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Abstract

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ON THE MECHANISM OF THE ANODIC OXIDATION OF SILVER IN ALKALI

(Presented by Academician A. N. Frumkin on 24 VII 1961)

In a previous paper (1), the peculiarities of the passivation of silver in alkaline solutions were described. In particular, in studying the anodic oxidation of silver in alkali at constant potential, it was found that in the first minutes after switching on the anodic polarization there is a strong retardation of the overall rate of the process Ag → Ag_2O. This is expressed in a sharp drop in the current. Judging from the quantity of electricity, a layer of Ag_2O about 10^{-6} cm thick is formed in this process.* Having decreased upon formation of such a layer, the dissolution rate remains constant for some time (plateau *a* on the curve *i*, Fig. 1), after which it decreases again. The aim of the present work was to clarify the causes of these two successive retardations in the rate of anodic oxidation of silver.

Overvoltage curves were recorded for the process Ag → Ag_2O. Figure 2 shows such a curve (*a*) for a 0.1 *N* KOH solution. At a current density of about $1 \cdot 10^{-4}$ A/cm^2, a sharp rise is observed on the overvoltage curve, resembling the attainment of a limiting diffusion current. The constancy of the current over a certain time interval on the potentiostatic curves (plateau *a*, Fig. 1) could also be explained by a limiting current. However, the magnitude of the limiting current and its independence of the KOH concentration (within the range from 0.1 to 10 *N*) rule out the assumption of concentration polarization in the solution with respect to OH^- ions. In our opinion, this limiting current is associated with diffusion limitations in the Ag_2O layer that forms at the first moment after the anodic current is switched on. Indeed, regardless of the boundary at which the electrochemical process occurs (Ag/Ag_2O or Ag_2O/solution), the reacting particles of silver or oxygen must diffuse through the Ag_2O layer. To test the above assumption, it was necessary to determine whether diffusion difficulties of such magnitude actually exist for the oxidation of silver. We used the method of measuring the components of the electrode impedance in alternating current at various frequencies. Usually, as a criterion for the existence of concentration polarization, the dependence of the components of the electrode impedance on $1/\sqrt{\omega}$ is used (ω is the angular frequency of the alternating current). In this case,

Figure 1

Figure 1: Figure 1

in those instances where the capacitance of the double layer can be neglected, a rectilinear dependence is obtained (^{2}). In our case such a simplification is inadmissible, since the expected diffusion must proceed in a solid phase and, naturally, must have an impedance several orders of magnitude greater than with concentration polarization in solutions. Thus, in the case under study the dependence of the impedance components on $1/\sqrt{\omega}$ has a more complex character. We used the method proposed by Leikis and Knots (^{3}) for detecting concentration polarization under the conditions described above. If one assumes that the electrode in the absence of concentration polari-

* In the calculation it was assumed that the roughness factor of the electrode is equal to 3.

···can be modeled by a circuit consisting of a parallel-connected capacitance C_2 and resistance R_2, representing the capacitance of the double layer and the resistance of the process; then the impedance of the entire electrode is equal to:

$$\dot{Z} = R_0 - jX_0 = \frac{R_2}{1+(\omega R_2 C_2)^2} - j\frac{\omega R_2^2 C_2}{1+(\omega R_2 C_2)^2},$$

where R_0 is the active component, measured by the series circuit, and X_0 is the reactive component.

As is seen from this formula, when the frequency of the alternating current is decreased, R_0 increases and tends to R_2. If, however, a term equivalent to concentration polarization is included in the model circuit, then the active resistance increases without limit with increasing $1/\sqrt{\omega}$, since the resistance of the concentration term itself is an unbounded function of $1/\sqrt{\omega}$.

Fig. 1. Dependence of the oxidation current (i) and the resistance of the electrochemical stage of the process (R_2) on silver in $0.1\,N$ KOH solution at a constant potential of 0.32 V.

Figure 3 gives the experimental curve for the change in the ohmic component as a function of $1/\sqrt{\omega}$. As is seen from the figure, the active component R_0 in the frequency interval studied does not tend to a limiting value and exceeds the experimentally obtained value (R_2) for the resistance of the electrochemical stage of the process

$$\mathrm{Ag} \rightarrow \mathrm{Ag_2O},$$

indicated by the dotted line. This agrees with the assumption that the electrode circuit contains a concentration term. The resistance equivalent to con-

Figure 2

Figure 2: Figure 2

centration polarization, at the lowest frequencies we used, is 150 $\Omega \cdot \mathrm{cm}^2$, i.e., approximately 100 times greater than the resistance of concentration polarization measured at the same frequencies by Ershler and Rosenthal (^{2}), even in $0.001\,N$ aqueous solutions of the diffusing ion. Such a large resistance could be explained by concentration polarization in a solution in which the concentration of the diffusing ion is $\sim 10^{-5}\,N$. Thus, it may be assumed that concentration polarization could arise from silver ions, since the solubility of Ag_2O in $0.1\,N$ KOH is of the order of 10^{-5} g-eq/l.* However, when the alkali concentration is changed, the solubility of Ag_2O changes by many times and, consequently, the ohmic component R_0 should have changed by the same factor; in fact it does not change and has the same values at the same frequencies for $0.02\,N$, $0.1\,N$, and $10\,N$ KOH solutions. This independence of the resistance from the composition of the solution indicates that the observed concentration polarization cannot be explained by the low solubility of the product of the anodic process. Evidently, concentration polarization takes place in the solid phase, i.e., in the Ag_2O layer.* Thus, the process Ag → Ag_2O, after the silver surface is covered by an Ag_2O layer, is limited by diffusion of the reacting particles through the oxide. During the further course of the Ag → Ag_2O process, the thickness of the diffusion layer in the oxide film does not increase substantially. It is possible that the latter is explained by differences in the structure of the films (a dense Ag_2O layer is formed on the silver surface, while a loose Ag_2O layer is formed on the Ag_2O substrate) or by the action of the solution on the outer parts of the film. An analogous phenomenon, as is known, is observed during formation of an anodic film on aluminum in sulfuric

