# THE EFFECT OF THE NATURE OF THE ALKALI CATION ON THE DIFFUSION OF PROTONS IN NICKEL OXIDE

G. Ya. Slaidin* and P. D. Lukovtsev

Institute of Electrochemistry of the Academy of Sciences, USSR
(Presented by Academician A. N. Frumkin, September 20, 1961)
Translated from Doklady Akademii Nauk SSSR, Vol. 142, No. 5,
pp. 1130-1133, February, 1962
Original article submitted September 16, 1961

In spite of great achievements in the theory of electrochemical current sources, the role of which is growing in present day science and engineering, there are even today a number of questions which require further study. Included in the number of such questions is the kinetics of the electrochemical reduction and oxidation of solid oxides and insoluble salts. The present investigation is of importance for the theory of the oxide-nickel electrode, which has found wide application in alkaline iron-nickel, cadmium-nickel, and nickel-zinc storage batteries.

It has been shown in previous papers [1-9] that the electrochemical reduction of nickel oxides in alkaline solution, going according to Eq. (1), depends, in a fundamental way, on the proton diffusion rate in nickel oxides:

$$(Ni^{3+}\ O^{2-}\ OH^-)_s + H_2O_{p\text{-}p} + e \rightarrow (Ni^{2+}\cdot 2\,OH^-)_s + OH^-_{p\text{-}p}, \quad (1)$$

$$(Ni^{2+}\cdot 2OH^-)_s + (Ni^{3+}\,O^{2-}\,OH^-)_i \rightarrow (Ni^{3+}\,O^{2-}\,OH^-)_s + (Ni^{2-}\cdot 2OH^-)_i. \quad (2)^*$$

However, in the papers mentioned, there were only qualitative observations relative to the process.

The purpose of the present paper is to study the quantitative laws governing proton diffusion in nickel oxides, in particular, to find out how the proton diffusion rate varies as a function of the potential and electrolyte composition. To investigate the proton diffusion rate in nickel oxide, use was made of a diffusion Ni-electrode in the form of a foil, $7.5 \cdot 10^{-2}$ mm thick, on one side of which was an anodized oxide film. The anodizing was done at room temperature with a current strength of $22 \cdot 10^{-6}$ amp/cm$^2$ for 14 hr. This gave films of the order of 60 monolayers thick.

The thickness of the film was found approximately after completing a series of measurements from the values of the electrochemical capacity obtained from cathode polarization of the film with a current of $18 \cdot 10^{-6}$ amp/cm$^2$ up to $\varphi = 0$ with respect to an 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, to reduce one monolayer requires $3.2 \cdot 10^{-4}$ coulomb/cm$^2$.**

Figure 1 shows the change with time of the anode current, $i_a$, required to maintain a constant film potential $\varphi_a = 0.0.575$ v, in 2 N KOH solution with respect to the oxide-mercury electrode before and after turning on the cathode current $i_k = 0.073$ amp/cm$^2$ on the other side of the foil.***

As may be seen from Fig. 1, after turning on the cathode polarization a gradual increase in the anode current, $i_a$, was observed, which reaches a practically constant value after 1.5-2 hr time. It is known that when nickel is anodized continuous oxide films are formed. The anode current $i_a$, required under our experimental conditions to maintain the constant film potential, $\varphi_a$, is consumed mainly in liberating oxygen and partially (not more than 1-2%) in further oxidation of the nickel:

* In Eqs. (1) and (2), the indices s and i signify, respectively, the surface and internal layers of the grains.
** The roughness coefficient of the surface was taken equal to unity.
*** 3.3 N KOH solution was used in the cathode chamber in all experiments.

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

therefore $i_a$ as a function of the potential $\varphi_a$ is determined only by the laws governing the oxygen liberation reaction.

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

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

In the stationary state, a definite value of $X_{H^+}$ corresponds with a definite potential. A decrease in protons resulting from reaction (3) occurs only from transfer of protons from the internal layers of the film to the surface. Consequently, the rate of reaction (3) is limited by the diffusion rate of the protons in the film, i.e.,

$$i_a' = i_H = k\,(C_i - C_s), \quad (5)$$

where $C_s$ and $C_i$ are the values of $X_{H^+}$ at the surface and inside the layers respectively.

