The Kinetic Characteristics of Nickel Electrodeposition From Solutions with Amino Acids

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Kinetics of nickel electrodeposition from electrolytes containing glycine, alanine, serine and asparaginic acid was studied. It was shown, that the process occurs irreversibly under mixed kinetics conditions with dominant control by charge transfer and is complicated by adsorption. All the complexes present in the baths are electroactive and reduce simultaneously. The process rate and kinetic characteristics sufficiently depend on the nature of amino acids. Namely, the more stable complexes are formed, the larger charge transfer coefficient and the less heterogeneous rate constant of charge transfer.

Keywords: Nickel, Electrodeposition, Kinetics, Complexes, Glycine, Alanine, Serine, Asparaginic acid.

1. INTRODUCTION

At the present time the electrochemical methods are successfully used to produce metal coatings with a wide range of functional properties by varying of deposition parameters and electrolyte composition. One of the effective ways to do this is the use of different organic and inorganic substances, which can form complexes with nickel ions, that leads to substantial change in bath composition and, as consequence, in deposition kinetics and coating properties.

Advantages of use of amino acids as ligands were reported in [1, 2]. However, the kinetics of nickel deposition from electrolytes containing amino acids still remains unclear. So, the aim of this work is the comparative study of nickel electrodeposition kinetics from solutions containing glycine (HGly), alanine (HAla), serine (HSer) or asparaginic acid (H₂Asp). Selected acids differ in carbon chain length as well as nature and quantity of functional groups. This significantly influences the composition and stability of complexes formed by mentioned acids with nickel ions.

2. EXPERIMENTAL

Kinetics of nickel electroplating was studied in the following baths (mol/l): 0.08 NiCl$_2$ + y H$_x$L (pH 5.5), where L – Gly⁻, Ala⁻, Ser⁻ or Asp²⁻. The amino acid concentration was varied from 0.02 to 0.60 mol/l. Solutions were prepared from reagents of kh. ch. (chemically grade), and doubly distilled water. Required acidity was reached by adding 10% HCl or NaOH solutions and controlled by an EV-74 universal ionometer (accuracy±0.05).

Electrochemical studies were performed with an IPC-Compact potentiostatic complex. A three-electrode cell with separate cathodic and anodic compartments was used. Two Ni(99.99) working electrodes were employed; namely, stationary (S = 0.28 cm²) and a rotating disk (S = 0.71 cm²). A silver-silver chloride electrode served as the reference one and a platinum wire gauze as counter electrode. All the potentials are given relatively to a standard hydrogen electrode.

Before each experiment, the working electrode was mechanically sand by abrasive paper with decreasing grain size, then polished with soft suede leather, and degreased with ethanol. Thus prepared electrode was polarized from the steady state potential (E_{st}) to -1.6 V. Scan rate v was varied from $1\cdot10^{-3}$ to $1\cdot10^{-1}$ V/s.

Partial curves of nickel deposition and hydrogen evolution were derived from potentiostatic steady-state polarization curves with account of nickel current efficiency (CE), measured by gravimetric method and calculated ed by formula:

$$CE = \frac{nF(m_2 - m_1)}{I \cdot \tau \cdot M},\qquad(2.1)$$

where m_1, m_2 – copper plate weights before and after deposition respectively; τ – deposition time; I – current; M – molar mass of Ni. Partial currents of nickel deposition and hydrogen evolution were calculated as $i_{Ni} = i_{tot} \cdot CE$ and $i_{H_2} = i_{tot} - i_{Ni}$ respectively.

3. RESULTS AND DISCUSSION

3.1 Partial curves of nickel deposition and hydrogen evolution

Typical cathodic voltammetric curves measured in the studied electrolytes are shown in Fig. 1.

Curves 1-4 are characterized by the presence of a clearly pronounced cathodic peak, whose position and magnitude depend on the amino acid nature. So, in the raw Gly⁻≥ Ala⁻> Ser⁻>Asp²⁻ peak potential becomes more positive, and peak current decreases. In the same order investigated acids can be arranged with respect to compactness of acid molecules [3]. The least compact form has asparaginic acid. It has a very «bulky fragment». Measured cathodic current includes both nickel ion electroreduction process and hydrogen evolution reaction (HER). The latter occurs simultaneously with nickel deposition. Therefore, partial curves of referred above reactions were obtained. Results are presented for glycine solution in Fig. 2 as the example.

