

UDC 544.65

DOI: 10.15372/CSD20170606

Electrochemical Processes in Nanostructured Systems Based on Nickel and Cadmium

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(Received October 01, 2017)

Abstract

Regularities of electrodeposition and electrooxidation of nanostructured mono- and bimetallic systems based on nickel and cadmium were examined in sulphate and ammonia buffer electrolytes when using the inert glassy carbon substrate for deposition. Nanometallic precipitates with complex phase composition were formed, as shown by means of anodic voltammetry. Their electrooxidation was accompanied by generating a series of peaks in voltammetric curves. Conditions of electrochemical synthesis of nanostructured electrolytic systems based on nickel and cadmium were determined.

Keywords: binary systems, nickel, cadmium, voltammetry, electrodeposition, anodic oxidation

INTRODUCTION

The interest towards electrochemistry of nanoscale bimetal systems is driven by the following factors. In the first place, electrochemical methods are efficient during the preparation of such systems, as a variation of potential, current, and electrolyte composition allows managing relative rates of metal deposition and accordingly forming electrodeposits of various compositions and structural types [1]. Secondly, electrochemical methods of analysis, in particular, voltammetry allow determining both elemental and phase compositions of nanoobjects and are able to compete in this respect with the known methods for exploring material structure. Lately, research relevance in the area of preparation

and analysis of bimetallic nanostructured systems based on iron subgroup transition metals, in particular, the nickel–cadmium system, has been increasing. Two-component transition metal systems show distinct magnetic and catalytic properties, while nanostructured materials of this class are considered among the most promising ones for practical use.

An electrochemical method for preparation of nanostructured bimetal systems has a number of advantages over other synthesis methods. However, complex multicomponent precipitates that, in addition to separate elements, may contain their interaction products, such as solid solutions and intermetallic compounds may form during electrochemical deposition of several metals on the electrode surface. The study of phase composition peculiarities of such

systems and opportunities of regulating their properties during variation of synthesis conditions is necessary to be carried out in situ mode *via* a method capable of detecting the phases under study at the level of nano-gram amounts [1]. One of the most facile and informative methods of analysis of nanoscale materials, including thin metal films, is voltammetry using solid inert electrodes.

The Ni–Cd system considered as a model is the subject of fundamental research related to clarifying formation mechanisms of nanoscale intermetallic phases during chemical and electrochemical synthesis and their stability [2–4].

Earlier, acid electrolytes containing boric acid and citrate ions [4, 5] were used during studying processes of deposition and anodic oxidation of a nickel and cadmium binary system. A very complex composition of deposition medium complicates the interpretation of the results acquired by electrochemical methods, as nickel oxidation peaks have an irregular shape varying with an increase in concentration and requires electrolyte replacement before anodic dissolution. To exclude the indicated problems, the search for the optimum compositions of electrolytes that allow efficiently carrying out electrochemical processes is required.

The goal of the present work is to study processes of electrochemical formation and anodic oxidation of nanostructured Ni–Cd precipitates in sulphate and ammonia buffer electrolytes by means of anodic voltammetry.

EXPERIMENTAL

Electrochemical studies were carried out using a PU-1 universal polarograph and a Versastat 3 potentiostat/galvanostat in the three-electrode cell with working and auxiliary glassy carbon electrodes, and a silver chloride reference electrode in a 0.1 M KCl solution that

was placed in a separate cell. Potentiostatic deposition of binary nanometallic systems was performed at a potential of -1.6 V under constant stirring conditions. Compositions of background electrolytes were as follows: 0.1 M NH_4Cl + 0.1 M NH_4OH (pH 9.8), and sulphate – 0.1 M Na_2SO_4 + H_2SO_4 (pH 1.5, 2.1, and 3.0). Cadmium and nickel ions were introduced into electrolytes as sulphuric acid salts. Extra pure bidistilled water and chemically pure reagents were used to prepare solutions. The study of oxidation processes of the resulting precipitates was carried out by means of anodic stripping voltammetry with a linear potential sweep ($v = 100$ mV/s). Measuring the pH of solutions was performed using an Ecotest 2000 pH meter/ionomer.

