PHYSICAL CHEMISTRY

Ya. I. Turyan and A. I. Tsinman

1961

SovietRxiv

Fig. 1

Figure 1: Fig. 1

Abstract

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PHYSICAL CHEMISTRY

Ya. I. Turyan and A. I. Tsinman

THE INFLUENCE OF THE CONCENTRATION AND NATURE OF THE ALKALI ON THE OXYGEN OVERVOLTAGE AT A NICKEL ANODE

(Presented by Academician A. N. Frumkin, 19 IX 1960)

Data (^{1,2}) on the influence of alkali concentration $[OH^-]$ on the oxygen overvoltage η at a smooth Ni anode are contradictory and cover only low current densities i. A remark in the discussion (^{3}) concerning the change of η with a change in the nature of the alkali: $K^+ < Na^+ < Li^+$, contains no further details.

The conditions of our experiment* were analogous to (^{4}), except for the absence in our work of electrode rotation ($i \leqslant 1$ A/cm^2) and for the use, for more accurate allowance for the ohmic voltage drop, of several electrolytic keys (^{5}), whose openings were located at different distances from the electrode surface (galvanic Ni on Pt wire). It was established that the dependence of the potential on this distance at $i = \text{const}$ was a straight line. This facilitated extrapolation to zero distance. Such a dependence differed somewhat from that considered in (^{6}).

Fig. 1. Curves η—$\lg i$ in KOH. 1—7.5 M; 2—5.0 M; 2′—the same, 48 hr.; 3—3.7 M; 4—2.2 M; 5—1.3 M; 5′—the same, 12 hr.; 5″—the same, 48 hr.; 6—0.6 M.

The study was carried out at 25° in thoroughly purified KOH, NaOH, and LiOH. The curves η—$\lg i$, corresponding to potentials established in time, were recorded from larger i to smaller after 24-hour anodic polarization with a current $i = 1$ A/cm^2. In concentrated alkali (2.5–7.5M) this time is sufficient for attaining $\eta = \text{const}$, whereas in dilute solutions ($[OH^-] \ll 1M$), especially in KOH, at large i (~ 1 A/cm^2) a further increase of η with time was observed (Fig. 1).

On the curves η—$\lg i$ in KOH and NaOH (Figs. 1 and 2), at $[OH^-] = 2.0$–$9.5M$, there are three regions: I—linear, gently sloping, at $i \cong 10^{-5}$–10^{-3} A/cm^2; II—steep, at $i \cong 10^{-3}$–10^{-1} A/cm^2; III—linear, again gently sloping, at $i > 10^{-1}$ A/cm^2.

Thus, the presence at a Ni anode of a wave-like polarization curve ($^{4,7-11,15}$) is also confirmed by investigation in alkali of various

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* L. F. Gushchina took part in the experimental part of the work.

the nature and concentration, and the fact that in (2) only two regions, I and II, were observed is explained by the use in (2) of lower i.

According to (7-9), for KOH solutions in region I the limiting stage is

$$\mathrm{Ni_2O_3 + 2OH_{ads} \rightarrow 2NiO_2(Ni_2O_4) + H_2O} \tag{1}$$

or

$$\mathrm{2OH_{ads} \rightarrow H_2O + O_{ads}}$$

with the kinetic equation

$$\eta = \mathrm{const} + \frac{RT}{2F}\ln i, \tag{2}$$

and in region III

$$\mathrm{OH^- - e \rightarrow OH_{ads}} \tag{3}$$

with the kinetic equation (12)

$$\eta = \mathrm{const} + \frac{RT}{\alpha F}\ln i - \frac{1-\alpha}{\alpha}\frac{RT}{F}\ln[\mathrm{OH^-}] - \psi_1\frac{1-\alpha}{\alpha}. \tag{4}$$

The influence of the nature of the alkali on η in the region of i of regions I and III is evident from Figs. 1-3; at higher $[\mathrm{OH^-}]$ (2—$7.5\,M$) η increases in the order $K^+ < Na^+ < Li^+$, which agrees with (3), whereas at lower $[\mathrm{OH^-}]$ the picture changes: $Na^+ < K^+ < Li^+$. The fact that the character of the influence of the nature of the alkali cation is the same for regions I and III and opposite to that observed at a Pt anode (13) confirms the opinion (3) that it is impossible to explain the effect under consideration solely by the influence of the cation on the structure of the electrical double layer. Most probably, for the Ni anode the predominant significance is the change in the catalytic properties of the anode surface due to incorporation of alkali-metal ions into the oxide lattice (3).

Fig. 2. Curves η—$\lg i$ in NaOH. 1—9.5 M; 2—7.5 M; 3—5.0 M; 4—2.5 M; 5—1.0 M; 6—0.4 M

With a change in the concentration and the nature of the alkali cation, leading to different effects upon incorporation of cations into the oxide lattice, the length

Fig. 2. Curves η—$\lg i$ in NaOH. 1—9.5 M; 2—7.5 M; 3—5.0 M; 4—2.5 M; 5—1.0 M; 6—0.4 M

Figure 2: Fig. 2. Curves η—$\lg i$ in NaOH. 1—9.5 M; 2—7.5 M; 3—5.0 M; 4—2.5 M; 5—1.0 M; 6—0.4 M

Fig. 3

Figure 3: Fig. 3

of region III (complete coverage by NiO_2 (14)) increases in the order $Na^+ < K^+ < Li^+$, so that in LiOH, up to $i = 1 \cdot 10^{-5}$ A/cm^2, region I can no longer be noticed (Fig. 3). With decreasing [OH$^-$] and increasing time of preliminary polarization, region III contracts until it disappears completely (NaOH, Fig. 2) and a new region IV appears (KOH, LiOH, Figs. 1 and 3), which was also observed in 7.5 M KOH, but at higher i (4).

