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THE INFLUENCE OF THE NATURE OF THE ALKALI CATION ON THE DIFFUSION OF PROTONS IN NICKEL OXIDE

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Despite major achievements in the theory of electrochemical current sources, whose role in modern science and technology is increasing, at the present time there still remain a number of questions requiring further study. Among such questions is the kinetics of electrochemical reduction and oxidation processes of solid oxides and insoluble salts. The present investigation is of importance for the theory of the nickel oxide electrode, which has found wide application in alkaline iron-nickel, cadmium-nickel, and nickel-zinc storage batteries.

In previous works ([1–9]) it was shown that the process of electrochemical reduction of nickel oxides in an alkaline solution, proceeding according to equation (1), depends essentially on the rate of diffusion of protons in nickel oxides:

$$(\mathrm{Ni^{3+}\ O^{2-}\ OH^{-}})_{\mathrm{p}} + \mathrm{H_2O_{p-r}} + e \rightarrow (\mathrm{Ni^{2+}} \cdot 2\mathrm{OH^{-}})_{\mathrm{p}} + \mathrm{OH^{-}_{p-r}}, \qquad (1)$$

$$(\mathrm{Ni^{2+}} \cdot 2\mathrm{OH^{-}})_{\mathrm{p}} + (\mathrm{Ni^{3+}\ O^{2-}\ OH^{-}})_{\mathrm{v}} \rightarrow (\mathrm{Ni^{3+}\ O^{2-}\ OH^{-}})_{\mathrm{p}} + (\mathrm{Ni^{2-}} \cdot 2\mathrm{OH^{-}})_{\mathrm{v}}. \quad (2)$$

However, in the cited works only qualitative observations concerning this process were available.

The aim of the present work is to study the quantitative laws of the process of proton diffusion in nickel oxides, in particular, to study the dependence of the rate of proton diffusion on the potential and composition of the electrolyte. To investigate the rate of proton diffusion in nickel oxide, a diffusion Ni electrode was used in the form of foil, $7.5 \cdot 10^{-2}$ mm thick, on one side of which an oxide film had been deposited by anodizing. Anodizing was carried out at room temperature with a current of $22 \cdot 10^{-6}$ A/cm^2 for 14 h. Films of a thickness of about 60 monolayers were thereby obtained.

The film thickness was estimated approximately after completion of a series of measurements from the values of the electrochemical capacity obtained upon cathodic polarization of the film with a current of $18 \cdot 10^{-6}$ A/cm^2 to $\varphi = 0$

relative to the oxide-mercury electrode in the same solution. In calculating the film thickness it was assumed that NiO(OH) is reduced to $Ni(OH)_2$. In this case, $3.2 \cdot 10^{-4}$ C/cm^2 is required for the reduction of one monolayer.**

Figure 1 presents the time course of the change in the anodic current i_a required to maintain a constant film potential $\varphi_a = 0.575$ V in 2 N KOH solution relative to the oxide-mercury electrode before and after switching on a cathodic current $i_k = 0.073$ A/cm^2 on the other side of the foil.***

As can be seen from Fig. 1, after switching on the cathodic polarization, a gradual increase in the anodic current i_a is observed, which after 1.5-2 h reaches a practically constant value.

As is known, continuous oxide films are formed during anodizing of nickel. The anodic current i_a, required under the conditions of our experiments to maintain —

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* In equations (1) and (2), the subscripts p and v denote, respectively, the surface and the internal layer of the grain.
** The surface roughness coefficient was taken to be unity.
*** In the cathodic chamber, a 3.3 N KOH solution was used in all experiments.

of maintaining the constant potential of the film φ_a is spent mainly on oxygen evolution and partly (not more than 1-2%) on further oxidation of the film:

$$(Ni^{3+}O^{2-}OH^-)_n + OH^- \rightarrow (Ni^{4+} \cdot 2O^{2-})_n + H_2O + e, \tag{3}$$

therefore the dependence of i_a on the potential φ_a is determined only by the regularities of the oxygen-evolution process.

The rate of process (3) depends on the concentration of protons in the surface layer of the film X_{H^+} ([2,3]), i.e.,

$$i_a = k_a X_{H^+} [OH^-] \exp\left(\frac{\beta_1 \varphi F}{RT}\right). \tag{4}$$

In the steady state, a definite value of X_{H^+} corresponds to a definite potential. The loss of protons as a result of reaction (3)

[Figure 1 and Figure 2]

Fig. 1. Change in the anodic current i_a with time before and after switching on cathodic polarization from the reverse side of the electrode in a 2 N KOH solution

Fig. 2. Curves of dependence on potential in a 2 N KOH solution: 1—logarithm of the anodic current before switching on cathodic polarization, 2—the same

after switching on cathodic polarization, 3–logarithm of the proton-diffusion current i_{H}

is replenished only by the transfer of protons from the inner layers of the film to the surface. Consequently, the rate of process (3) is limited by the rate of proton diffusion in the film, i.e.,

$$i'_a = i_{\mathrm{H}} = k(C_{\mathrm{v}} - C_{\mathrm{p}}), \tag{5}$$

where C_{p} and C_{v} are the values of X_{H^+}, respectively, in the surface and inner layers.

