by our model calculations is in qualitative agreement with the behavior found in [8] when studying the kinetics of europium ion discharge in the presence of N,N-dimethylformamide.

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IMPEDANCE STUDY OF THE BEHAVIOR OF POLYCRYSTALLINE NICKEL ELECTRODES IN ALKALINE SOLUTIONS

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An examination of the behavior of nickel electrodes in electrolyte solutions is of interest since nickel is widely used in practice (protective coatings, iron–nickel storage batteries, etc.). In a number of its properties the nickel electrode is close to platinum and iron electrodes. Over a rather wide range of potentials (300 to 400 mV) the nickel surface holds an appreciable amount of hydrogen [1-4], a region of ideal polarizability is practically missing, and oxygen compounds with different nickel oxidation states are formed at sufficiently anodic potentials on Ni [3, 8]. The qualitative behavior of hydrogen adsorption and oxide-film formation on Ni was revealed on the basis of data obtained by measurements of the potential decay following cathodic polarization [4], of differential capacitance at individual faces of single crystals and at polycrystalline electrodes [3], and by ellipsometric studies [5]. It was of substantial interest in this connection to examine the effect of additives to the solution upon electrode processes by impedance measurements.

Sheets of spectroscopically pure Ni which had first been annealed in hydrogen served as the electrodes in the experiments. Prior to the measurements the electrodes were polished with glass powders and degreased with alcohol. The idle part of the surface was insulated with polystyrene lacquer in toluene. The working surface area was about 0.1 cm^2. Measurements of the impedance components were performed with an R-5021 impedance bridge hooked up to a P-5827 potentiostat. We used a series equivalent network of capacitance and resistance; the range of ac frequencies was from 90 to 50 000 Hz. The impedance was measured over the potential range from −1.4 to +0.5 V (relative to a mercury–mercuric oxide electrode in the

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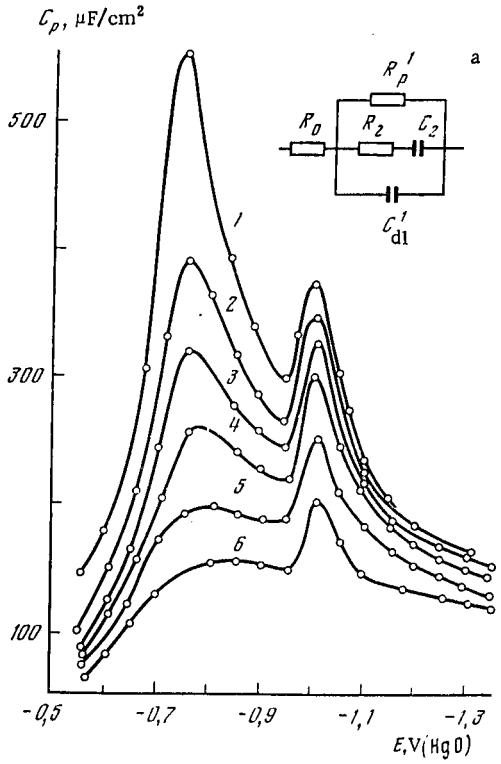

Fig. 1. C_p vs. E curves of the nickel electrode in 1 N KOH solution at different ac frequencies: 1) 90, 2) 210, 3) 410, 4) 800, 5) 2000, and 6) 5000 Hz; a) the equivalent network simulating electrode impedance.

same solution). The values of the impedance components refer to apparent surface area of the electrode. The solutions were carefully purified prior to the measurements.

Figure 1 shows the differential capacitance (recalculated while allowing for solution resistance to the parallel equivalent) as a function of potential in 1 N KOH solution. According to literature data [3], the maximum found at E = −1.0 V corresponds to the formation and elimination of adsorbed hydrogen following the scheme of

$$H_{ads} + OH^- - e = H_2O. \quad (1)$$

The maximum at −0.75 V is associated with the oxidation of Ni to the divalent state:

$$Ni + 2\,OH^- - 2e = Ni(OH)_2. \quad (2)$$

The region of the passive state follows at potentials more anodic than this peak. The ohmic resistance measured simultaneously with capacitance is highest in this region of potentials (Fig. 2). At E = 0.2 V one sees a capacitance rise due to oxidation of Ni to the trivalent state:

$$Ni(OH)_2 + OH^- + e = NiOOH + H_2O. \quad (3)$$

We made an attempt to use the dispersion of impedance in order to calculate the parameters of the network of Fig. 1a [6] for potentials corresponding to reaction (1); here C_{dl}^1 is the double-layer capacitance, R_p^1 is the polarization resistance, C_2 is the hydrogen adsorption capacitance, and R_2 is the resistance associated with the exchange current of reaction (1):

$$i_0 = RT/FR_2.$$

The calculations have shown, however, that in order to obtain reliable values for the equivalent-network parameters (Fig. 1a) one must have experimental data for much lower ac frequencies (on the order of 0.01 to 0.1 Hz, because of the low i_0-value) than can be obtained with the R-5021 bridge. Two processes occur simultaneously at the maximum of E = −0.75 V: the elimination of adsorbed hydrogen, and the oxidation of Ni to $Ni(OH)_2$; this makes the equivalent network much more complicated.

