

calculated from Eqn. (1) with allowance for the constancy of the gas temperature in the reaction zone at discharge intensities below the critical value. They show the limiting concentrations of ozone obtainable in these ozonisers when the temperature of the cooling liquid is 20°. Their difference from curves 1 is due to the fact that the temperature of the gas in the reaction zone of the ozonisers cannot be less than the critical value however small the discharge intensity.

It is important to note that the limiting ozone concentrations rapidly decrease with increase in the discharge gap. To obtain a high concentration of ozone (of the order of 10–12 vol. %), it is necessary to use ozonisers with discharge gaps of the order of 1 mm.

SUMMARY

A study has been made of the effect of discharge intensity on the electrical synthesis of ozone in ozonisers having discharge gaps of 2.1, 2.9, and 4.2 mm. Increase in the width of the discharge gap reduces the concentration of ozone, because of the consequent rise in the temperature of the gas in the reaction zone. Equilibrium concentrations calculated for the case where the temperature of the gas in the reaction zone is 20° are independent of the discharge gap. The quadratic relation between the temperature drop in the gas and the width of the discharge gap makes it impossible to obtain high concentrations of ozone (of the order of 10–12 vol. %) in ozonisers with wide discharge gaps.

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Lomonosov Moscow
State University

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OXYGEN OVERPOTENTIAL AND POTENTIAL DECAY CURVES AT THE NICKEL OXIDE ELECTRODE

P. D. Lukovtsev and G. Ya. Slaidin¹

The use of curves showing the change in potential E with time t after the polarising current has been switched off, in order to obtain data on the kinetics of an electrochemical process, has been discussed in several papers^{1–5}. The general case was examined by Grahame⁴, who derived an equation for the potential decay curve when there are several limiting stages in the process. However, his equation proved to be too complicated for practical application.

Most of the experimental papers^{6–8} have utilised relations obtained by integrating the equation

$$C \frac{dE}{dt} + i = 0 \quad (1)$$

with certain simplifying assumptions, for example that the capacitance of the electrode C is constant and that the Tafel relation between the current i and the potential is maintained after the current has been switched off. Integration of Eqn. (1) yields

$$E = E' - b \log(t + \theta), \quad (2)$$

where $\theta = bc/2.3i_0$, b is the constant of the Tafel equation, and i_0 is the steady-state current immediately before the cell is disconnected.

Eqn. (2) and relations deduced on similar assumptions were used to determine the capacitance of Hg,⁷ Ni,^{6–8} Fe,⁸ and other cathodes. In these papers the application of equations analogous to (2) was restricted to narrow ranges of change in overpotential, within which the assumptions made in deriving these equations could be regarded as correct to a sufficient degree of approximation.

An investigation of the kinetics of the self-discharge of the nickel oxide electrode showed⁹ that the potential decay curves plotted as E against $\log(t + \theta)$ after the anodic current has been switched off consist of two linear portions with different slopes: i.e. equations similar in form to (2) hold for each section, the values of b being 0.028–0.040 V at high potentials and 0.016–0.023 V at low potentials.

It follows from Eqn. (2) that the slope of the decay curves is equal to that of the overpotential–current curves. Therefore Conway and Bourgault⁹ assume that the values which they obtained for the slope of the decay curves are equal to the constant b in the Tafel equation for the oxygen overpotential at a nickel oxide electrode, i.e. for the overpotential of the reaction governing the kinetics of the decay in potential after the anodic current has been switched off. On the basis of the numerical values thus obtained for b , they draw far-reaching conclusions about the mechanism of the processes taking place at a nickel oxide electrode, and in particular about the mechanism of oxygen evolution.

The slopes of the $E - \log i$ and the $E - \log(t + \theta)$ curves are equal only if the assumptions made in deriving Eqn. (2) are valid. With the nickel oxide electrode, at least one of the above postulates does not hold, since the capacitance of the electrode depends on the potential. Some of the conclusions reached by Conway and Bourgault⁹ from a comparison of Eqn. (2) with the experimental results are therefore open to doubt.

Lukovtsev and Temerin^{10,11} showed, by using the experimental relation between the potential of the nickel oxide electrode and the capacitance Q lost by discharge, that the quantities $b_1 = \partial \log i$, $b_2 = -\partial E / \partial \log t$, and $b_c = -\partial E / \partial \log Q$ are related as follows:

$$\frac{b_1 - b_2}{b_1} = \frac{b_1}{b_c + b_1}, \quad (3)$$

whence

$$b_1 = \frac{b_c b_2}{b_c - b_2}; \quad b_2 = \frac{b_1 b_c}{b_1 + b_c}; \quad b_c = \frac{b_1 b_2}{b_1 - b_2}. \quad (4)$$

Therefore calculation of the constant b in the Tafel equation for the oxygen overpotential requires knowledge not only of the constant b_2 of the decay curve but also the constant b_c .

