INTERPRETING DATA ON THE ANODIC EVOLUTION OF OXYGEN

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During the anodic evolution of oxygen on metals of the iron-copper group under various conditions, values of b close to 1/2 RT/F, 2/3 RT/F, and RT/F have been observed (cf. the survey [1]). Usually the value b = 1/2 RT/F is explained by the slowness of some chemical step or other, while the value 2/3 RT/F is associated with the slowness of the reaction which is the analog of electrochemical desorption

$$OH_{ads} + OH^- \rightarrow O_{ads} + H_2O + e. \quad (1)$$

Krasil'shchikov [1, 2] considers that this reaction occurs in two steps

$$OH_{ads} + OH^- \rightarrow O^-_{ads} + H_2O \quad (1a)$$

$$O^-_{ads} \rightarrow O_{ads} + e. \quad (1b)$$

He associates the slope 2/3 RT/F with the second step, and the slope RT/F with Eq. (1a).

The slow reaction of Eqs. (1) or (1b), or a different reaction of the electrochemical desorption type, e.g., Eq. (2), is in an important sense the process reverse to the reduction of molecular oxygen

$$OOH_{ads} + OH^- \rightarrow O_2 + H_2O + e, \quad (2)$$

with the corresponding value $b = \frac{1}{1+\alpha}\frac{RT^*}{F}$. With $\alpha = 1/2$, $\alpha = 1/2$ $b = 2/3\frac{RT}{F}$

However, α may take on other values. We have shown the possibility in principle of two limiting electrode reactions: activation-free ($\alpha = 0$) at sufficiently high overvoltages, and barrier-free ($\alpha = 1$) at sufficiently low overvoltages [3-5]. If Eqs. (1) or (2) proceeds barrier-free, $\alpha = 1$ and b = 1/2 RT/F, if activation-free, $\alpha = 0$ and b = RT/F.

Thus an account of the possibility of barrier-free or activation-free path of the process allows one to explain the observed values of the slope of the polarization curve without having to make assumptions about the various limiting steps, and by assuming a change in the nature of only one process or another.

Using the ordinary methods of calculation, and considering the adsorption of hydroxyl or, correspondingly, hydroperoxide to be of the Langmuir type, one can obtain the following expression for the potential as a function of current (in an alkaline solution):

$$\varphi = \text{const} + \frac{RT}{(1+\alpha)F}\ln i - \frac{1-\alpha}{1+\alpha}\psi_1 - \frac{2}{1+\alpha}\frac{RT}{F}\ln c_{OH^-}. \quad (3)$$

The second order of this reaction with respect to OH^- ion, as is observed under corresponding conditions on a Ni anode [6], follows when there is an excess of the base electrolyte, i.e., at a constant ψ_1-potential. In pure alkali, if the dependence of ψ_1 on c_{OH^-} follows the Stern theory, the reaction order at constant potential is $1 + \alpha$ on a negatively charged surface. The latter situation seems likely, since the equilibrium points of metal oxides can be at very positive potentials [7]. It is possible that it is with this circumstance that the reaction order 2.5 observed on nickel in pure alkial [1, 2] is connected.

The values of the corresponding coefficients which follow from Eq. (3) (and from the analogous expression for the discharge from acidic solutions) are summarized in Table 1. A comparison with experimental data (done in detail in [5]) shows a satisfactory agreement for the evolution of oxygen on Ni (under different conditions, $\alpha = 1, 1/2$,

* Equation (2), just as Eq, (1), can in principle occur in two steps, with prior formation of adsorbed O_2^-.

