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Porous Nickel Deposits Formed in the Oxidation of Alcohols in an Alkaline Medium

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Abstract—Highly porous nickel matrices with varied content of nickel were formed on a glassy graphite electrode by the electrochemical deposition method. The nickel deposits were studied by pulsed chronoamperometry, impedance spectroscopy, and cyclic voltammetry on a rotating disk electrode in a 1 M KOH solution and in alkaline solutions containing methanol or ethanol. The process in which a hydroxide film is formed on the nickel surface in an alkaline solution and the influence exerted by this process on the catalytic oxidation of alcohols on nickel in an alkaline medium are discussed.

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At present, there is a considerable interest in application of nickel-based electrodes for electro-oxidation of small organic molecules. The oxidation mechanism of some organic compounds on a nickel anode in alkaline solutions was considered in [1, 2], and the catalytic activity of nickel in the reactions of methanol and ethanol oxidation in an alkaline medium, in [3–5]. The oxidation of methanol was studied on nickel electrodes modified with nickel complexes, on nickel oxides [7–9], and also on nickel alloys [10–16]. The catalytic oxidation of ethanol in alkaline solutions was examined on nickel nanoparticles supported by substrates made of various materials [17, 18].

As follows from the published evidence, an important role is played in the electrocatalytic activity of nickel-containing electrodes by the redox pair Ni(OH)₂/NiOOH. However, the oxidation mechanisms of alcohols vary between reports by different authors. Therefore, of interest is a more detailed study of the process of recharging of nickel oxides on the electrode surface in alkaline solutions and of its influence on the catalytic oxidation of alcohols.

EXPERIMENTAL

We prepared working solutions and made

electrochemical measurements by the procedures previously described in detail in [19, 20]. All the reagents used in the study were thoroughly purified and solutions were prepared with twice-distilled water. The cell and vessels used in the experiments were also washed with twice-distilled water.

The study was carried out in a hermetically sealed three-electrode glass cell having separate cathode and anode spaces, with an inert gas (argon) bubbled through the solution. An installation with a rotating disk electrode was used. The working disk electrode had the form of a glassy-carbon (GC) rod embedded in Teflon, with a disk surface area of 0.07 cm², on which a porous nickel layer was electrochemically deposited. Prior to deposition of nickel, the glassy-carbon electrodes were polished to mirror shine with fine emery paper and then thoroughly washed with twice-distilled water. Porous nickel was deposited onto the glassy-carbon electrode by the procedure suggested in [21] from a 0.2 M NiCl₂ + 2 M NH₄Cl solution with pH 3.6 in the galvanostatic mode during a certain time. It was found [21] that, owing to the joint discharge of ammonium ions as proton donors, highly porous metallic nickel matrices are formed under these electrodeposition conditions, with a large roughness factor and good mechanical strength. Using the data of [21], obtained when determining the

fraction of the current consumed by the nickel deposition process under these conditions, we estimated the amount of deposited nickel. It was found to be 1.3, 2.6, 4.4, 5.2, and 13 mg cm⁻², depending on the current density and deposition duration.

As auxiliary electrode served a glass-sealed platinum wire. The role of the reference was played by a calomel electrode in a saturated KCl solution (SCE). All the working-electrode potentials are given in the study relative to this reference electrode. The study was carried out at room temperature (18 ± 2°C). Before measurements, the solution under study was saturated with argon in the course of 0.5 h to remove molecular oxygen. When current–voltage curves were recorded, argon was passed over the solution under study. Electrochemical measurements were made with an Autolab PGSTAT 12 automated electrochemical complex (Eco Chemie, The Netherlands) interfaced with a personal computer.

The electrochemical impedance spectroscopy (EIS), in which the impedance of an electrochemical system is measured under ac voltage conditions, is a powerful method for a study of the electrical properties of substances and phase boundaries at the electrode surface. For all the fabricated nickel electrodes, we obtained electrochemical impedance spectra in a wide range of frequencies (0.1–10 000 Hz) with an amplitude of 0.01 Hz at various electrode potentials. Prior to impedance measurements, the electrode was polarized during a long time (500 s) at an appropriate potential until a steady-state current was reached. The electrodes with various amounts of deposited nickel were studied in an alkaline solution. Cyclic voltammetric (CVA) curves were recorded in a 1 M KOH solution in a wide range of potentials at various potential sweep rates.

As noted previously [19, 20], anodic and cathodic peaks are observed on the nickel electrode in an alkaline solution at potentials higher than 0.35 V. These peaks correspond to the process of nickel hydroxide recharging on the electrode, which can be described by the equation [1, 2]:



With increasing potential sweep rate, the currents of the recharging peaks grow. We plotted dependences of the currents I_p of the anodic and cathodic peaks on the potential sweep rate V , which were straight lines with

slope ratios of about 0.7–0.8 in the $\ln I_p$ – $\ln V$ coordinates.