RESULTS AND DISCUSSION

Electrodeposition of monometallic nickel and cadmium phases

The main factor affecting the electrochemical behaviour of metals is the type of the background electrolyte. To carry out electrolytic deposition followed by voltammetric analysis of precipitates of binary systems, it is necessary to determine conditions for forming analytical signals (present in the precipitation of phases, primarily), phases of single metals. The greatest number of difficulties arise when selecting electrolyte pH value for nickel deposition, as this metal catalyses hydrogen evolution process. Therefore, local medium alkalization occurs and a passivation layer of nickel hydroxide is formed on the electrode surface [6, 7]. Thus, the electrodeposition process in sulphate electrolyte with the pH of 3 is complicated because of the reasons indicated and it is impossible to register the anodic peak of nickel. Sulphate electrolyte with lower pH values should be used

TABLE 1

Parameters of the peaks of nickel and cadmium oxidation in various electrolytes

Background electrolyte	Peak potential, mV		Equation based on $I_p = f(c_{Me})$	
	Nickel	Cadmium	Nickel	Cadmium
0.1 M Na_2SO_4 + H_2SO_4 , pH 1.5	-110	-720	$I = 6.3 \cdot 10^3 c$	$I = 1.0 \cdot 10^6 c$
0.1 M Na_2SO_4 + H_2SO_4 , pH 2.1	-110	-720	$I = 6.5 \cdot 10^3 c$	$I = 1.1 \cdot 10^6 c$
0.1 M NH_4Cl + 0.1 M NH_4OH , pH 9.8	-420	-820	$I = 8.0 \cdot 10^5 c$	$I = 1.2 \cdot 10^6 c$

to avoid these phenomena, as established. The electrodeposition process at the pH of 2.1 and 1.5 proceeds efficiently; nickel oxidation peak near potential of -110 mV linearly increases with the nickel ion concentration in a solution (Table 1). In both cases, there is the linear dependence of current strength on the concentration. According to the anodic voltammetry data, nickel electrodeposition in ammonia buffer electrolyte proceeds with a much higher rate (c.a. by two orders of magnitude); metal phase oxidation peak substantially shifts to the negative potential region, which attests to the involvement of ammonia complexes of nickel in the electrode process.

The analytical signal of cadmium in ammonia and sulphate electrolytes is presented by a narrow peak in the range of more negative potentials relative to the nickel peak. The amount of metal precipitate on the electrode surface is linearly related to the cadmium ion concentration. It is worth noting that cadmium electrodeposition rate almost does not depend on electrolyte nature. During the transition from the sulphate medium to the ammonia one, oxidation peak potential drops by only 100 mV (see Table 1) because of the fact that the stability constant of cadmium ammonia species is lower by four orders of magnitude than that of nickel complexes.

The concentration limits of the preservation of the linear dependencies ($I_p = f(c_{Me})$) for cadmium ions in sulphate and ammonium buffer electrolytes are $(0.2-50) \cdot 10^{-5}$ and $(0.8-20) \cdot 10^{-5}$ mol/L, for nickel ions – $(1.3-14) \cdot 10^{-4}$ and $(1.2-16) \cdot 10^{-5}$ mol/L, respectively. Therefore, nanostructured electrolytic nickel and cadmium precipitates, and also a binary system can be obtained using both electrolytes considering the differences in deposition rates of these metals.

Electrodeposition of the cadmium–nickel binary system

To assess the effect of deposition sequence on the electrochemical behaviour of the binary cadmium–nickel system, the experiments were performed in two options of the introduction of metal ions into the analyzed system: Cd→Ni and Ni→Cd.

Sulphate electrolyte

In the first option (Cd→Ni), the cadmium electrodeposition was carried out on the electrode surface and cadmium anodic oxidation curve was registered. There are a decrease of the cadmium peak (Fig. 1) and the formation and growth of two additional peaks (-500 and -310 mV) with increasing nickel ion content. The nickel peak becomes apparent at a potential of -110 mV beginning with a concentration of 0.2 mmol/L (Fig. 2). According to the phase diagram for the cadmium–nickel system [8], with joint deposition of these metals, the formation of intermetallic compounds with the composition of Cd_5Ni and $CdNi$ is probable, therefore, additional peaks most likely refer to oxidation of cadmium from alloy that includes the structural elements indicated and is generated on the electrode surface.

It is noteworthy that currents of additional peaks in this option almost do not depend on the nickel ion concentration. A similar picture was observed with a two-fold increase in the initial concentration of nickel ions.