The observed increase in the anode current at constant potential after turning on the cathode polarization on the other side of the foil (see Fig. 1) can only be due to an increase in the rate of reaction (3) resulting from an increase in the concentration of protons which are passed through the metallic nickel into the internal layers of the

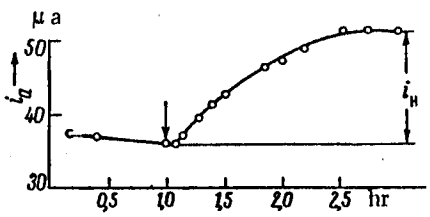


Fig. 1. Change in anode current, $i_a$, with time before and after turning on cathode polarization at the opposite side of the electrode in 2 N KOH solution.

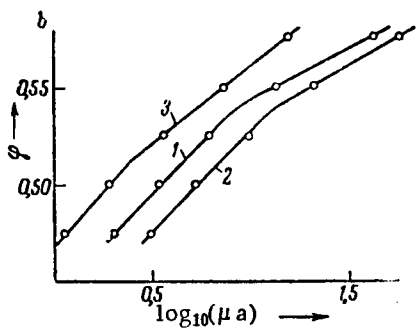


Fig. 2. Curves showing as a function of potential in 2 N KOH solution: 1) Logarithm of the anode current before turning on the cathode polarization, 2) the same after turning on the cathode polarization; 3) logarithm of proton diffusion current, $i_H$.

Therefore, the difference between the anode currents found before and after turning on the cathode current in the stationary state is equal to the rate of diffusion of protons through the nickel oxide film, $i_H$.

Figure 2 gives the functional relationship with the potential of the values of $i_a$ established* before and after turning on the cathode polarization, as well as the values of the current $i_H$ for $i_k$ equal to 0.073 amp/cm$^2$ in 2 N KOH. The $\varphi_a$-$\log_{10} i_a$ and $\varphi_a$-$\log_{10} i_H$ curves given in Fig. 2 change their slope on going from low potentials to higher potentials. In the low potential region the values of the constant b in Tafel's equation are equal to 0.1.04 v for $i_a$, and 0.114 v for $i_H$. In the high potential region b is equal to 0.052 v for $i_a$ and 0.078 v for $i_H$. It follows from the data given in Fig. 2 that the proton diffusion current, $i_H$, increases with increase in the potential $\varphi_a$. It has been shown in the papers of P. D. Lukovtsev [2, 3] that with increasing potential of the oxide-nickel electrode the proton concentration in the surface layer of the nickel oxides is reduced. As follows from Eq. (5) the

*The measurements were made from large to small potentials. The values of $i_a$ before turning on the cathode current at large potentials was established in one hour, and on turning on the cathode polarization in two hours, while at all lower potentials this value was established in 15 min.

reduction in $C_s$ causes an increase in the proton concentration gradient, and, consequently, an increase in the proton diffusion rate, which is observed experimentally.

Figure 3 gives $\varphi_a$-$\log_{10} i_a$ curves, i.e., curves of the overvoltage when oxygen is liberated at the oxide film, the curves being obtained potentiostatically in 2 N alkaline solutions of LiOH, NaOH, and KOH. It is clear from the data given that at a potential above 0.54 v, the $\varphi_a$-$\log_{10} i_a$ curves have practically the same slope equal to 0.052-0.054 v. In the region of lower potentials, breaks are observed in the curves, and the slope increases to a value equal to 0.104 v. It may be seen from Fig. 3 that in LiOH solution the oxygen overvoltage is greater than in NaOH solution, and is greater in NaOH solution than in KOH solution, which agrees with the data already published [2, 10-12].

Figure 4 shows the logarithm of the proton diffusion current, $i_H$, through the nickel oxide film as a function of the potential. It follows from Fig. 4 that a linear relationship between $\log_{10} i_H$ and $\varphi_a$ is not observed over the

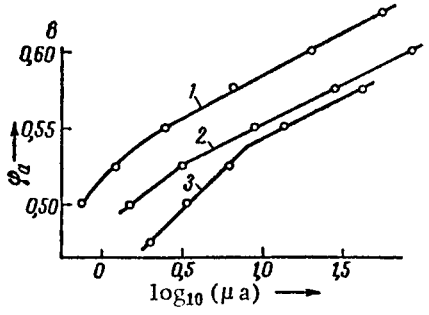


Fig. 3. The potential $\varphi_a$ as a function of $\log_{10} i_a$ before turning on cathode polarization in 2 N solutions of (1) LiOH, (2) NaOH, and (3) KOH.

