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Abstract

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THE MECHANISM OF THE CHANGE IN OXYGEN OVERVOLTAGE WITH TIME ON A NICKEL ANODE AT CONSTANT CURRENT DENSITY

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The phenomenon of the growth of the oxygen overvoltage η with time t on a Ni anode at i = const has so far not found a quantitative explanation. We have assumed ([1,2]) that the cause of the growth of η, due at large i to the slowness of the discharge of OH' ions ([1–3]), is that η on NiO_2 (Ni_2O_4) ([4]), the concentration of which in the surface solid solution $Ni_2O_3 + Ni_2O_4$ gradually increases, is greater than η on Ni_2O_3 (the anode, already at $t = 0$, is considered to be completely covered with Ni_2O_3). The assumption that η on Ni_2O_4 is greater than η on Ni_2O_3 is to some extent confirmed by work ([5]), which showed that η on Ni_2O_3 is greater than η on NiO.

For the purpose of quantitatively checking these ideas, experimental data on the dependence of η on t at i = const from ([1]) and ([6]) were used (Fig. 1, 6–7.5 N KOH). The results from ([6]) at small t and 18° showed an anomalous course of the η–t curve, possibly because of the nonstationarity of the anode surface area ([1]) or incomplete coverage by Ni_2O_3. These data were discarded, and $(\eta)_{t=0}$ was found by extrapolation (Fig. 1).

At large i, the evolution of O_2 through the formation and decomposition of Ni_2O_4 must be insignificant in comparison with another parallel process ([2]), for example

$$2OH \rightarrow H_2O + O. \tag{1}$$

Taking this into account, the kinetics of the accumulation of Ni_2O_4

$$Ni_2O_3 + 2OH \rightarrow Ni_2O_4 + H_2O \tag{2}$$

with simultaneous decomposition of Ni_2O_4

$$Ni_2O_4 \rightarrow Ni_2O_3 + O \tag{3}$$

can be described by the expression

$$\frac{dS}{dt} = K_1(1 - S) - K_2S; \tag{4}$$

S is the part of the anode surface occupied by Ni_2O_4 (the closeness of the molar surfaces of Ni_2O_3 and Ni_2O_4 is assumed); $K_1 = K_1'[OH]^2$; K_1' and K_2 are the rate constants of processes (2) and (3), respectively.

According to the theory of slow discharge ([7]), taking into account the discharge of OH' ions on the surface of the solid solution $Ni_2O_3 + Ni_2O_4$ ($[OH'] = \text{const}$), we obtain:

$$i = K_3(1 - S)\exp\left(\frac{\eta F}{2RT}\right) + K_4 S \exp\left(\frac{\eta F}{2RT}\right). \quad (5)$$

From (4) and (5) (at $t = 0$, $S = 0$), assuming $K_3 \gg K_4$, we find:

$$\eta = \frac{2RT}{F}\ln i - \frac{2RT}{F}\ln\frac{K_1K_3}{K_1 + K_2} - \frac{2RT}{F}\ln\left[\left(\frac{K_2}{K_1} + \frac{K_4}{K_3}\right) + e^{-(K_1+K_2)t}\right]. \quad (6)$$

Table 1

T, °C	Current density, A/cm^2: 0.01			Current density, A/cm^2: 0.05			Current density, A/cm^2: 0.1			Current density, A/cm^2: 0.3		
	a	b	$\varphi_{t=0}$, mV (N.H.E.)	a	b	$\varphi_{t=0}$, mV (N.H.E.)	a	b	$\varphi_{t=0}$, mV (N.H.E.)	a	b	$\varphi_{t=0}$, mV (N.H.E.)
18	$6.94\cdot 10^{-3}$		632	$2.3\cdot 10^{-4}$	$7.9\cdot 10^{-2}$	690	$2.7\cdot 10^{-4}$	0.158	750			
25										$1.4\cdot 10^{-4}$	1.37	794
60							$5.0\cdot 10^{-4}$	$3.6\cdot 10^{-2}$	660			
80										$1.0\cdot 10^{-3}$	$7.0\cdot 10^{-2}$	696

Note. $a = \dfrac{K_2}{K_1} + \dfrac{K_4}{K_3}$, b (h^{-1}) $= K_1 + K_2 \approx K_1$.

Equation (6) agrees well with the experimental results (Fig. 1) for the values of the constants indicated in Table 1, and under the condition

$$(\eta)_{t=0} = \frac{2RT}{F}\ln i - \frac{2RT}{F}\ln\frac{K_1K_3}{K_1 + K_2}. \quad (7)$$

(Figure: Fig. 1)

Fig. 1. Dependence of φ on t. Points are calculated data; curves are experimental. 1–0.3 A/cm^2, 25° (1); 2–0.1 A/cm^2, 18° (6); 3–0.05 A/cm^2, 18° (6); 4–0.3 A/cm^2, 80° (1); 5–0.1 A/cm^2, 60° (6); 6–0.01 A/cm^2, 18° (6).

Since

$$\left(\frac{K_2}{K_1}+\frac{K_4}{K_3}\right)\ll 1$$

(Table 1) and $K_3 \gg K_4$, it follows that $K_1 \gg K_2$. This is also confirmed by expression (7), which at $t = 0,\ S = 0$ must be transformed into

$$(\eta)_{t=0}=\frac{2RT}{F}\ln i-\frac{2RT}{F}\ln K_3, \tag{8}$$

which is possible for $K_1 \gg K_2$.