With a change in metal deposition order (Ni→Cd option), the addition of cadmium ions to a solution does not lead to a change in parameters of the analytical signal of nickel. There are the cadmium peak and two additional ones in the same region of potentials at voltammetric curves, as in previous deposition option; in other words, phase composition of the precipitate generated on the electrode surface

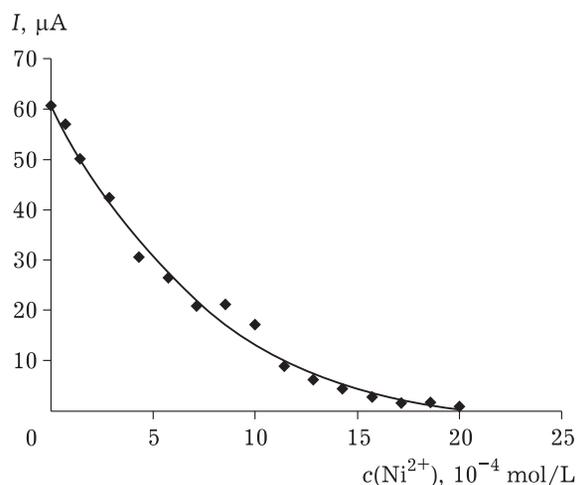


Fig. 1. Cadmium peak current versus nickel ion concentration in a 0.1 M Na_2SO_4 solution (pH 1.5), with $c(Cd^{2+}) = 4 \cdot 10^{-5}$ mol/L.

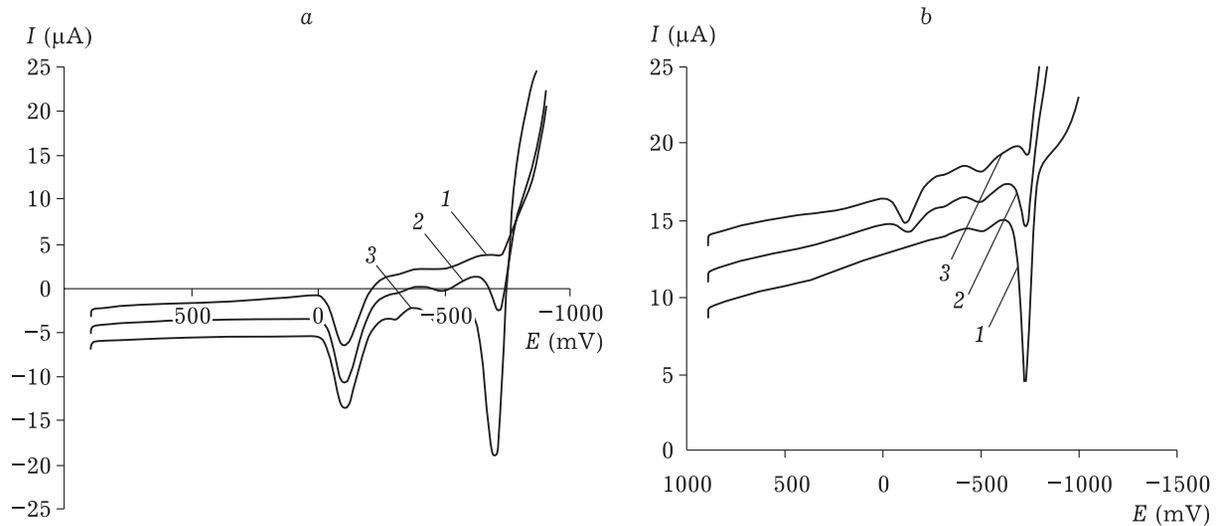


Fig. 2. Voltammetric oxidation curves of the Cd–Ni binary system in 0.1 M Na_2SO_4 (pH 1.5) Ni→Cd option (a) ($c(\text{Ni}^{2+}) = 1.5 \cdot 10^{-3}$ mol/L and $c(\text{Cd}^{2+}) = 10^{-5}$ mol/L: 2 (1), 4 (2), 7 (3)); Cd→Ni (b) $c(\text{Cd}^{2+}) = 2 \cdot 10^{-5}$ mol/L and $c(\text{Ni}^{2+}) = 10^{-4}$ mol/L: 0.7 (1), 2.5 (2), 5 (3)