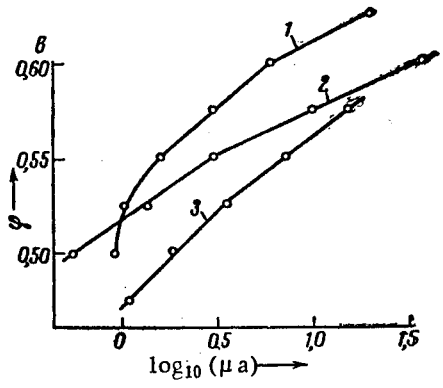


Fig. 4. Logarithm of proton diffusion current nickel oxide film as a function of the potential in 2 N solutions of (1) LiOH, (2) NaOH, and (3) KOH.

whole range of potentials studied. As in the case of the variation of oxygen overvoltage with current density, the $\varphi_a$-$\log_{10} i_H$ curves have a greater slope at the lower potentials. In the higher potential region, the slope, b of the Tafel curves varies from 0.045 v for NaOH to 0.075 v for KOH. It may also be seen from Fig. 4 that over the whole range of potentials studied the proton diffusion current is greater when using KOH solution, and smaller when using LiOH solution.

In NaOH solution in the high potential range, the proton diffusion current is greater than in LiOH solution, and less 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.

It is known from the theory of semiconductors that adding cations of smaller valence than the cation of the fundamental oxide to the lattice of an oxide semiconductor with p-type conductivity is supposed to cause an increase in electrical conductivity, and a decrease in the diffusion rate of matter in the solid phase [13]. The fact that the electrical conductivity of nickel oxides increases when $Li^+$ is added to them is rather well known [14, 15]. As follows from the data given in Fig. 3 and 4, replacing the alkali cation $K^+$ with $Na^+$, and then with $Li^+$ causes an increase in the oxygen overvoltage, and a reduction in the proton diffusion rate. The observed relation between the proton diffusion rate and the nature of the cation is found to be in agreement with semiconductor theory, if we assume that the energy barrier for proton diffusion is located in the nickel oxide, which has p-type conductivity, and that the monovalent cations $Li^+$, $Na^+$, and $K^+$ penetrate into the nickel oxide lattice instead of the cations $Ni^{2+}$ or $Ni^{3+}$. Since the sorptivity of cations by nickel oxides increases in the series $K^+ < Na^+ < Li^+$, it is to be expected that the effect of $Li^+$ on the proton diffusion rate when it penetrates into the oxide lattice will be greater than that of $Na^+$, and that of $Na^+$ will be greater than that of $K^+$. This is found to be in agreement with the experimental data.

## LITERATURE CITED


1. P. D. Lukovtsev and S. A. Temerin, Transactions of 1950 Conference on Electrochemistry [in Russian] Academy of Sciences Press, USSR, 1953, p. 494.
2. P. D. Lukovtsev, Doctors Dissertation, Institute of Physical Chemistry Academy of Sciences, USSR, 1952.
3. P. D. Lukovtsev, Transactions of Fourth Conference on Electrochemistry, 1956 [in Russian] Academy of Sciences Press, USSR, 1959, p. 773.
4. E. Jones and W. F. K. Wynne-Jones, Trans. Farad. Soc. 52, No. 9, 1260 (1956).
5. G. W. D. Briggs and W. F. K. Wynne-Jones, Trans. Farad. Soc. 52, No. 9, 1272 (1956).
6. H. Winkler, Dtsch. Elektrotechnik, 9, 1272 (1956).
7. H. Winkler, Intern. Comm. Electrochem., Thermod. and Kinet. (8th Meet. Madrid, 1956) (London, Butterworths Sc. Pub., 1958) p. 383.
8. S. U. Falk, J. Electrochem. Soc. 107, No. 8, 661 (1960).
9. E. M. Kuchinskii and B. V. Ershler, ZhFKh 20, 539 (1946).
10. S. A. Gantman and P. D. Lukovtsev, Transactions of 1950 Conference on Electrochemistry [in Russian] Academy of Sciences Press, USSR, 1953, p. 504.
11. P. D. Lukovtsev, Transactions of Fourth Conference on Electrochemistry, 1956 [in Russian] Academy of Sciences Press, USSR, 1959, p. 302.
12. Ya. I. Tur'yan and A. I. Tsinman, DAN 136, No. 5, 1154 (1961).
13. K. Hauffe, Reaktionen in und an festen Stoffen (Berlin, 1955).
14. E. J. W. Verwey, Chem. Week. blad. 44, 1195 (1954).
15. F. J. Morin, Phys. Rev. 93, 1195 (1954).


---

**All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.**

---