In the present work relations (3), which have been confirmed with lamellar nickel oxide electrodes^{10,11}, have been studied on smooth electrodes of this type. The oxygen overpotential and the potential decay curves were therefore investigated experimentally with these electrodes in solutions of KOH, NaOH, and LiOH, and also in KOH solutions containing added WO_3 and ZnO .

The test electrode consisted of nickel foil 75 μ thick having an oxide film formed by anodising. The foil had first been degreased in hot 4 N KOH, washed with distilled and twice-distilled water, and then placed in the cell described in Ref. 12. Anodising was carried out in the test solutions at a current density of 22 $\mu\text{A cm}^{-2}$ for 14 h, films of thickness 100–400 Å being obtained.

Fig. 1 shows curves obtained potentiostatically for the relation between the potential E of the nickel oxide electrode, measured relative to that of the Hg/HgO electrode in the same solution, and the logarithm of the current density in electrolytes of various compositions†. It follows from Fig. 1 that, at potentials below 0.55 V, the slopes of the E – $\log i$ curves are practically the same, varying within the limits 0.100–0.128 V. At potentials above 0.55 V the slope of the curves decreases to 0.050–0.060 V.

Fig. 2 shows the potential decay curves at the same electrodes‡. The curves are seen to have practically the same slope $b_a = 0.041$ –0.047 V. Lower values of b_a were obtained⁹ for a non-lamellar (porous) nickel oxide electrode: 0.034 V in 2.9 M KOH, and 0.038 V in 7.1 M KOH.

The results plotted in Figs. 1 and 2 indicate that the cation of the alkali and additives in it have a marked effect on the oxygen overpotential and the position of the decay curves: the overpotential is higher and the curve is located

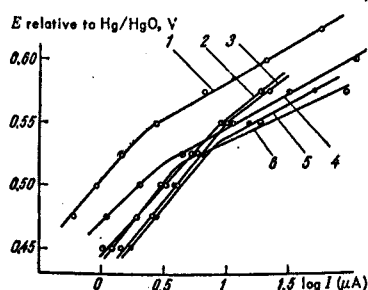


Fig. 1. Dependence of potential E on $\log I$ in solutions of: 1) 2 N LiOH; 2) 3.3 N KOH + ZnO (10 g of Zn per litre); 3) 3.3 N KOH; 4) 2 N NaOH; 5) 2 N KOH; 6) 3.3 N KOH + WO_3 (10 g of W per litre).

† Measurements were made passing from higher to lower potentials. At the highest potential a constant value of i was established after 1 h; at all other, lower potentials this value was established after 15 min.

‡ Before the decay curves were determined, the electrodes were polarised anodically at 22 $\mu\text{A cm}^{-2}$ for 14 h, and then maintained for 1 h at 0.625 V in the case of 2 N LiOH, 0.600 V with 2 N NaOH, and 0.575 V with all the other solutions.

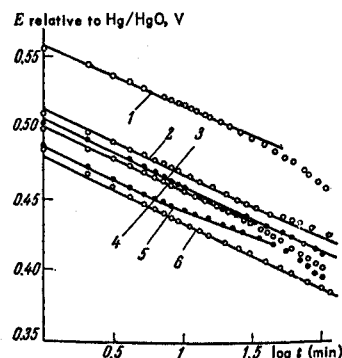


Fig. 2. Dependence of potential E on $\log t$ in solutions of: 1) 2 N LiOH; 2) 2 N NaOH; 3) 2 N KOH; 4) 3.3 N KOH + ZnO (10 g of Zn per litre); 5) 3.3 N KOH + WO_3 (10 g of W per litre); 6) 3.3 N KOH.

at higher potentials in the case of LiOH than in that of NaOH, and the same applies to the latter compared with KOH. Furthermore, in the more concentrated solutions (4 N KOH) the decay curve is located at less positive potentials.

Comparison of experimental data on the relation between oxygen overpotential and current at a nickel oxide electrode, obtained by direct polarisation measurements, with the potential decay curves shows that the latter differ in slope from the overpotential curves, contrary to the assumption made in Ref. 9. In all cases the decay curves have a smaller slope than the overpotential curves, in agreement with Eqn. (4).

Table 1 gives numerical values of the constants b_1 and b_a obtained experimentally, and of b_c calculated for a smooth electrode by means of Eqn. (4). It follows from Table 1 that the constant b_c has a higher value for a smooth than for a lamellar nickel oxide electrode¹¹.

For comparison, Table 1 gives also values calculated from experimental data¹³. The value of b_a was obtained by plotting the data shown in Fig. 3 of Ref. 13 as E against $\log t$. The value of b_c was obtained on the basis of the

TABLE 1.