We examined the reproducibility of the nickel hydroxide recharging curves on nickel electrodes operating during several days. The corresponding data are presented in Fig. 1. The arrows show the direction in which the potential changes. It can be seen that the height and position of the anodic and cathodic recharging peaks vary with time on the same electrode. All the curves have a single anodic recharging peak, which shifts toward positive potentials in the course of time. A bifurcation of the cathodic recharging peak is observed, with the cathodic peak lying at more negative potentials being more strongly pronounced on freshly deposited electrodes. This peak gradually decreases and is transformed to the peak at more positive potentials. This variation of the cathodic recharging peak can be attributed to the presence of two nickel hydroxide phases, α -Ni(OH)₂ and β -Ni(OH)₂ [7], on the nickel surface and to the transformation of nickel hydroxide from phase α to phase β in the course of time. Similar curves were obtained on electrodes with various nickel contents, which may indicate that the recharging process of nickel hydroxides occurs in a thin surface layer, rather than throughout the deposit volume.

The catalytic activity of all the porous nickel electrodes we obtained was studied in the reaction of ethanol and methanol oxidation in an alkaline medium. The cyclic voltammetric curves were recorded at various potential sweep rates in a wide range of potentials. Figure 2 shows as an example the CVA curves obtained on the nickel electrode at a potential sweep rate of 0.05 V s⁻¹ in an alkaline solution with addition of 1 M of ethanol. The data obtained in alkaline alcoholic solutions fully agree with those published previously [19, 20]. The oxidation of the alcohols is only observed on the nickel electrode on the oxidized nickel surface, in agreement with published data [3, 13]. The potentials of the oxidation peaks of the alcohols in forward (anodic) and reverse (cathodic) potential sweeps coincide. The voltammetric curves corresponding to the anodic potential sweep show a superposition of two processes, recharging of nickel and oxidation of ethanol (methanol). The curves obtained in a cathodic potential sweep clearly demonstrate, after the anodic peak corresponding to the alcohol oxidation, the cathodic peak of nickel recharging. The currents of the alcohol oxidation peaks grow with increasing potential sweep rate. In the process, the nickel recharging peaks also

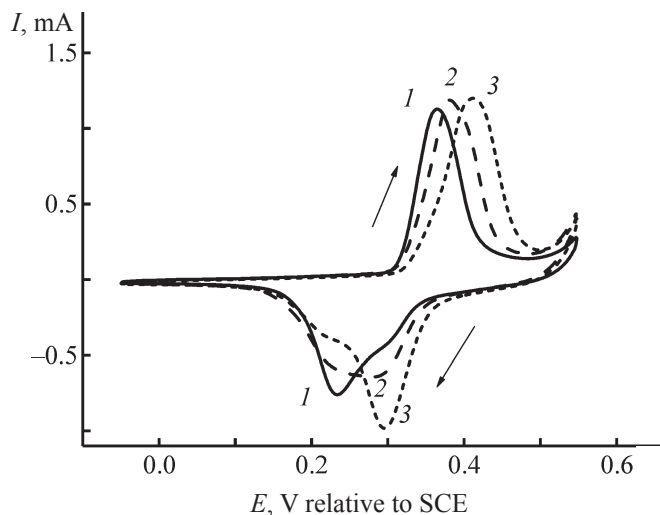


Fig. 1. Cyclic voltammetric curves obtained in a 1 M KOH solution at a potential sweep rate of 0.05 V s^{-1} on a nickel electrode deposited at a current density of 0.1 A cm^{-2} in the course of 100 s, with the electrode operating for several days. (*I*) Current and (*E*) potential; the same for Figs. 2 and 5. (*I*) On the day of nickel deposition, (*2*) in 5 days, and (*3*) in 7 days.

