PHYSICAL CHEMISTRY

Yu. V. PLESKOV

1957

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

Yu. V. PLESKOV

FORMATION OF DIVALENT AND TRIVALENT SILVER IN ALKALINE SOLUTIONS ON A ROTATING DISK ELECTRODE

(Presented by Academician A. N. Frumkin on 21 V 1957)

A number of studies have been devoted to the electrooxidation of silver. The anodic voltage curves of a silver electrode in NaOH solutions have two steps, the potentials of which are close to the equilibrium potentials $\varphi_{Ag|Ag_2O} = 0.344$ V and $\varphi_{Ag_2O|Ag_2O_2} = 0.57$ V. The third step corresponds to the evolution of oxygen. Apparently, at sufficiently low current densities Ag is reversibly oxidized to Ag_2O and then to Ag_2O_2 ([1]). According to another point of view, Ag_2O_2 arises not directly as a result of the electrode process, but through decomposition of a higher silver oxide initially formed at the electrode ([2]).

When powders of Ag and Ag_2O are oxidized by ozone in NaOH solutions, they acquire a potential close to the equilibrium potential $\varphi_{Ag_2O_2|Ag_2O_3} = 0.79$ V. When the oxidant is removed, the potential falls to $\varphi_{Ag_2O|Ag_2O_2}$. Apparently, in alkaline solutions trivalent silver is practically unstable ([3]). During anodic oxidation of Ag^+ ions in neutral and acid solutions containing the anions NO_3^-, ClO_4^-, SO_4^{2-}, and F^-, mixed compounds of mono-, di-, and trivalent silver are formed ([4]).

Ions of di- and trivalent silver are thermodynamically unstable in aqueous solutions ([5]).

Together with B. N. Kabanov ([6]), we determined the solubility of Ag_2O in concentrated KOH solutions and showed that monovalent silver ions form a trinuclear singly charged complex, the composition of which can be expressed by the formula $[Ag_3O(OH)_2]^-$.

The mechanism of oxidation of the silver electrode in alkaline electrolytes has still not been clarified. In particular, it is not known whether oxidation occurs in the solid phase or whether silver ions pass into solution and are then discharged at the electrode. Therefore it seemed of interest to us to study the anodic oxidation and reduction of alkaline Ag_2O solutions.

As the anode we used a gold electrode, which, for activation before the start of individual measurements, was subjected alternately to cathodic and anodic

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

polarization in 1 N H_2SO_4. We recorded curves in KOH solutions (8.4-13.4 g-equiv/l), saturated with Ag_2O, at various electrode rotation rates; one of the curves is shown as an example in Fig. 1 (curve 1).

Simultaneously with the oxidation of Ag_2O at the anode, a parallel process occurs—oxygen evolution. In order to separate the current going to the silver oxidation process, which depends on the intensity of stirring, from the current going to the discharge of hydroxyl ions, which at the given alkali concentrations and current strengths does not depend on stirring, we applied the rotating disk electrode method. The quantitative theory of convective diffusion to a rotating disk was developed by V. G. Levich ([7]) and then confirmed experimentally ([8]). According to Levich' s theory, in the case of electrochemical processes whose rate is determined by diffusion of the reacting particles to the electrode, with a constant concentration difference in the bulk of the solution and at the surface of the disk electrode, there is a direct proportionality between the current strength and the square root of the angularifysgol

rotation rate of the electrode ω; extrapolation to $\omega = 0$ at a constant value of the concentration polarization should give a current value $i = 0$. In our case it turned out that, at a fixed potential, the current i depends linearly on $\sqrt{\omega}$ (Fig. 2). By extrapolating the straight lines obtained experimentally for different potentials to $\omega = 0$ (Fig. 2), we isolated that part of the total current which does not depend on the rotation rate of the electrode (Figs. 1, 2). Calculated curve 2 corresponds to oxygen evolution.

Subtracting the current-density values corresponding to curve 2 from the total anodic current (Fig. 1, 1), we obtained the calculated polarization curve

Fig. 1

Fig. 2

Fig. 1. Anodic polarization curves recorded on a rotating gold disk electrode in $2.3 \cdot 10^{-4}$ N Ag_2O solution in 13.4 N KOH. Rotation rate of the electrode: 3100 rpm.
1 —experimental curve; 2 —calculated curve of O_2 evolution; 3 —calculated curve of Ag_2O oxidation

Fig. 2. Dependence of the current density (Fig. 1, 1) on the angular velocity of rotation of the electrode

for the oxidation of Ag_2O (Fig. 1, 3). The curve has two waves, whose heights are proportional to the value $\sqrt{\omega}$ and to the concentration of monovalent silver in solution and are therefore determined by the rate of diffusion of the ions $[Ag_3O(OH)_2]^-$ to the electrode. The first wave corresponds to oxidation of

these ions to Ag_2O_2, which gradually covers the electrode with a black deposit

$$2[Ag_3O(OH)_2]^- + 4OH^- \rightleftarrows 3Ag_2O_2 + 4H_2O + 6\bar{e}.$$

The limiting-current density (wave height) is equal to the limiting current obtained experimentally from the cathodic polarization curve for reduction of silver ions in the same solutions to metallic silver (Fig. 3). The second wave is twice as high as the first and, consequently, corresponds to oxidation of $[Ag_3O(OH)_2]^-$ to the oxide of trivalent silver. Oxidation in both cases is accompanied by a noticeable overvoltage, since the slopes of both waves in semilogarithmic coordinates (respectively 0.09 and 0.06) are greater than those calculated from the concentration-polarization formula (0.058 and 0.029).

