, *Appl. Surf. Sci.*, 2002, vol. 202, p. 33. doi 10.1016/S0169-4332(02)00798-5
16. Bard, A.J. and Faulkner, L.R., *Electrochemical Methods: Fundamentals and Applications*, 2nd ed., New York: Wiley-VCH, 2001.
17. Damaskin, B.B. and Petrii, O.A., *Vvedenie v Elektrokhmicheskuyu Kinetiku* (Introduction to electrochemical kinetics), Moscow: Vysshaya Shkola, 1975.

18. Kravtsov, V.I., Kinetics and mechanism of electrode reactions of metal complexes in aqueous solutions of electrolytes, *Usp. Khim.*, 1976, vol. 45, p. 284.

19. Protsenko, V.S., Kityk, A.A., and Danilov, F.I., Voltammetry study of Cr(III)/Cr(II) system in aqueous methanesulfonate solutions, *J. Electroanal. Chem.*, 2011, vol. 661, p. 213. doi 10.1016/j.jelechem.2011.08.003

20. Kityk, A.A., Protsenko, V.S., and Danilov, F.I., Voltammetry study of Cr(III)/Cr(II) system in methanesulfonate and sulfate solutions: Temperature dependences, *J. Electroanal. Chem.*, 2012, vol. 689, p. 269. doi 10.1016/j.jelechem.2011.08.003

21. Kozin, V.F. and Omel'chuk, A.A., Kinetics and mechanism of the formation of monovalent indium ions in the system In^0–$In_2(SO_4)_3$–In_2SO_4, *Izv. Vyssh. Uchebn. Zaved., Tsvetn. Metall.*, 2006, vol. 2, no. 2, p. 45.

22. Kozin, V.F., Formation of monovalent indium ions in concentrated solutions of the system In^0–$InCl_3$–$CaCl_2$, *Ukr. Khim. Zh.*, 1995, vol. 61, no. 9, p. 3.

23. Nazmutdinov, R.R., Shapnik, M.S., and Malyucheva, O.I., Reduction pathways of indium ions—multistep discharge or disproportionation, *Russ. J. Electrochem.*, 1993, vol. 29, p. 428.

24. Miomandre, F., Sadki, S., Audebert P., and Meallet-Renault, R., *L'Electrochimie,* Dunod, 2005 (translated into Russian).

25. Galus, Z., *Fundamentals of Electrochemical Analysis*, New York: Harwood, 1976.

26. Delahay, P., Theory of irreversible waves in oscillographic polarography, *J. Amer. Chem. Soc.*, 1953, vol. 75, p. 1190.

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