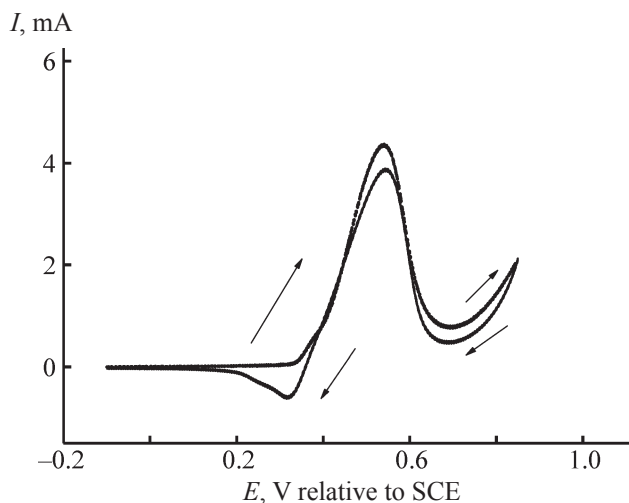


Fig. 2. Cyclic voltammetric curves obtained on a porous nickel electrode in a 1 M KOH solution with addition of 1 M of ethanol at a potential sweep rate of 0.05 V s^{-1} .

become higher. The dependences of the peak currents on the potential sweep rate are linear in the $\ln I_p - \ln V$ coordinates. The slope ratios of these dependences for the recharging process of nickel hydroxides were 0.7–0.8. The same parameters for the processes of methanol and ethanol oxidation were substantially smaller (~ 0.2 – 0.3).

Porous nickel electrodes were studied by pulsed chronoamperometry. In doing so, we applied a pulse of a potential in the range from -0.8 V (the value at which no Faraday processes occur at the nickel electrode according to the preliminarily measured CVA curves) to $-0.4, 0.0, +0.4, +0.5,$ and $+0.6 \text{ V}$ and the variation of the current with time was recorded. Figure 3 shows the $I-\tau$ curves obtained in a 1 M KOH solution (Fig. 3a) and in an alkaline solution with addition of 1 M of ethanol (Fig. 3b). It can be seen that, at potentials in the range in which no Faraday processes occur at the nickel electrode, a sharp fall of the current is observed when the potential instantaneously changes upon an abrupt change in the current, which corresponds to charging of the electric double layer. At the potentials corresponding to the nickel hydroxide recharging (Fig. 3a) or to the alcohol oxidation (Fig. 3b), delays appear in the $I-\tau$ curve, during which the current grows as the positive pulsed potential becomes higher.

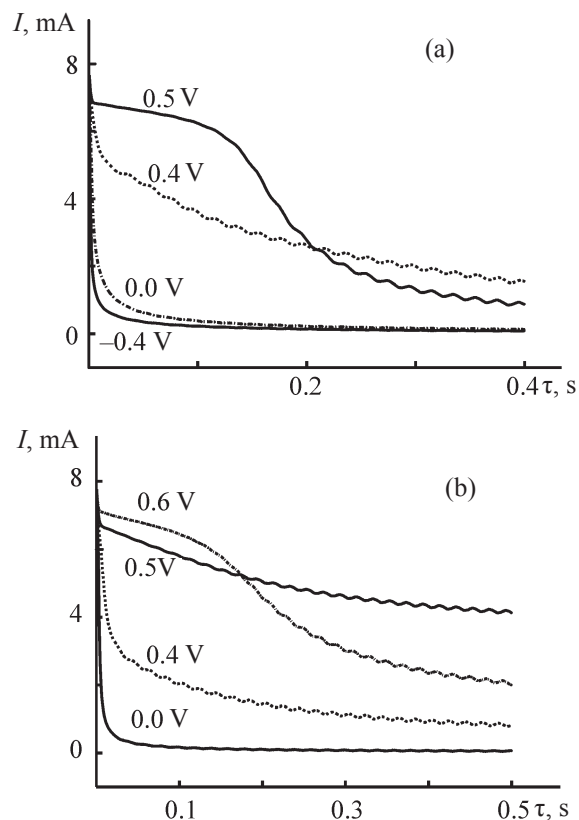


Fig. 3. Chronoamperograms obtained on a nickel electrode in solutions of (a) 1 M KOH and (b) 1 M KOH + 1 M ethanol, with the potential changed in the pulsed mode from -0.8 V to various values. (*I*) Current and (τ) time.