Fig. 2. Overvoltage of the process Ag → Ag_2O in $0.1\,N$ KOH. *a*—on an active electrode; *b*—on a passivated electrode.

$\lg i$ (a/cm^2) ⟶

b

0.4, 0.3, 0.2

−6, −5, −4

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* The equilibrium solubility of Ag_2O in $6.6\,N$ KOH is $54 \cdot 10^{-5}$ g-eq/l; in $0.25\,N$ KOH it is $3.5 \cdot 10^{-5}$ g-eq/l; in $0.02\,N$ KOH it is $0.67 \cdot 10^{-5}$ g-eq/l (^{4}).

Fig. 3. Dependence of the active component of the impedance of a silver electrode on frequency in 0.1 N KOH

Figure 3: Fig. 3. Dependence of the active component of the impedance of a silver electrode on frequency in 0.1 N KOH

acid. We believe that Ag^+ ions and electrons diffuse through the dense Ag_2O film, while the electrochemical stage of the reaction occurs at the Ag_2O/solution boundary.

Fig. 3. Dependence of the active component of the impedance of a silver electrode on frequency in 0.1 N KOH

This diffusion-limited process, as we indicated earlier, does not proceed at a constant rate until the silver is completely consumed, but slows down as a result of passivation, which is expressed in a decrease in the oxidation rate. At a potential of 0.32 V it falls to a value of $2 \cdot 10^{-6}$ a/cm^2. In this state the electrode is passive: it is sufficient to increase the anodic current, for example, to a value of $1 \cdot 10^{-5}$ a/cm^2, and the electrode potential within seconds rises to the potential of a new process, $Ag_2O \rightarrow AgO$. Passivation is also indicated by a shift of the overvoltage curve. As can be seen from Fig. 2, overvoltage curve 6, recorded on a passive electrode (when, during potentiostatic measurement, the dissolution rate fell to $2 \cdot 10^{-6}$ a/cm^2), is located to the left of the curve recorded on an active electrode.

The observed passivation is not associated with diffusional difficulties. This is shown by the dependence, in this region, of the active component of the electrode impedance on frequency. Increasing as the frequency decreases, it tends to a limiting value at low frequencies. The presence of a limit in the active component (^{3}) indicates the absence of concentration polarization here.

It should be noted that the resistance of the electrochemical process, calculated from the slope of the overvoltage curve and from the value of i, increases throughout the entire oxidation process, reaching at its end a constant value equal to approximately 20 000 ohm $\cdot$ cm^2. Direct measurements of the resistance by alternating current (R_2) characterize a faster stage of the $Ag \rightarrow Ag_2O$ process. We assume that this stage is the electrochemical adsorption of oxygen on the surface of Ag_2O oxide. The resistance of this stage, which remains two orders of magnitude smaller than the rate of the electrochemical oxidation process itself, also increases and likewise becomes constant at its end (Fig. 1). It may be considered that further retardation of the overall reaction of electrochemical oxidation of silver is caused by adsorption of oxygen on the surface of Ag_2O oxide. The slowest stage of the entire process is probably the ionization of an atom

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* From the data obtained, assigning the thickness of the diffusion layer an av-

erage value of $5 \cdot 10^{-7}$ cm, we determined the diffusion coefficient of Ag^+ ions in Ag_2O. The diffusion coefficient was determined from the equations for the limiting current under stationary diffusion

$$i_d = \frac{nFD \cdot C}{\delta}$$

and the equation for concentration resistance in alternating current:

$$R_k = \frac{RT}{n^2F^2}\frac{1}{C}\sqrt{\frac{1}{2D\omega}}.$$

The value obtained for D is of the order of 10^{-12} cm^2/sec, i.e., comparable with the values of the diffusion coefficients of Ag^+ ions in Cu_2S or Cu^+ in Ag_2S at room temperature.

silver on the surface of Ag_2O. Passivation from this point of view consists in the fact that, as a result of the accumulation of firmly adsorbed oxygen on the surface of the oxide, both the rate of oxygen adsorption and the rate of ionization of silver atoms decrease.

Thus, at the moment the anodic polarization is switched on, the rate of anodic dissolution of silver is limited by the electrochemical stage. When an amount of electricity of approximately 20 $\mu C/cm^2$ is passed, a continuous Ag_2O film forms on the silver, and the rate of anodic oxidation of silver begins to be limited by the rate of diffusion of silver ions through the film that has formed. For some time the process proceeds at this constant rate, and then passivation occurs at the oxide/solution boundary, consisting in a slowing of the electrochemical stage of the silver oxidation process.

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