Thus, with the aid of a new method for separating diffusion and non-diffusion currents on a rotating disk electrode, it has been unambiguously proved that, under anodic polarization of Ag_2O solutions in concentrated alkali, silver is oxidized to Ag_2O_2, and at sufficiently high potentials—to trivalent silver. The magnitude of the current is determined by the rate of diffusion of monovalent silver ions to the electrode; consequently, the process of oxidation and reduction of silver oxides can proceed through solution at high rates.

In carrying out these experiments we found that the potential of an electrode covered with oxides of di- and trivalent silver at $\varphi = 1.0$ V, when anodic polarization is stopped, immediately begins to fall and after several minutes assumes a value of 0.6 V; no appreciable delay at the potential of the Ag_2O_2/Ag_2O_3 system was observed. Evidently, trivalent silver is very unstable in alkaline solutions.

We attempted to estimate the stability of Ag^{II} ions. In a KOH solution above a precipitate of Ag_2O_2 (obtained by oxidation of $AgNO_3$ with the aid of $K_2S_2O_8$ ([9])), the potential of a rotating unpolarized platinum electrode assumes a value of 0.34 V (the stationary potential of Ag in alkaline solutions of Ag_2O). A cathodic polarization curve taken in such a solution has a limiting current, showing that the solution is saturated with Ag_2O. This solution was subjected to anodic oxidation on a gold electrode at a potential of 0.73 V (with a remote cathode) for several days in order to remove traces of possible reducing agents. The potential of the rotating unpolarized platinum electrode immersed in the solution gradually changes from 0.34 to 0.57-0.62 V. Thus, a sufficiently high concentration of divalent silver is produced in the solution; together with monovalent silver it is potential-determining. Stopping the rotation of the platinum electrode causes a sharp decrease in its potential, which, when rotation is resumed, again assumes a value of about 0.6 V. When anodic polarization of the gold electrode is stopped, the potential of the rotating platinum electrode slowly (over several hours) falls to 0.34 V. Apparently, the reason for this phenomenon is that divalent-silver ions are unstable in aqueous solutions and are gradually reduced to monovalent silver (at the expense of O_2 evolution or oxidation of

Fig. 3

Figure 2: Fig. 3

dust particles that accidentally enter the solution). It is possible that platinum is slowly oxidized in depth, reducing silver ions to Ag^{I} and further to the metal.

Fig. 3. Cathodic polarization curve recorded on a rotating disk electrode in $2.3 \cdot 10^{-4}\,N$ Ag_2O solution in $13.4\,N$ KOH. Electrode rotation rate 3100 rpm.

The instability of Ag^{II} ions is also indicated by the fact that, when the chemical or anodic precipitate of Ag_2O_2 obtained on a gold electrode is dissolved in a concentrated KOH solution, silver passes into solution only in the form of Ag^{I} ions (as was determined by recording the cathodic polarization curve in this solution).

Despite the low stability of Ag^{II} ions in solution, the data obtained make it possible to conclude that oxidation-reduction processes on a silver electrode in an alkaline electrolyte can proceed not only in the solid phase, but also through the solution.

I express my deep gratitude to Academician A. N. Frumkin for suggesting the topic and to Professor B. N. Kabanov for valuable advice given during discussion of the results obtained.

Institute of Physical Chemistry
Academy of Sciences of the USSR

Received
14 V 1957

CITED LITERATURE

1. R. Luther, F. Pokorny, *Zs. anorg. Chem.*, **57**, 291 (1908).

2. A. Hickling, D. Taylor, *Disc. Farad. Soc.*, **1**, 277 (1947).

3. F. Jirsa, J. Jelinek, *Zs. anorg. Chem.*, **158**, 61 (1929).

4. M. C. Skanev-Grigor' eva, I. L. Shimanovich, *ZhOKh*, **24**, 1490 (1954); **26**, 1540 (1956).

5. P. Delahay, M. Pourbaix, R. van Rysselberghe, *J. Electrochem. Soc.*, **98**, 65 (1951).

6. Yu. V. Pleskov, B. N. Kabanov, *Zhurn. neorg. khim.*, **2**, 1807 (1957).

7. V. G. Levich, *ZhFKh*, **18**, 335 (1944).

8. Yu. G. Siver, B. N. Kabanov, *ZhFKh*, **22**, 53 (1948); **23**, 428 (1949).

9. J. H. de Boer, J. van Ormondt, *Proc. Intern. Symposium Reactivity of Solids*, Gothenburg, 1952, p. 557.

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