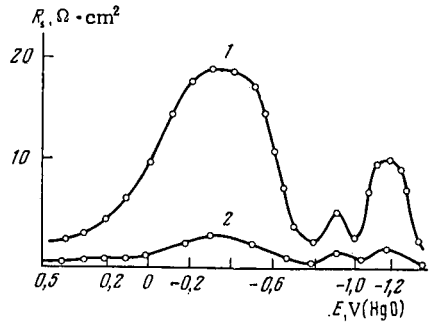

Fig. 2. R_S vs. E curves of the nickel electrode in 1 N KOH solution at different ac frequencies: 1) 410, and 2) 5000 Hz.

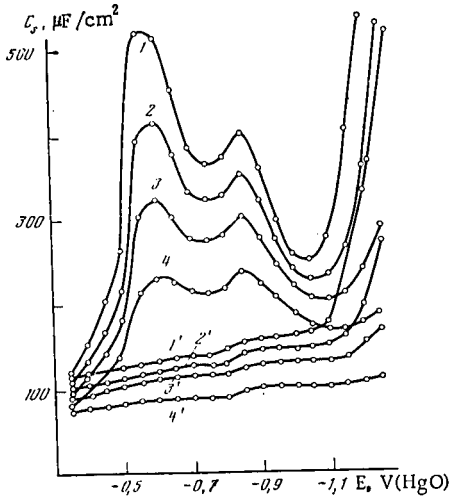

Fig. 3

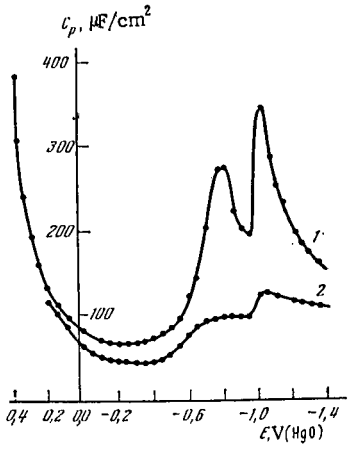

Fig. 4

Fig. 3. C_S vs. E curves of the nickel electrode in 1 N Na_2SO_4 + 0.01 N KOH solution at different ac frequencies: 1) 210, 2) 410, 3) 800, and 4) 2000 Hz, and in 1 N $(NH_4)_2CO_3$ solution at: 1') 210, 2') 410, 3') 800, and 4') 2000 Hz.

Fig. 4. C_p vs. E curves of the nickel electrode for ν = 800 Hz in: 1) 1 N KOH solution, 2) 1 N KOH + 10^{-3} N Na_2S solution.

We studied the effect of cations NH_4^+, anions S^{2-}, and Sb(III) as additives upon impedance. It was found that NH_4^+ strongly depress the capacitance and reduce the dispersion at potentials between −1.25 and −0.35 V over the frequency range investigated (Fig. 3). Qualitatively similar is the effect of S^{2-} on the processes occurring at Ni at these potentials (Fig. 4). This probably is due to the strong adsorption of these ions on Ni and to the kinetic retardation occurring for this reason in hydrogen oxidation (possibly also due to a lower degree of hydrogen coverage of the electrode surface) and initial Ni oxidation.

The different effects of S^{2-} exerted on the initial oxidation of Ni and on that of Fe (here the process is accelerated) possibly are due to the fact that sulfide ions hinder the formation of an oxide film on Fe [7], while according to ellipsometric data [5], the Ni surface has no oxide film at the potentials of beginning oxidation. The addition of Sb(III) leads to a depression of differential capacitance and dispersion in the region of the cathodic maximum, i.e., the rate of reaction (1) decreases. The initial oxidation is practically not affected by Sb(III).

At potentials where nickel is in the passive state, the measured impedance is practically not affected when the above ions are added to the solution.

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EFFECT OF THE SURFACE ANALOG OF FRIEDEL OSCILLATIONS UPON INTERACTION BETWEEN ADSORBED SPECIES

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The interaction between ions adsorbed from solution on the electrode surface has an important effect on the organization of the compact double-layer part. It is one of the factors governing the form of the adsorption isotherm and the value of the parameters contained in it. One of its chief components is the electrostatic interaction between the ionic charges.

In studies of electrostatic interaction near the metal/solvent or metal vacuum interface, one often uses [1-4] the model of a sharp boundary, i.e., of specular reflection of the polarization waves at the phase boundary [5-7]. In this approximation, the electrostatic potential $\Phi(R, x, a, c)$ is stated in terms of the bulk dielectric functions of the metal, $\varepsilon_1(k)$, and of the medium holding the charge, $\varepsilon_2(k)$. For a dielectric function of the metal in the Hubbard-Sham form [8-11], the behavior of this potential at $R \to \infty$ can be written as [3, 4]:

$$\Phi(R, x, a, c) \simeq \Phi_1(R, x, a, c) + \Phi_2(R, x, a),$$
$$\Phi_1(R, x, a, c) \equiv \Phi_1(R, c);\ \Phi_2(R, x, a) \equiv \Phi_2(R),$$

where $\Phi_1(R, c)$ is the monotonically diminishing part of the potential due to interaction of the adsorbed species across the solution space which allows for field penetration into the metal; $\Phi_2(R)$ is the surface analog of the Friedel oscillations; R and x are coordinates in a cylindrical coordinate system where the x-axis is perpendicular to the plane of the electrode; a is the distance to the center of an adsorbed ion; and c is the electrolyte concentration.

It had been shown in work [3] dealing with metal/dielectric systems that for a dielectric permittivity of the medium of $\varepsilon \gg 1$ or for $a \neq 0$ one has $\Phi_1(R, 0) \gg \Phi_2(R)$.

In metal/electrolyte systems with low electrolyte concentration [4], the electrolyte ions screen the inter-

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