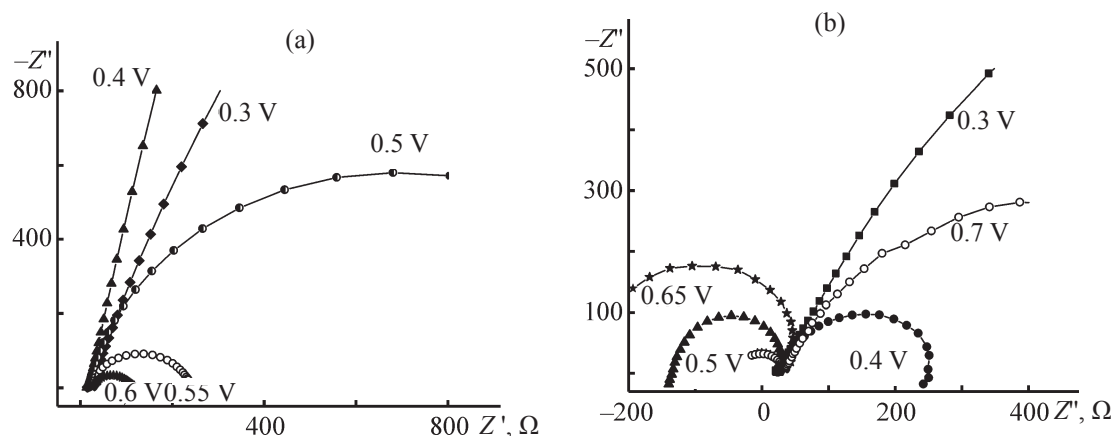


Fig. 4. Nyquist diagrams obtained on a Ni electrode at various potentials in (a) 1 M KOH alkaline solution and (b) alkaline solution with addition of 1 M of ethanol. (Z' , Z'') Real and imaginary components of the impedance.

Electrochemical impedance spectra were obtained on all the nickel electrodes in alkaline 1 M KOH solutions and alkaline solutions of the alcohols. Figure 4 shows Nyquist diagrams obtained on a Ni electrode at various potentials in a 1 M KOH solution (Fig. 4a) and in an alkaline solution with addition of 1 M of ethanol (Fig. 4b).

It is noteworthy that the run of the Nyquist diagrams varies with the electrode potential and solution composition. In all of the solutions studied, the Nyquist diagrams obtained on nickel electrodes at the potentials at which no Faraday processes are observed in the CVA curves ($-0.4...+0.3$ V) are linear. At more positive potentials, semi-circles corresponding to the occurrence of a charge-transfer process at the electrode appear in the Nyquist diagrams. In addition, negative values of the real component of the impedance are observed in alcohol solutions at potentials corresponding to the descending branch of alcohol oxidation in the CVA curve. At even more positive potentials, when a next Faraday process starts to occur at the electrode, semi-circles are again observed in the Nyquist diagrams.

When obtaining the electrochemical impedance spectra, we preliminarily polarized the electrodes during 500 s at a required potential until a steady-state current was attained. We plotted dependences of the steady-state currents on the potentials at which these currents were attained. Figure 5 shows dependences of this kind, obtained on a nickel electrode in a 1 M KOH solution (Fig. 5a) and in a solution of 1 M KOH + 1 M ethanol (Fig. 5b).

It can be seen in Fig. 5 that the steady-state currents

are extremely low at potentials in the range in which there are no Faraday processes at the nickel electrode. At potentials of nickel recharging and alcohol oxidation, the steady-state currents sharply grow. In this case, the steady-state currents in alcohol-containing solutions pass through a maximum.

Comparison of the dependences in Figs. 4 and 5 shows that an increase in the steady-state currents is observed at positive potentials in a 1 M KOH solution (Fig. 5a), which is correlated with the appearance of semi-circles in the Nyquist diagrams (Fig. 4a). The steady-state currents in alcohol-containing solutions pass through a maximum with increasing positive value of the potential (Fig. 5b). The decrease in the steady currents is accompanied by the appearance of negative values of the real component of the impedance in the Nyquist diagrams (Fig. 4b). At the most positive potentials, when the next electrode process starts to occur, the steady-state currents again increase, which is accompanied by the appearance of semi-circle in the Nyquist diagrams.

No influence of the thickness of the nickel deposit on the run of the dependences obtained was observed.

The experimental data obtained on the nickel electrode in the 1 M KOH solutions indicate that the surface layer of nickel hydroxide s changed in the course of electrochemical measurements. In this case, both conversion of nickel hydroxide from one phase into the other [from the α -Ni(OH)₂ phase to the β -Ni(OH)₂ phase] in a cathodic sweep of the potential (Fig. 1) and, presumably, a slow growth of the nickel hydroxide layer on the electrode surface are observed. The formation

