THE MECHANISM OF ANODE OXIDATION OF SILVER IN ALKALI

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(Presented by Academician A. N. Frumkin July 24, 1961)
Translated from Doklady Akademii Nauk SSSR, Vol. 142, No. 1,
pp. 109-112, January, 1962
Original article submitted July 18, 1961

A previous paper [1] has described the special features of the passivation of silver in solutions of alkali. In particular, in studying the anode oxidation of silver in alkali at constant potential, it was observed that in the first few minutes after applying the anode polarization, a marked retardation in the overall rate of the reaction Ag→Ag_2O occurs. This makes itself known by a sharp drop in the current strength. Judging from the quantity of electricity passed, what is formed here is a layer of Ag_2O about 10^{-6} cm thick*. After having dropped off while the layer was being formed, the rate of solution remains constant for some time (the flat portion a on the curve i, Fig. 1) after which it again drops. The problem of the present paper was to dicover the causes of these two stages of retardation in the silver anode oxidation rate.

Curves were taken of the overvoltage of the reaction Ag→Ag_2O. Figure 2 gives a curve of this sort (a) for 0.1 N KOH solution. For a current density of about $1 \cdot 10^{-4}$ amp/cm^2 a sharp rise is observed in the overvoltage curve, similar to reaching a limiting diffusion current. A limiting current might also be used to explain the fact that the current is constant over a certain length of time on the static potential curves (flat region a, Fig. 1). However, the magnitude of the limiting current, and the fact that it is independent of the KOH concentration (over the range from 0.1 to 10 N) exclude any assumption of concentration polarization in this solution from OH-ions. In our opinion, this limiting current is a matter of diffusional limitations in the Ag_2O layer, which forms immediately after the anode current is turned on. Actually, independently of what boundary the electrochemical reaction is occurring on (Ag/Ag_2O, or Ag_2O/solution), the reacting particles of silver or oxygen must diffuse through a layer of Ag_2O. In order to check the above assumption, it was necessary to find out whether or not there are in fact diffusional hinderances of this magnitude in the silver oxidation reaction. We have employed the method of measuring the components of the electrode impedance with alternating current at various frequencies. The usual criterion for the existence of concentration polarization is that the components of the electrode impedance are a function of $1/\sqrt{\omega}$ (ω is the angular frequency of the alternating current). Here, in those cases where it is possible to neglect the capacitance of the double layer, a linear relationship is obtained [2]. In our case, this simplication was inadmissable since the expected diffusion was supposed to take place in the solid phase and naturally would have an impedance several orders of magnitude greater than for concentration polarization in solutions. Thus, in the case under study, the relation between the impedance components and $1/\sqrt{\omega}$ is of a more complicated nature. We used a method, proposed by Leikis and Knots [3], to observe concentration polarization under the conditions described above. If we assume that in the absence of concentration polarization the electrode may be represented by an equivalent circuit consisting of a capacitance C_2 and a re-

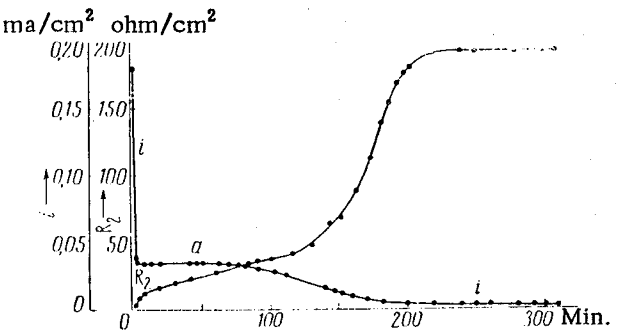

Fig. 1. Curve of oxidation current (i) and resistance of the electrochemical stage of the process (R_2) on silver in 0.1 N KOH solution at a constant potential of 0.32 v.

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

sistance R_2 in parallel, representing the capacitance of the double layer and the resistance of the process, the impedance of the whole 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 for the equivalent circuit, and X_0 is the reactive component.

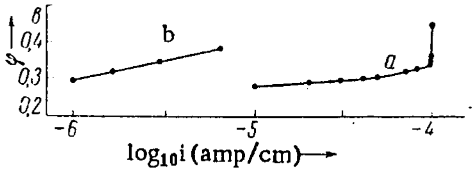

Fig. 2. Overvoltage of the reaction Ag→Ag_2O in 0.1 N KOH. a) On active electrode; b) on passivated electrode.

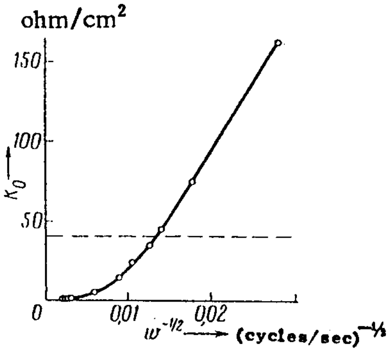

Fig. 3. Active component of impedance of silver electrode as a function of the frequency in 0.1 N KOH.

As may be seen from this formula, as the frequency of the alternating current is reduced, R_0 increases and approaches R_2. If, however, an element is inserted into the equivalent circuit to correspond with concentration polarization, the active resistance increases without limit as $1/\sqrt{\omega}$ increases, since the resistance of the concentration term is itself an unbounded function of $1/\sqrt{\omega}$.