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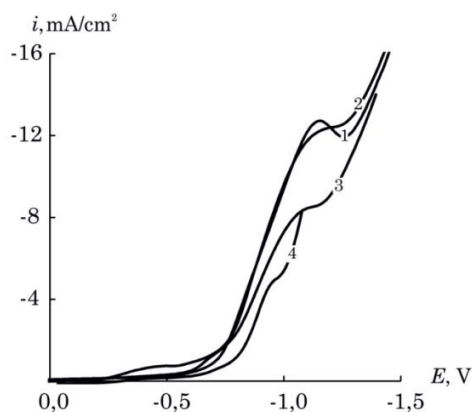† nvs@chem.vsu.ru
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Fig. 1 – Voltammetric curves obtained in nickel-plating baths containing different amino acids: HGly (1), HAla (2), HSer (3), H_2Asp (4); $C(H_xL) = 0.2$ mol/l; $v = 0.05$ V/s
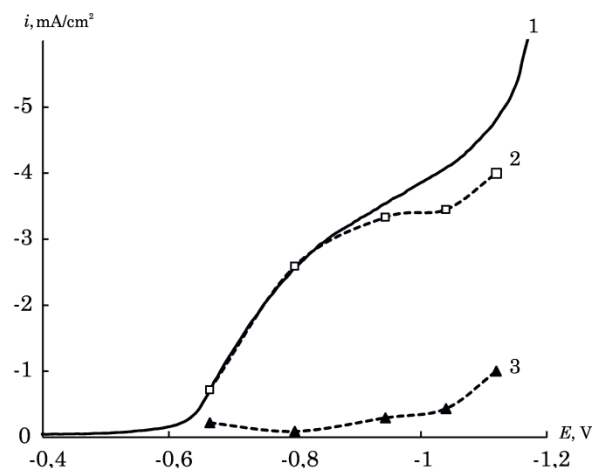

Fig. 2 – Total polarization curve (1) and partial polarization curves of nickel deposition (2) and hydrogen evolution (3) from glycine-containing electrolyte 0.08 M $NiCl_2$+0.20 M HGly

Table 1 – Steady-state potentials of nickel electrode (E_{st}), peak potentials (E_p) and peal currents (i_p) for different concentrations of studied amino acids

$C(H_xL)$, mol/l	HGly			HAla		
	E_{st}, V	E_p, V	i_p, mA/cm²	E_{st}, V	E_p, V	i_p, mA/cm²
0.02	0.16±0.003	-1.16±0.07	-15.30±0.15	0.16±0.004	–*	–*
0.04	0.16±0.003	-1.19±0.02	-19.04±0.24	0.15±0.005	-1.36±0.09	-18.56±0.19
0.08	0.16±0.004	-1.11±0.02	-15.80±0.22	0.14±0.008	-1.27±0.04	-15.73±0.17
0.10	0.15±0.005	-1.12±0.08	-17.08±0.18	0.14±0.003	-1.23±0.08	-14.89±0.18
0.20	0.15±0.002	-1.09±0.02	-12.56±0.21	0.13±0.004	-1.23±0.09	-12.45±0.15
0.50	0.14±0.004	-1.01±0.03	-10.57±0.19	0.12±0.007	-1.13±0.07	-10.69±0.20
	HSer			H_2Asp		
0.02	0.15±0.006	-1.54±0.04	-18.34±0.13	0.15±0.004	-1.06±0.02	-8.12±0.12
0.04	0.14±0.005	-1.21±0.08	-14.80±0.19	0.12±0.006	-1.12±0.03	-12.13±0.14
0.08	0.13±0.007	-1.20±0.06	-13.17±0.17	0.11±0.007	-1.05±0.01	-8.69±0.11
0.10	0.12±0.006	-1.14±0.07	-12.06±0.21	0.09±0.005	-0.97±0.02	-8.56±0.17
0.20	0.11±0.009	-1.25±0.09	-10.68±0.14	0.08±0.007	-0.96±0.01	-4.88±0.16
0.40	0.08±0.008	-1.07±0.04	-7.74±0.20	0.07±0.006	-0.94±0.02	-4.68±0.13
0.60				0.07±0.004	-0.91±0.01	-4.57±0.15