Solution	b_1 , V	b_a , V	b_c , V
2 N LiOH	0.120	0.041	0.062
2 N NaOH	0.100	0.045	0.082
2 N KOH	0.120	0.047	0.077
3.3 N KOH	0.126	0.047	0.075
3.3 N KOH + ZnO	0.112	0.045	0.075
3.3 N KOH + WO_3	0.128	0.047	0.074
4 N KOH ¹³	0.123	0.047	0.076

* Region of low potentials, which corresponds to the range of potentials for the decay curves.

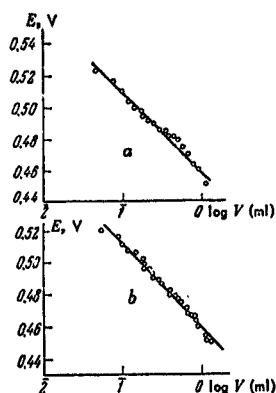


Fig. 3. Dependence on potential of the logarithm of the volume of oxygen evolved during the self-discharge of a nickel oxide electrode in:
 a) 0.015 M KOH (from data of Fig. 6a in Ref. 9);
 b) 0.145 M KOH (from data of Fig. 6b in Ref. 9).

data in Fig. 5 (curve 8) of Ref. 13. That of b_1 was calculated from b_a and b_c by means of Eqn. (4). It is seen from Table 1 that values calculated for the constants b_1 , b_a , and b_c from our data agree well with those obtained from experimental data¹³ for a smooth nickel oxide electrode.

It is also of interest to calculate these constants from the experimental data in Ref. 9 for a non-lamellar porous electrode. Numerical values of b_c can be obtained comparatively simply from the data in Ref. 9. For this purpose, the experimental results plotted in Fig. 6 of Ref. 9 are shown in Fig. 3 as E plotted against $\log V$, where V is the volume of oxygen evolved as a result of self-discharge, which corresponds to the capacitance Q .

It is seen from Fig. 3 that there is a linear relation over the whole range of values of E , with a slope b_c of 0.050 V for 0.015 M KOH and of 0.054 V for 0.145 M KOH.

The numerical values thus obtained for b_c together with values of b_a from Table 1 in Ref. 9 were used to calculate the constants b_1 by means of Eqn. (4), the results being shown in Table 2.

At high potentials the constant b_1 of the Tafel equation for the oxygen overpotential at a nickel oxide electrode is seen from Table 2 to be 0.117–0.177 V, which agrees in some measure with the values for the smooth electrode

(see Table 1). At low potentials $b_1 = 0.033$ – 0.043 V, in agreement with values obtained in several papers^{14–17} from direct measurements of the oxygen overpotential at low current densities. In this connection we must point out that we are unacquainted with papers in which direct polarisation measurements have yielded slopes for the oxygen overpotential at a nickel or a nickel oxide electrode of 0.016–0.023 V, as is assumed for low potentials in Ref. 9.

The results given in the present paper show that potential decay curves at a nickel oxide electrode can be used to determine the constant b in the Tafel equation for oxygen evolution only if the variation of the electrode capacitance with potential is taken into account. Disregard of this dependence leads to erroneous results and conclusions, as occurred in Ref. 9.

SUMMARY

1. Curves for the fall in potential with time and the overpotential for oxygen evolution at a smooth nickel oxide electrode have been studied in solutions of KOH, NaOH, and LiOH, and in KOH solutions containing added WO_3 and ZnO.
2. The experimental results thus obtained, together with data from the literature^{9,13}, were used to verify relation (3).
3. Errors made by Conway and Bourgault⁹ in determining the constant b_1 from the potential decay curves at a nickel oxide electrode are indicated.

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TABLE 2.

Solution	b_a^* , V	b_a^{**} , V	b_c , V	b_1^* , V	b_1^{**} , V
0.015 M KOH	0.039	0.020	0.050	0.177	0.033
0.145 M KOH	0.037	0.024	0.054	0.117	0.043

* At high potentials.

** At low potentials.

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Institute of Electrochemistry,
USSR Academy of Sciences

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KINETICS OF SORPTION AND ION EXCHANGE IN A CURRENT OF LIQUID WITH EXTERNAL DIFFUSION AS THE RATE-LIMITING PROCESS

V. S. Golubev and G. M. Panchenkov

Equations representing the kinetics of sorption and of ion exchange have been examined and discussed by several workers¹⁻³. Those obtained in Ref. 1 are generally accepted. The equations describe the kinetics of ion exchange for the following cases: (1) rate of exchange limited by external diffusion (external diffusion kinetics); (2) rate of exchange limited by internal diffusion (internal diffusion kinetics); and (3) rate of exchange limited by the rate of the ion-exchange reaction. The equations were derived for the case in which the kinetics are studied in a current of the liquid phase. However, as will be shown below, neglect by these workers¹ of the hydrodynamic conditions of the experiment makes their kinetic equation valid only for cases in which there is no flow of the liquid phase, i.e. those in which the kinetics of the process are studied under static conditions. The presence of a flux of the liquid phase results in a change in the numerical constants in the equations of external diffusion kinetics.