Figure 3 gives an experimental curve of the change in ohmic resistance as a function of $1/\sqrt{\omega}$. As may be seen from the figure, in the frequency range studied, the active component R_0 does not approach a limit, and exceeds the experimentally obtained value (R_2) for the resistance of the electrochemical stage of the reaction Ag→Ag_2O, which is shown dotted. This supports the assumption that the electrode circuit contains a concentration term. The resistance, equivalent to the concentration polarization at the lowest of the frequencies which we used, is equal to 150 ohm · cm^2, i.e., approximately 100 times greater than the resistance of the concentration polarization measured at these same frequencies by Ěrshler and Rosental' [2] even in 0.001 N aqueous solutions of the diffusing ion. A resistance this large could be explained by concentration polarization in a solution, in which the concentration of the diffusing ions is ~10^{-5} N. Thus, it may be assumed that concentration polarization could arise with the silver ions, since the solubility of Ag_2O in 0.1 N KOH is of the order of 10^{-5} gram-equiv/liter*. However, if the alkali concentration is varied, so that the solubility of Ag_2O varies many times, and, consequently, the ohmic resistance ought to change by just as many times, R_0 does not change, and has the same values for the same frequencies in 0.02 N, 0.1 N, and 10 N KOH solutions. The fact that the resistance of the solution is independent in the composition indicates that the concentration polarization observed cannot be explained by low solubility of the product of the anode reaction. Obviously, the concentration polarization occurs in the solid phase, i.e., the Ag_2O layer**. Thus, after the silver surface is closed off by the Ag_2O

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* The equilibrium solubility of Ag_2O in 6.6 N KOH is $54 \cdot 10^{-5}$ gram-equiv/liter, in 0.25 N KOH it is equal to $3.5 \cdot 10^{-5}$ gram-equiv/liter, and in 0.02 N KOH is equal to $0.67 \cdot 10^{-5}$ gram-equiv/liter [4].

** From the data obtained, taking the mean value of the thickness of the diffusion layer to be $5 \cdot 10^{-7}$ cm, we found the diffusion coefficient of the Ag^+ ions in Ag_2O. The diffusion coefficient was found from the equations for the limiting current with stationary diffusion, $i_d = nFD \cdot C/\delta$, and the equation for the concentration resistance with alternating current: $R_K = \frac{RT}{n^2F^2}\frac{1}{C}\sqrt{\frac{1}{2D\omega}}$. The values of D found are 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.

layer, the reaction Ag →Ag_2O is limited by diffusion of the reacting particles through the oxide. During the subsequent course of the reaction Ag →Ag_2O, the thickness of the diffusion layer in the oxide film is not substantially increased. This fact can possibly be explained by a difference in structure of the films (a dense layer of Ag_2O is formed on the silver surface, while on the Ag_2O backing, a loose layer of Ag_2O is formed), or it may be explained by the effect of the solution on the oxide portions of the film. A similar phenomenon is, as we known, observed, in the formation of the anode film on aluminum in sulfuric acid. We assume that Ag^+ ions and electrons diffuse through the dense Ag_2O film and that the electrochemical stage of the reaction goes on the Ag_2O/solution boundary.

This limited diffusion process, as we have shown earlier, does not go at a constant rate until all the silver is used up, but is retarded as a result of passivation, which is reflected as a reduction in the oxidation rate. At a potential of 0.32 v it drops to a value of $2 \cdot 10^{-6}$ amp/cm². In this state, the electrode is passive: It is sufficient to raise the anode current, for example, to the value of $1 \cdot 10^{-5}$ amp/cm² to make the electrode potential increase in the course of seconds to the potential of the new reaction $Ag_2O \rightarrow AgO$. The shift in the overvoltage curve also gives evidence of passivation. As may be seen from Fig. 2, the overvoltage curve, b, taken on the passive electrode (when, in the static potential measurement, the solution rate has fallen to $2 \cdot 10^{-6}$ amp/cm²), is located to the left of the curve taken on the active electrode.

The passivation observed has nothing to do with diffusional hinderances. This is shown by the way the active component of the electrode impedance varies with frequency. Increasing with decreasing frequency, it approaches a limit at low frequencies. The fact that a limiting value of the active component exists [3] indicates that no concentration polarization is present here.

It should be noted that the resistance of the electrochemical reaction, calculated from the slope of the overvoltage curve and the value of i, increases in the course of the whole oxidation process, reaching at the end a constant value, equal approximately to 20,000 ohm · cm². However, direct measurements of the resistance with alternating current (R_2) show a more rapid stage of the reaction Ag →Ag_2O. We assume that this stage is one of electrochemical adsorption of oxygen on the surface of the oxide Ag_2O. The resistance of this stage, which remains two orders of magnitude below the rate of the electrochemical oxidation process itself, increases and also becomes constant in the end (Fig. 1). It may be assumed that the subsequent retardation of the over-all electrochemical silver oxidation reaction is caused by the adsorption of oxygen on the surface of the oxide Ag_2O. The slowest stage of the whole reaction is probably the ionization of the silver atom on the Ag_2O surface. From this point of view, the passivation consists in the fact that, as a result of accumulation of strongly adsorbed oxygen on the oxide surface, both the adsorption rate of the oxygen, and the ionization rate of the silver atoms is reduced.

Thus, at the moment the anode polarization is applied, the anode silver solution rate is limited by the electrochemical stage. If the electric charge is passed at a density of approximately 20 millicoulomb/cm², a continuous Ag_2O film is formed on the silver, and the anode silver oxidation rate begins to be limited by the rate of diffusion of silver ions through the film being formed. The reaction continues at this constant rate for a certain length of time, and then passivation occurs at the oxide/solution boundary, consisting in retardation of the electrochemical stage of the silver oxidation reaction.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.