–* – no peak is observed;

It can be seen that in the vicinity of E_p contribution of HER to the total current is about 10%, at higher potentials it reaches 30%. The same dependences is observed for electrolytes with alanine and serine, but in asparaginic solutions maximum CE of Ni is 55%. The peak current values were updated in conformity with obtained CE magnitudes. The peak current values were update in conformity with obtained CE magnitudes.

3.2 Establishment of nickel electrodeposition mechanism

To establish the mechanism of nickel electrodeposition it is necessary to obtain the dependences of parameters i_p, E_p on some factors.

Influence of amino acid concentration $C(H_xL)$ on steady-state potential and peak current is represented by Table 1. It can be seen that E_{st} becomes sufficiently more negative with increase of $C(H_xL)$. The specific feature of glycine and asparaginic electrolytes is reaction acceleration by low amino acid concentration (0.02–0.04 mol/l) with subsequent rate decay. At the same time for alanine and serine solutions deposition rate decreases in the whole concentration range.
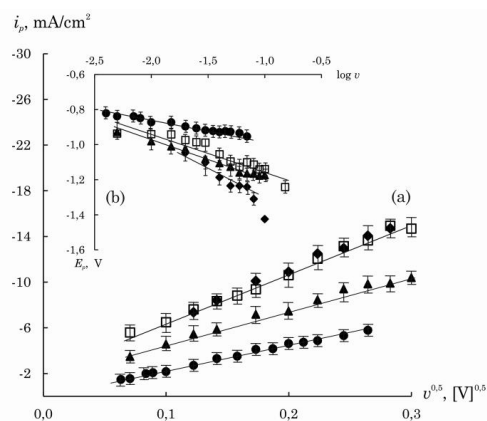

Fig. 3 – The effect of potential scan rate on the peak current density (a) and potential (b) of voltammograms measured in nickel-plating baths with different amino acids: (□) – HGly; (♦) – HAla; (▲) – HSer; (●) – H_2Asp ($C(H_xL) = 0.2$ mol/l)

It should be noted that direct proportionality between peak current and $C(H_xL)$ is absent, as well as definite regularity of peak potential change (see Table 1).

The investigation of potential scan rate (v) and disk rotation speed (w) effects on the cathodic voltammo-

gram parameters was performed in electrolytes containing the isomolar amino acid concentrations. It was found that for all systems under study peak current proportionally increases with $v^{1/2}$ and peak potential linearly depends on log v (Fig. 3).
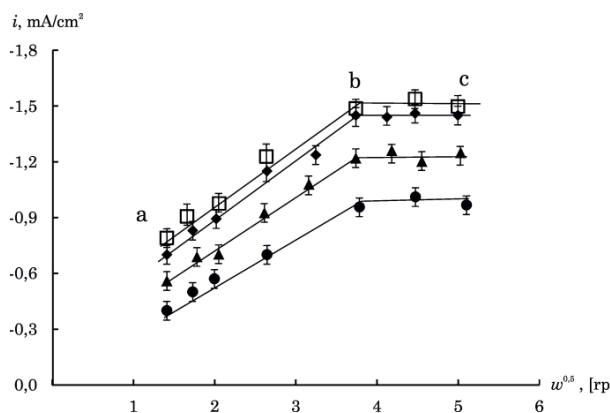

Fig. 4 – The effect of disk rotation speed on the current density of voltammograms measured in nickel-plating baths with different amino acids: (□) – HGly; (♦) – HAla; (▲) – HSer; (●) – H_2Asp ($C(H_xL)$=0.2 mol/l; v=0.05 V/s)

The influence of disk rotation speed on the process rate in studied nickel plating electrolytes is shown in Fig. 4. Two linear sections can be distinguished at the $i = f(w^{0.5})$ dependences. Section ab observed in a wide range of the rotation speed denotes the presence of diffusion limitations in our systems. At the same time the i independence of $w^{0.5}$ observed at higher electrode rotation speed (section bc) points to the limiting charge transfer stage [7].