Derivation of Equation of External Diffusion Kinetics for Equilibrium Sorption (Ion Exchange)

Let us suppose that, through a column filled with an adsorbent, a solution of the substance to be adsorbed is passed. The experiment is carried out under conditions (thin layer of adsorbent, sufficiently high concentration of substance entering the column) such that the concentration of the solution at any instant at a point in the column remote from an adsorbent grain can be regarded as constant. The case is considered in which equilibrium at the adsorbent surface is established instantaneously. The rate of sorption (ion exchange) will then be limited by diffusion of the adsorbate to the surface of the adsorbent. In this case the process is taking place in the region of so-called external diffusion kinetics.

We shall assume laminar flow of the adsorbate through the column. Then the whole of the liquid can be divided into two regions, one remote from the surface of the adsorbent, where the concentration of the solution is constant, and one close to this surface, where the concentration varies owing to diffusion and adsorption. The latter

region represents a boundary diffusion layer. To find the concentration distribution in this layer, we shall use a method developed by Levich⁴, and set up the material balance equation for an arbitrary volume V of the column surrounding an adsorbent particle. The total flux of matter in unit time through 1 cm² of surface surrounding the volume V is

$$\vec{j} = \vec{j}_D + \vec{j}_c = -D \text{grad } c + c\vec{u}, \quad (1)$$

where $\vec{j}_D$ is the diffusional flux, $\vec{j}_c$ the convective flux due to the motion of the liquid, c the concentration of the adsorbate (in g cm⁻³), $\vec{u}$ the rate of flow of the liquid (in m sec⁻¹), and D the diffusion coefficient. The amount of material entering the volume V in 1 sec is

$$Q = -\oint \vec{j} dS,$$

where the integral is taken over the surface surrounding the volume V . On applying to the material balance equation

$$\oint \kappa \frac{\partial c}{\partial t} dV = \oint \vec{j} dS \quad (2)$$

(where κ is the fraction of the cross-section of the column which is available) the Ostrogradskii-Gauss formula, we shall obtain, in view of the incompressibility of the liquid ($\text{div } \vec{u} = 0$), the following equation of convective diffusion:

$$\kappa \frac{\partial c}{\partial t} + (\vec{u} \text{ grad}) c = D \nabla^2 c, \quad (3)$$

where ∇^2 is the Laplace operator. Assuming the adsorbent particles to be spherical and of identical size, we can write Eqn. (3) in spherical coordinates for steady-state experimental conditions:

$$u_r \frac{\partial c}{\partial r} + \frac{u_\theta}{r} \frac{\partial c}{\partial \theta} = D \left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \frac{\partial c}{\partial r} \right), \quad (4)$$

where u_r is the radial component of the rate of flow of the liquid phase $\vec{u}$, and u_θ the tangential component of $\vec{u}$. The boundary conditions for this process will be

$$\begin{cases} c = f(q), & r = r_0 \text{ (at the adsorbent surface),} \\ c = c_0 & r \rightarrow \infty \text{ (remote from the adsorbent surface),} \\ c = c_0, & r = r_0, \theta = 0, \end{cases} \quad (5)$$

where r_0 is the particle radius, and q the adsorbate concentration in grammes per cm³ of adsorbent. The expression $c = f(q)$ is the equation to the molecular sorption isotherm. The third condition in (5) implies that the concentration of the solution at the point where the flux strikes the particle ($r = r_0, \theta = 0$) is the same as the bulk concentration, owing to the fact that diffusion is absent in the inflowing current⁵.

The solution of Eqn. (4) with the boundary conditions (5) is based on reducing the equation for convective diffusion to an equation of the thermal conductivity type, the integration of which, given in Levich's book⁴, is considerably simpler than that of Eqn. (4). On the assumption that the thickness of the layer within which the sharp change in adsorbate concentration occurs is small compared with the particle size, integration of Eqn. (4) taking into account (5) yields the following distribution of concentration in the boundary diffusion layer:

$$c(z) = \frac{c_0 - f(q)}{1.16} \int_0^z e^{-\frac{1}{2}z^2 + \frac{1}{2}z} dz + f(q). \quad (6)$$

Here $z = z(r, \theta; D, u)$ is a new variable introduced to simplify the integration of Eqn. (4).