The dependence of the length of region III on the composition of the electrolyte used in nickel plating (15) is also explained, in our view, by the difference in the catalytic properties of the anode surface. The authors (15) explained this effect by a change in the magnitude of the true surface; however, as is evident from the data of (15), this would require a change in the true surface by a factor of 10—100, which is hardly possible.

In support of the assumption of incorporation of the alkali cation into the oxide lattice there is also the slow increase in η at $i =$ const observed by us after adding a certain amount of LiOH to a KOH solution.

From Fig. 3 it is evident that the effect of increasing η in LiOH, compared with NaOH or KOH, is significant only at $10^{-3} < i < 10^{-2} \div 10^{-1}$ A/cm^2. Hence, it seems to us, it follows that when charging an alkaline accumulator with a current

$i > 10^{-1}$ A/cm^2 (per square centimeter of true surface), the effect of the LiOH addition on the capacity of the accumulator should be insignificant.

Fig. 3. Curves of $\eta - \lg i$ in LiOH, KOH, and NaOH.
1—5 M LiOH; 2—2.5 M LiOH; 3—0.5 M LiOH; 4—5 M KOH; 5—5 M NaOH.

The dependence of η on [OH$^-$] is presented in Fig. 4. Assuming that the change in the catalytic properties of the anode surface with a change in the concentration of the cation in the solution proceeds slowly, owing to the slow occurrence of secondary processes involving changes in the concentration and structure of oxides, in order to eliminate this effect as completely as possible when studying the dependence $\eta -$ [OH$^-$], we used rapid dilution of the alkali with water at $i =$ const without switching off the current. Before the beginning of these measurements, $\eta =$ const was attained in concentrated alkali.

From Fig. 4 there follows complete independence of η from [OH$^-$] in NaOH in

Fig. 4

Figure 4: Fig. 4

regions I and III. The catalytic influence of the Na^+ ion at low i is apparently so small that the same conclusion also follows from the curves of $\eta - \lg i$ (Figs. 2 and 4)*.

In KOH (Fig. 4), for regions I and III the dependence $\eta - \lg[OH^-]$ is a straight line with a slope of −0.012-0.015 (Fig. 4), while in LiOH, for region III, the slope is 0.010 (Fig. 4).

We believe that the slight influence of $[OH^-]$ on η in KOH and LiOH is entirely associated with a change in the catalytic activity of the anode surface with a change in $[K^+]$ or $[Li^+]$, and that in both KOH and LiOH, η in regions I and III does not depend on $[OH^-]$. These data in KOH for region I agree with (2) and do not agree with (1).

The slope of $\eta - \lg i$ for region I, 0.032-0.047 (7.5-0.6 M KOH) and 0.030-0.031 (9.5-0.4 M NaOH), and the independence of η from $[OH^-]$ confirm the chosen limiting stage (i^{-9}) (1).

The slope of $\eta - \lg i$ for region III, 0.090-0.130, corresponds to limiting stage (3), and to explain the independence of η from $[OH^-]$ one must assume

$$\psi_1 \simeq \text{const} - \frac{RT}{F} \ln[OH^-], \tag{5}$$

although theoretically[^12] this dependence is realized in the case of more dilute solutions. Possibly, specific adsorption of OH^- ions occurs here, which should also shift the ψ_1-potential in the negative direction.

Fig. 4. Curves of $\eta - \lg[OH^-]$.
a—KOH: 1—$i = 1 \cdot 10^{-4}$ A/cm^2, 2—$4 \cdot 10^{-4}$, 3—$1 \cdot 10^{-3}$;
b—NaOH: 1—$i = 7 \cdot 10^{-5}$ A/cm^2, 2—$7 \cdot 10^{-4}$;
v—NaOH from the curves of $\eta - \lg i$: 1—$i = 1 \cdot 10^{-4}$ A/cm^2, 2—$4 \cdot 10^{-4}$, 3—$1 \cdot 10^{-3}$;
g—LiOH: 1—$i = 7 \cdot 10^{-3}$ A/cm^2;
d—KOH: 1—$i = 0.16$ A/cm^2, 2—0.33, 3—0.55;
e—NaOH: 1—$i =$ 1-0.35 A/cm^2, 2—0.70, 3—1.05.

The applicability of equation (4) was also confirmed for a fully charged mercury-oxide electrode, but under the condition $\psi = 0$, i.e., there is a substantial

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* For other solutions, from the curves of $\eta - \lg i$ (Figs. 1 and 3) one cannot, as in (10), draw any definite conclusion about the dependence $\eta - [OH^-]$. The reason for this, apparently, is that during the prolonged recording of the $\eta - \lg i$ curves, the state of the anode surface changes as the concentration of the alkali cation changes.

difference in the behavior of this electrode and of the smooth nickel anode investigated by us.

Lisichansk Branch
of the State Scientific-Research
and Design Institute of the Nitrogen Industry
and Products of Organic Synthesis

Received
16 IX 1960

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