Experimental data on $C(H_xL)$, v and w effects on peak current and peak potential values were analyzed with the help of diagnostic criteria of linear voltammetry and rotating disk electrode methods in order to make conclusion about process mechanism.

Table 2 – Average coordination of metal complexes ($\bar{n}$) and average coordination number of electroactive complex ($\bar{k}$) in electrolytes containing different amino acids

$C(H_xL)$, mol/l	HGly		HAla	
	$\bar{n}$	$\bar{k}$	$\bar{n}$	$\bar{k}$
0.02	0.16	0.17	0.16	0.13
0.04	0.30	0.38	0.33	0.38
0.08	0.54	0.56	0.66	0.72
0.10	0.64	0.74	0.82	0.88
0.20	0.99	0.98	1.42	1.32
0.50	1.47	1.44	1.81	1.85
	HSer		H_2Asp	
0.02	0.20	0.16	0.25	0.12
0.04	0.39	0.46	0.49	0.49
0.08	0.71	0.81	0.93	0.85
0.10	0.84	0.95	1.09	1.14
0.20	1.30	1.25	1.52	1.42
0.40	1.68	1.68	1.79	1.88
0.60			1.87	1.96

Linear dependency $i_p - v^{0.5}$ (Fig. 3a) indicates that the process can be limited by both diffusion and (or) charge transfer stage. However, observed negative shift of peak potential with increase of scan rate and linear E_p vs. log v dependence (Fig. 3b) clearly point to the slow charge

transfer stage [6]. At the same time, values of the Semerano rate criterion $X_v = (\partial \lg i_p / \partial \lg v)_{C(H_xL)}$ which are 0.5 5 for asparaginic solution and $X_v = 0.36$, 0.38 and 0.39 for electrolytes with glycine, alanine and serine respectively, together with observed $i - w^{0.5}$ allow us to conclude that the process under investigation proceeds under mixed kinetics conditions [6-8].

Values of Semerano concentration criterion $X_C = (\partial \lg i_p / \partial \lg C(H_xL))_v < 1$ (-0.09, -0.23, -0.26 and -0.26 for the solutions with glycine, alanine, serine and asparaginic acid respectively) that indicates complication of the process by adsorption of reacting species. The presence of adsorption stage is also supported by sharp increase of $i_p / C(H_xL)$ parameter at low amino acid concentration.

Thus, on the basis of above analysis it can be assumed that the nickel ion electroreduction process from investigated solutions is irreversible, occurs under mixed kinetics conditions with dominant control by charge-transfer stage and is complicated by the adsorption stage.

3.3 Nature of the electroactive complex

Equilibrium composition of electrolytes under consideration is rather difficult. For all amino acids studied, nickel ions form complexes of different composition and stability. In aqueous solutions, besides $[Ni(H_2O)_6]^{2+}$ aquacomplexes, the species with amino acid anions also present, namely: $[NiL]^+$, $[NiL_2]^0$, $[NiL_3]^-$ for electrolytes with glycine, alanine, serine and $[NiL]^0$, $[NiL_2]^{2-}$ for asparaginic solution. All complexes are chelate, and coordination of ligands occurs via one carboxylic group and amino group [8, 9].

Equilibrium composition of solutions studied can be characterized by the Bjerrum function. It corresponds to average coordination number of metal complexes into solution:

$$\bar{n} = \frac{[L^{x-}] \cdot \partial \Phi(L) / \partial [L^{x-}]}{\Phi(L)}, \qquad (3.1)$$

where $\Phi(L) = 1 + \sum_m m \cdot \beta_m [L^{x-}]^m$ – complexation function; $m = 1, 2, 3$. The Bjerrum function values for different concentrations of studied acids are presented in Table 2.
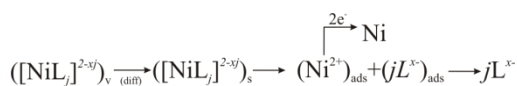
Complexity of ionic composition of solutions under consideration gives rise to a question on the nature of electroactive complex. Following versions are possible:
- all the species present in solution are discharged simultaneously;
- only a single definite type of complexes is discharged, whereas the other types are transformed into these complexes as a result of their pre-dissociation.