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TABLE 1

α	$b = \frac{\partial \eta}{\partial \lg i}$	$\left(\frac{\partial \eta}{\partial \psi_1}\right)_{pH}$	$\left(\frac{\partial \eta}{\partial pH}\right)_{\psi_1}$	$\frac{\partial \eta^*}{\partial \lg c}$ charge on electrode surface		$\left(\frac{\partial \eta}{\partial \lg x_{H_2O}}\right)^{**}_{pH, \psi_1}$
				positive	negative	
Discharge of OH^- ions						
0	$2,3\frac{RT}{F}$	-1	$-2,3\frac{RT}{F}$	0	$-2\cdot 2,3\frac{RT}{F}$	$-\frac{1}{2}\cdot 2,3\frac{RT}{F}\left(1+\frac{\partial \lg \gamma_{H_2O}}{\partial \lg x_{H_2O}}\right)$
1/2	$\frac{2}{3}2,3\frac{RT}{F}$	$-\frac{1}{3}$	$-\frac{1}{3}2,3\frac{RT}{F}$	0	$-\frac{2}{3}2,3\frac{RT}{F}$	$-\frac{1}{2}2,3\frac{RT}{F}\left(1+\frac{1}{3}\frac{\partial \lg \gamma_{H_2O}}{\partial \lg x_{H_2O}}\right)$
1	$\frac{1}{2}2,3\frac{RT}{F}$	0	0	0	0	$-\frac{1}{2}2,3\frac{RT}{F}$
Discharge of H_2O molec.						
0	$2,3\frac{RT}{F}$	0	0	0	0	$-2,3\frac{RT}{F}\left(\frac{3}{2}+\frac{1}{2}\frac{\partial \lg \gamma_{H_2O}}{\partial \lg x_{H_2O}}\right)$
1/2	$\frac{2}{3}2,3\frac{RT}{F}$	$\frac{1}{3}$	$\frac{1}{3}2,3\frac{RT}{F}$	$-\frac{2}{3}2,3\frac{RT}{F}$	0	$-2,3\frac{RT}{F}\left(\frac{5}{6}+\frac{1}{2}\frac{\partial \lg \gamma_{H_2O}}{\partial \lg x_{H_2O}}\right)$
1	$\frac{1}{2}2,3\frac{RT}{F}$	$\frac{1}{2}$	$\frac{1}{2}2,3\frac{RT}{F}$	$-2,3\frac{RT}{F}$	0	$-2,3\frac{RT}{F}\left(\frac{1}{2}+\frac{1}{2}\frac{\partial \lg \gamma_{H_2O}}{\partial \lg x_{H_2O}}\right)$

* c is the concentration of the pure alkali (OH^- discharge) or acid (H_2O discharge).

† x_{H_2O} is the mole fraction of water, and γ_{H_2O} is its activity coefficient.

and 0), Co (α = ½ and 0), Fe (α = ½ and 0 in alkaline and α = 1 and ½ in acid solutions), Cu (α = ½ and 0, for the formation of cupric oxide α = 0), and Au (α = 0 in acidic and alkaline solutions; during very slow recording of the polarization curves the slope of the curve is somewhat smaller than RT/F, apparently because of a gradual change in the state of the surface).

The different values of the slopes corresponded for the majority of electrodes to different conditions of electrode preparation. On the copper oxide electrodes only were there observed simultaneously two regions with slopes of 2/3 RT/F and, at higher current densities, RT/F [8]. It is this picture which should be observed in the transition with increase in potential, i.e., with a lowering of the activation energy from the ordinary Eqs. (1) or (2) (α = ½) to the activation-free process (α = 0). It is of interest to note that at not too high alkali concentrations the dependence of the overvoltage on the concentration, for both branches of the curve, corresponds to the theoretical dependence for the negatively charged surface.

The kinetics behaviors shown above were with reference to the case of Langmuir adsorption. If the filling of the surface by active oxygen-containing particles cannot be considered small, i.e., if there is a noticeable adsorption capacitance observed experimentally, then the picture becomes considerably more complicated. An analysis incorporating several approximations shows that the combination of large capacitance and small values of b is improbable according to Eq. (1), but completely possible during the slow step, Eq. (2), [5].*

The value of the coefficient b = RT/F can be explained in three different ways: by the slowness of the chemical step, Eq. (1a), by the activation-free flow of the electrochemical reaction, or by the influence of the nature of the adsorption thermal.

It is probable for anodes of iron group oxides that important amounts of electrochemically active oxygen are present on their surfaces. This allows one in principle to explain the low values of b, as was done by Conway et al. (cf., e.g., [10]), by the particularities of the kinetics of heterogeneous reactions with non-Langmuir adsorption components (although other mechanisms are not excluded). For copper and gold anodes, however, the capacitance is close to that of the double layer [11-13], so that this explanation is not possible for them.

* It was assumed in this analysis that the adsorption isotherm was close to logarithmic, and that the influence of any adsorbed particles on the energy of adsorption of all particles is practically the same (the latter idea can be based on the model of interaction of adsorbed atoms through a surface electronic gas, proposed by Temkin [9]). The reason for the difference in the behaviors for Eqs. (1) and (2) lies in the fact that the first of these occurs without change, and the second with a change, in the number of chemisorbed particles.

The assumption of the slowness of Eq. (1a) – the electrolytic dissociation of adsorbed hydroxyl – seems to demand a special basis. The flow of the reaction along this path in strongly acid solutions, in which the degree of dissociation of OH_{ads} must be very small, seems especially improbable. On the gold anode, b = RT/F is observed even in strongly acid solutions [11, 14]. For this anode, at least, it seems to us more intelligent to explain the experimental data by an activation-free reaction of the electrochemical desorption type, Eqs. (1) or (2).

The process by which oxygen evolves is very complicated, and we do not pretend that the treatment in this paper is universal. The goal of our analysis was only to demonstrate that an account of the possibility of barrier-free or activation-free electrode processes can be useful in an interpretation of the behaviors of these reactions.

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