remains the same. The experiment was carried out with two initial concentrations of nickel ions in a solution. Unlike the Cd→Ni option, the currents of additional peaks corresponding to binary phases linearly increase with an increase in the cadmium ion concentration in a solution. Table 2 gives the main parameters of peaks with different nickel concentrations. It can be seen that during the introduction of nickel ions, the cadmium peak is shifted to the positive range of potentials, which points to the formation of the binary phase on the basis of cadmium with variable composition. In addition, the dependence, *i.e.* the current of the cadmium peak versus cadmium ion concentration substantially deviates from straightforward (see Table 2). This is typical for the peak of a more active component and is related to the fact that more thermodynamically favourable binary phases are initially generated in the electrode surface, and only later, cadmium phases.

Thus, a deposition order does not affect the qualitative picture of anodic oxidation. However, to study the nature of additional peaks corresponding to the cadmium–nickel alloy, it is advisable to select the Ni→Cd option, where reproducible signals of two metallic phases generated on the electrode surface may be registered and there may be logical changes in their values.

Ammonia buffer electrolyte

Electrodeposition of binary precipitates was also carried out in two options of the preliminary introduction of components. Unlike sulphate electrolyte, the total picture of anodic oxidation into an ammonia buffer solution is much more complex. Apart from phase peaks of metals, there is a series of overlapping additional peaks, which argues in favour of the formation of four binary phases, different by composition (Fig. 3). Herewith, only one of them has the constant composition in the region that is richer in nickel ($E_p = -460$ mV). This may be a phase of a solid solution of Ni_xCd_y , where the

TABLE 2

Parameters of the cadmium peak (I_{Cd}) and of additional peaks (I) in anodic voltammetric curves of Ni→Cd system versus nickel ions concentration

$c(\text{Ni}^{2+}), 10^{-3}$ mol/L	Equation	E_p , mV
0	$I_{\text{Cd}} = 1.0 \cdot 10^6 c$	-720
1.5	$I_{\text{Cd}} = 4.59 \cdot 10^5 c - 14$	-705
	$I = 5.11 \cdot 10^4 c - 1.7$	-490
	$I = 2.58 \cdot 10^4 c - 0.4$	-310
5.7	$I_{\text{Cd}} = 5.76 \cdot 10^5 c - 25$	-690
	$I = 4.12 \cdot 10^4 c - 0.7$	-490
	$I = 2.58 \cdot 10^4 c - 0.1$	-310

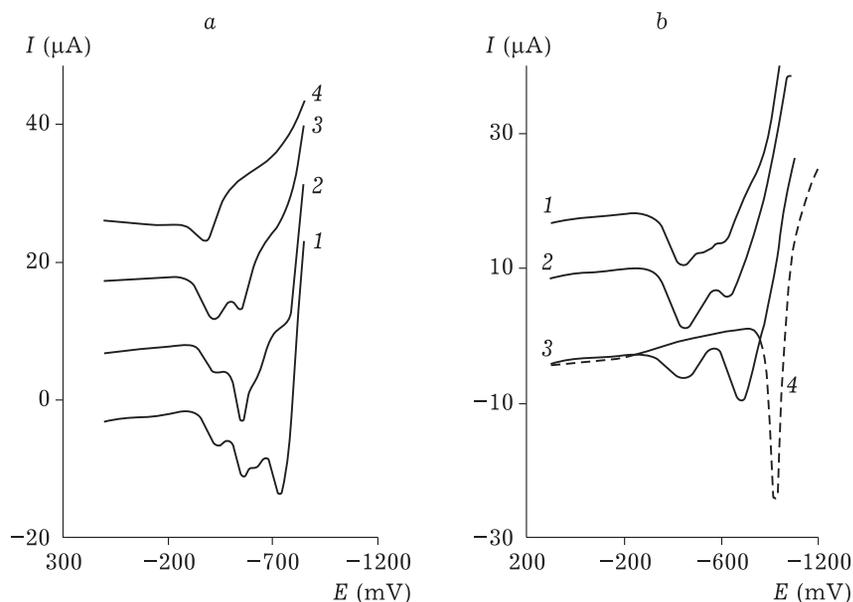


Fig. 3. Voltammetric oxidation curves of cadmium–nickel electrolytic precipitation in a solution of $0.1\text{MNH}_4\text{Cl} + \text{NH}_4\text{OH}$ in precipitation options: Ni→Cd (a) and Cd→Ni (b), $c_{\text{in}}(\text{Ni}^{2+}) = 5 \cdot 10^{-5} \text{ mol/L}$. The ratio of metal ion concentrations Ni/Cd in electrolytes for each curve: a – 1:1 (1), 3:2 (2), 5:1 (3), Ni (4); b – 3:1 (1), 1:1 (2), 1:2 (3), Cd (4).