To elucidate the nature of the discharged species, we used the approach introduced by authors [10]. It is based on calculation of average coordination number of electroactive complex $_c$ from experimental dependences of steady-state potential and current density at a constant overvoltage $i_{(-)}$ on the ligand concentration by equation:

$$\bar{k} = \frac{\partial \ln i_{(-)}}{\partial \ln[L^{x-}]} + \frac{\partial \ln \Phi}{\partial \ln[L^{x-}]} + \frac{\alpha n_\alpha F}{RT} \cdot \frac{\partial E_{st}}{\partial \ln[L^{x-}]} \quad (3.2)$$

Then, derived dependences $\bar{k} = f(C_{L^{x-}})$ were compared with $\bar{n} = f(C_{L^{x-}})$ obtained by equation (3.1). Parameter $\bar{k}$ values are listed in Table 2. It can be seen that $\bar{k}$ and $\bar{n}$ values are in good agreement. This fact allows us to conclude that all complexes existing in the solution bulk and in near-cathode layer are electroactive. On the basis of above analysis, the scheme of nickel electrodeposition from solutions with glycine, alanine, serine and asparaginic acid can be suggested:

$$([NiL_j]^{2-xj})_v \xrightarrow[\text{(diff)}]{} ([NiL_j]^{2-xj})_s \longrightarrow (Ni^{2+})_{ads} + (jL^{x-})_{ads} \xrightarrow{2e^-, Ni} jL^{x-}$$

3.4 Kinetic parameters of nickel deposition process

In terms of experimental dependences of voltammogram parameters on the potential scan rate the kinetic characteristics of nickel deposition process were calculated such as charge transfer coefficient αn_α and heterogeneous rate constant of charge transfer k_s by equations [6, 7]:

$$\alpha n_\alpha = -\frac{2.3RT}{F(\partial E_p / \partial \lg v)}, \quad (3.3)$$

and

$$k_s = \frac{4.405 i_p}{nFC_{Ni} \exp\left[-\frac{\alpha n_\alpha F}{RT}\left(E_p - E_{st}\right)\right]}. \quad (3.4)$$

It was found that an_a coefficient is equal to 0.12, 0.22, 0.28 and 0.59 for electrolytes with alanine, glycine, serine and asparaginic acid respectively. Corresponding k_s values are $1.1 \cdot 10^{-5}$, $3.5 \cdot 10^{-7}$, $1.6 \cdot 10^{-8}$, $1.7 \cdot 10^{-12}$, $1.1 \cdot 10^{-5}$ cm/s. It appears that with increasing of complex stability the charge transfer coefficient increases and the heterogeneous rate constant of charge transfer decreases.

4. CONCLUSION

In this work the correlation between the nickel electrodeposition rate from solutions containing glycine, alanine, serine and asparaginic acid and the compactness of amino acid molecules was established. The contribution of hydrogen evolution reaction into total process rate of metal deposition was detected by partial curves of nickel deposition. It was found that the hydrogen evolution reaction for electrolytes with HGly, HAla and HSer at peak region of voltammetric curves makes up approximately 10%, while it exceeds 40% for asparaginic solution. Possible scheme of nickel ion electrodeposition mechanism from solutions with amino acid studied was suggested. According to this scheme, nickel deposition process occurs irreversibly under mixed kinetics conditions with dominant control by charge transfer and is complicated by adsorption. All the complexes present in the baths are electroactive and reduce simultaneously. Charge transfer coefficient and the heterogeneous rate constant of charge transfer are calculated. The correlation of their values with increasing species stability presented in the solutions is brought out.

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