The observed increase in the anodic current at constant potential after switching on cathodic polarization from the other side of the foil (see Fig. 1) can be associated only with an increase in the rate of process (3) due to the growth in the concentration of protons that have passed through metallic nickel into the inner layer of the film. Therefore, the value of the difference of the anodic currents obtained before and after switching on the cathodic current in the steady state is equal to the rate of proton diffusion through the nickel oxide film $-i_{\mathrm{H}}$.

Figure 2 gives the dependence on potential of the established* values of i_a before and after switching on cathodic polarization, as well as the values of the currents i_{H} at i_k equal to 0.073 A/cm^2 in 2 N KOH. The curves $\varphi_a - \lg i_a$ and $\varphi_a - \lg i_{\mathrm{H}}$ shown in Fig. 2 change slope on passing from low potentials to higher ones. For the region of low potentials, the values of the constant b of the Tafel equation are 0.104 V for i_a and 0.114 V for i_{H}. In the region of high–

* The measurements were made from high potentials to low ones. The values of i_a before switching on the cathodic current at high potentials were established after 1 hour, and when cathodic polarization was switched on after 2 hours; at all other lower potentials this value was established after 15 min.

potentials b is equal to 0.052 V for i_a and 0.078 V for i_{H}. From the data shown in Fig. 2 it follows that the proton-diffusion current i_{H} increases with increasing potential φ_a. In the works of P. D. Lukovtsev ([2,3]) it was shown that, with increasing potential of the nickel oxide electrode, the proton concentration in the surface layer of nickel oxides decreases. As follows from equation (5), a decrease in C_{p} will lead to an increase in the proton concentration gradient and, consequently, to an increase in the rate of their diffusion, which is also observed experimentally.

Figure 3 gives the curves φ_a—$\lg i_a$, i.e., the overvoltage curves for oxygen evolution on an oxide film, obtained potentiostatically in 2N alkali solutions LiOH, NaOH, and KOH. From the data presented it is seen that, at potentials above 0.54 V, the curves φ_a—$\lg i_a$ have practically the same slope, equal to 0.052-0.054 V. In the region of lower

Fig. 3 and Fig. 4

Figure 1: Fig. 3 and Fig. 4

Fig. 3. Dependence of the potential φ_a on $\lg i_a$ before cathodic polarization is switched on in $2N$ solutions of LiOH (1), NaOH (2), KOH (3)

Fig. 4. Dependence of the logarithm of the proton-diffusion current through a nickel oxide film on the potential in $2N$ solutions of LiOH (1), NaOH (2), and KOH (3)

potentials, bends of the curves are observed, and the slope increases to a value equal to 0.104 V. From Fig. 3 it is seen that in LiOH solution the oxygen overvoltage is greater than in NaOH solution, and in NaOH solution greater than in KOH solution, which agrees with the data of previously published works ([2,10–12]).

Figure 4 presents the dependence of the logarithm of the proton-diffusion current i_{H} through a nickel oxide film on the potential. As follows from Fig. 4, a linear dependence of $\lg i_{\mathrm{H}}$ on φ_a is not observed over the entire range of potentials studied. As in the case of the dependence of the oxygen overvoltage on current density, the curves φ_a—$\lg i_{\mathrm{H}}$ at lower potentials have a higher slope. In the region of high potentials, the Tafel slope b varies within the limits from 0.045 V for NaOH to 0.075 V for KOH. From Fig. 4 it is also seen that, over the entire range of potentials studied, the proton-diffusion current is greater when KOH solution is used and smaller in LiOH solution.

In NaOH solution, in the region of high potentials, the proton-diffusion current is greater than in LiOH solution and smaller than in KOH solution, and only at a potential of 0.5 V is the diffusion current greater in LiOH solution than in NaOH solution.

From semiconductor theory it is known that introducing into the lattice of an oxide semiconductor with p-type conductivity cations of lower valence than the cation of the parent oxide should lead to an increase in electrical conductivity and to a decrease in the rate of diffusion of the substance in the solid phase ([13]). The facts of an increase in the electrical conductivity of Ni oxides upon introduction of Li^+ into them are quite well known ([14,15]). As follows from the data presented

in Figs. 3 and 4, replacement in the alkali of the cation from K^+ to Na^+ and then to Li^+ leads to an increase in the oxygen overvoltage and to a decrease in the rate of proton diffusion. The observed dependence of the rate of proton diffusion on the nature of the cation is in agreement with semiconductor theory, if it is assumed that the energy barrier for proton diffusion is located in nickel oxide, which has p-type conductivity, and that the monovalent cations Li^+, Na^+, and K^+ enter the nickel oxide lattice in place of Ni^{2+} or Ni^{3+} cations. Since the sorbability of cations by nickel oxides increases in the series $K^+ < Na^+ < Li^+$,

it should be expected that the effect of Li^+, when incorporated into the oxide lattice, on the rate of proton diffusion will be greater than that of Na^+, and that of Na^+ greater than that of K^+. This is in agreement with the experimental data.

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Note: Figure translations are in progress. See original paper for figures.