maximum value of y does not exceed 7 mol. % proceeding from the data of powdery systems of similar compositions [2, 3]. In some cases, it is possible to observe stabilization of a peak near -620 mV , however, only in a comparatively small range of ratios of nickel and cadmium ion concentrations. The potential of other peaks is changed with $c(\text{Cd}^{2+})/c(\text{Ni})$ ratio variation (Table 3).

The cadmium phase disappears from the electrode surface even with very low nickel ion contents in an electrolyser, *i.e.* the mutual effect

of binary system components is expressed to a larger degree in ammonia electrolyte than in sulphate one. As can be seen from the data of Fig. 3, the component introduction sequence has a substantial effect on electrodeposition results, and precisely, on qualitative and quantitative phase compositions of the precipitate. Table 3 gives the oxidation peak parameters of the binary nickel–cadmium system.

Anodic peaks in the voltammetric curve are substantially overlapped, therefore, measuring the maximum current strength was not carried

TABLE 3

Potentials of additional oxidation peaks for cadmium–nickel electrolytic system in ammonium buffer electrolyte (for Ni with $c(\text{Ni}^{2+}) = 5 \cdot 10^{-5} \text{ mol/L}$, $I = 8.8 \text{ } \mu\text{A}$, $E = -373 \text{ mV}$)

$c(\text{Cd}^{2+}), 10^{-5} \text{ mol/L}$	$E_1, \text{ mV}$	$E_2, \text{ mV}$	$E_3, \text{ mV}$	$E_4, \text{ mV}$
1	-420	–	–	–
2	-426	-545	–	–
3	-430	-550	–	–
5	-440	-555	-620	-730
7	-450	-560	-620	-720
8	-440	–	–	-700
9	-450	–	–	-690

Note: dash means the peak absence.

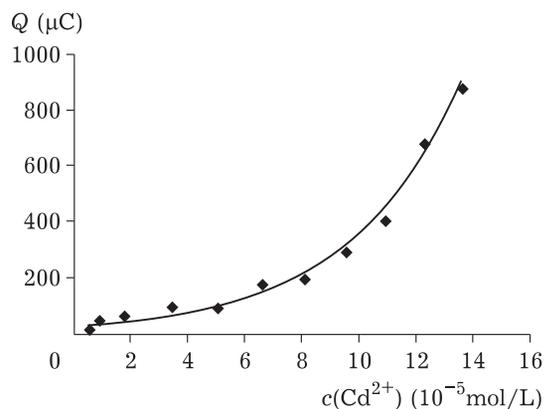


Fig. 4. Total area under oxidation peaks of the Cd–Ni binary system versus cadmium ion concentration in ammonia buffer electrolyte, $c(\text{Ni}^{2+}) = 2.5 \cdot 10^{-5}$ mol/L.

out for each of them. The measurement of the total area under all peaks is most correct in this case. Figure 4 gives the corresponding dependence for the Ni→Cd option. It can be seen that binary precipitate accumulation proceeds nonlinearly.

The observed dependence type may be explained by a change in precipitate growth direction from two-dimensional to three-dimensional with the appearance of excessive amounts of cadmium in the surface. However, even in this case, it is impossible to register the oxidation peak of a single phase of cadmium.

CONCLUSION

It has been found that from two to four binary phases with different compositions are generated during co-electrodeposition of cadmium and nickel depending on electrolyte types and metal ion concentration ratio. The order of introduction of components into an electrolyser and the nature of the background electrolyte have a significant impact on electrodeposition results, which was previously noted in studying a number of other binary systems. The carried out experiments allow recommending sulphate and ammonia buffer electrolytes for electrolytic preparation of nanostructured cadmium–nickel systems in potentiostatic mode.

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