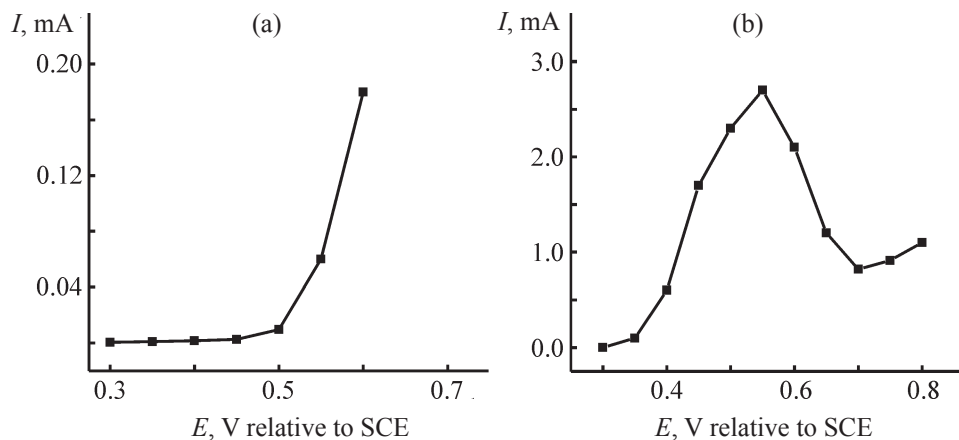


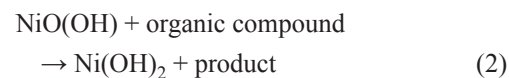
Fig. 5. Dependence of the steady-state current on the potential for a Ni electrode in (a) 1 M KOH alkaline solution and (b) 1 M KOH alkaline solution + 1 M ethanol.

of a bulk layer of nickel hydroxide is evidenced by the slope ratios of the linear dependences in the coordinates $\ln I_p - \ln V$ (0.7–0.8), found from CVA curves for peaks of nickel recharging in a 1 M KOH solution. For example, according to Laviron [22], a directly proportional dependence of the peak current on the potential sweep rate must be observed for charge-transfer processes in the adsorbed state. If the process occurs with diffusion hindrance, the slope ratio of the corresponding dependence must be 0.5 [23]. The intermediate value we obtained is in good agreement with the results of the study [12] in which the nickel recharging process in a 1 M KOH solution was studied in an exceedingly wide range of potential sweep rates (0.002–2.0 V s⁻¹). The authors of [12] obtained a dependence of the current of the nickel recharging peaks on the potential sweep rate on the surface of an electrode containing about 65 monolayers of nickel, which had two linear portions with slope ratios of 1.0 at potential sweep rates of 0.002–0.040 V s⁻¹ and 0.5 at higher potential sweep rates.

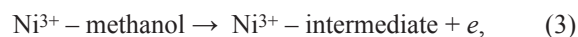
The diffusion hindrance is presumably created in nickel recharging by the nickel hydroxide layer because no diffusion limitations were found for the solution. This was confirmed in [20] by demonstrating on a rotating disk electrode that the recharging peaks are independent of its rotation speed.

A study in alkaline solutions with addition of alcohols demonstrated the following. In full agreement with published data, the cyclic voltammetric curves for oxidation of alcohols on a nickel electrode in alkaline solutions indicate that the oxidation of alcohols occurs on the oxidized surface of the nickel electrode. There

are several approaches in the literature to description of the mechanism by which alcohols are oxidized on nickel. For example, Fleischmann and co-workers [1] suggested a mechanism of alcohol oxidation with simultaneous reduction of Ni(III) to Ni(II), described by the equation

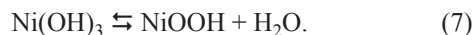


In [12], it was suggested to describe the oxidation of alcohols at more positive potentials in terms of the mechanism of electrochemical oxidation of an alcohol at active areas of the oxidized nickel surface by the reactions



The results obtained in the present study: the coincidence of the potentials of the alcohol oxidation peaks in potential sweep in the anodic and cathodic directions; slope ratios of the dependences of the peak current on the potential sweep rate in the $\ln I_p - \ln V$ coordinates, equal to 0.2–0.3; and the dependence with a maximum of steady-state currents on the potential (Fig. 5b), may indicate that the oxidation of alcohols occurs in their adsorbed state, has no diffusion limitation from the solution, and is controlled by processes occurring in the surface film of nickel hydroxide. The recharging of nickel hydroxide in alkaline solutions may occur via formation of intermediate products in

accordance with the equation



It can be assumed that alcohols are oxidized on the nickel surface via interaction of an alcohol with intermediate compounds in the hydroxide film of nickel in an alkaline solution.

CONCLUSIONS

(1) A nickel hydroxide film slowly grows on the surface of a nickel electrode in an alkaline solution. This film can be regarded as a polymeric film with redox properties.

(2) Oxidation of alcohols on a nickel electrode in alkaline solutions is only observed on the oxidized surface of nickel, in agreement with published data.

(3) The decrease in the steady-state currents of alcohol oxidation is accompanied by the appearance of negative values of the real component of the impedance in Nyquist diagrams.

(4) The oxidation of alcohols may occur via interaction with intermediate compounds in the hydroxide film of nickel in alkaline solutions.

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