The dependence found by us of $(\eta)_{t=0}$ on $\lg i$ is a straight line with slope

$$\frac{2RT}{F}\cdot 2.3$$

(Fig. 2), in good agreement with (8).

Thus, equation (6) takes the form

$$\eta=(\eta)_{t=0}-\frac{2RT}{F}\ln\left[\left(\frac{K_2}{K_1}+\frac{K_4}{K_3}\right)+e^{-K_1 t}\right]. \tag{9}$$

At small values of t, and taking into account the magnitudes of K_1 and

$$\left(\frac{K_2}{K_1}+\frac{K_4}{K_3}\right)$$

(Table 1), equation (9) can be transformed into a linear dependence of η of t:

$$\eta=(\eta)_{t=0}+\frac{2RT}{F}K_1 t, \tag{10}$$

which agrees with experiment (Fig. 1).

With increasing t, η tends to the value established in time (η_{st}):

$$\eta_{\text{st}}=(\eta)_{t=0}-\frac{2RT}{F}\ln\left(\frac{K_2}{K_1}+\frac{K_4}{K_3}\right), \tag{11}$$

which also agrees with experiment (Fig. 1).

As is seen from Table 1, K_1 depends on i, which apparently is connected with a certain inhibition also at other stages of the process (change in [OH]), considerably less than at the stage of discharge of $OH^{'}$ ions. A similar picture was observed [8] also in the study of η on a Pb anode.

(Figure: Figure 2)

Fig. 2. 1 –dependence of φ_{st} on $\lg i$ (a –according to [2], b –according to [9]); 2 –dependence of $\lg k_1$ on $\lg i$; 3 –dependence of $\varphi_{i=0}$ on $\lg i$

Since at constant temperature K_1 increases with increasing i (Table 1), at large i one may expect

$$\frac{K_4}{K_3} \gg \frac{K_2}{K_1},$$

and at small i

$$\frac{K_4}{K_3} \ll \frac{K_2}{K_1}.$$

Hence at large i, from (11), taking (8) into account,

$$\eta_{st} = \frac{2RT}{F} \ln i - \frac{2RT}{F} \ln K_4, \tag{12}$$

and at small i

$$\eta_{st} = \frac{2RT}{F} \ln i - \frac{2RT}{F} \ln K_3 -$$

$$-\frac{2RT}{F} \ln \frac{K_2}{K_1}. \tag{13}$$

If it is taken into account that $K_1 = K_1' i^{1.55}$ (Fig. 2) and (13), then

$$\eta_{st} = 2.55\frac{2RT}{F} \ln i - \frac{2RT}{F} \ln K_3 - \frac{2RT}{F} \ln K_2 + \frac{2RT}{F} \ln K_1'. \tag{14}$$

Equation (12) agrees with experiment already at $i > 0.1$ A/cm^2. This is the upper linear segment (Fig. 2) of the dependence of η_{st} on $\lg i$, with slope $\sim \frac{2RT}{F}$ 2.3 [2,9,10]. The presence of this segment, corresponding, according to (12), to complete coverage of the anode by Ni_2O_4, was also confirmed [11].

Equations (13) and (14) are confirmed at smaller i ($i < 0.01$–0.02 A/cm^2, but not below 10^{-3} A/cm^2, when the mechanism of η changes [2]) in the region of the

steep segment of the dependence of η_{st} on $\lg i$ [2,10]—a straight line with angular coefficient 0.320 (Fig. 2), which is close to the theoretical value 0.303 (equation (14)). From (5) and (13) it follows that in this segment the discharge process of OH' ions proceeds mainly on Ni_2O_3. To each value of η_{st} there corresponds a definite value of S. As the surface concentration of Ni_2O_4 increases (with increasing i), the process also proceeds on Ni_2O_4.

On the basis of (14) and the experimental dependences of η_{st} on $\lg i$ [2], $\eta_{t=0}$ on $\lg i$, and K_1 on i, we calculated that $K_2 = 1 \cdot 10^{-5}$ h^{-1} at 25°, i.e., as also follows

one should expect, $K_1 \gg K_2$. Approximately the same value of K_2 was obtained from the dependence of η on t. Such a low value of K_2 does not confirm assumption [4] about process (3) as the rate-controlling stage even at very low i, since in this case the calculation gives an unrealistically large concentration of Ni_2O_4 (for example, at $i = 10^{-5}$ a/cm^2, $[Ni_2O_4] = 1.1 \cdot 10^{22}$ molec./cm^2).

The assumption of the process

$$2\,Ni_2O_4 \rightarrow 2\,Ni_2O_3 + O_2 \tag{15}$$

is not confirmed by the dependence of η on t.

On the basis of the dependence of η_{ust} on $\lg i$ (at $i > 0.1$ a/cm^2) and the dependence of $\eta_{t=0}$ on $\lg i$, we calculated $K_4/K_3 = 1.7 \cdot 10^{-4}$, which agrees exceptionally well with the value of K_4/K_3 from the dependence of η on t (Table 1).

It is seen from Table 1 that, with increasing temperature, K_1 decreases. This is the result of the predominant influence of temperature on lowering the surface concentration of OH radicals in comparison with the concomitant increase of K_1'.

In conclusion, we note that equation (5), also under the condition $K_3 \gg K_4$, has already been used [12] to describe the dependence of η on t for a Pt anode. However, the kinetics of oxide accumulation is represented in [12] not by the same dependence as in our work, and therefore the dependence of η on t in [12] came out completely different.

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