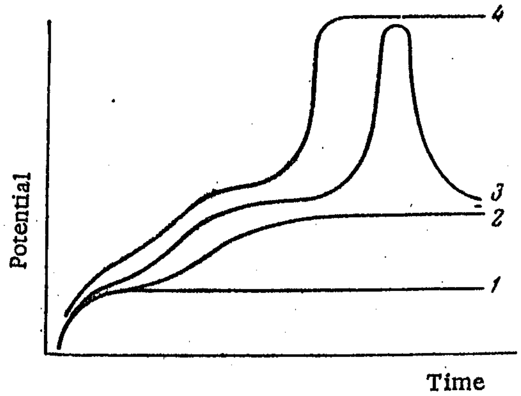
PASSIVITY AND CORROSION: DISCUSSION

Anode Oxidation of Copper in Hot Concentrated Solutions of Alkali by A. L. L'vov and A. D. Fortunatov

A. V. Finkel'shtein. The mechanism of anode oxidation of copper in alkali solutions proposed by A. L. L'vov seems very probable to me because by studying the behavior of copper in concentrated solutions of H_3PO_4, we observed analogous phenomena, which may be explained; equations derived theoretically give good agreement with those obtained experimentally if the ideas on the anode liberation of oxygen developed by A. I. Krasil'shchikov are used.

In the anode polarization of a copper electrode in orthophosphoric acid solutions, the following phenomena may be observed (the current density $\underline{i}$ should be strictly constant during the experiment and this is achieved by inclusion of a stabilizer in the cell circuit):

1. When $\underline{i} < i_1$*, the anode potential is stabilized immediately after the current is switched on and the value of $\varphi_a < \varphi_1$* remains constant with time. The electrode surface is corroded (figure, curve 1).



Potential-time curves for anode polarization of copper in H_3PO_4 solutions. 1) $i < i_1$; 2) $i_1 \leq i < i_2$; 3) $i_2 \leq i < i_3$; 4) $i > i_3$.

2. When $i_1 \leq i < i_2$*, the anode potential first increases and then is stabilized when $\varphi_a \geq \varphi_1$. The anode is polished (curve 2).

3. When $i_1 \leq i < i_2$*; the anode potential increases and when $\varphi_a > \varphi_1$, the anode begins to be covered with a black film (CuO according to analysis data). The anode potential then increase sharply until $\varphi_a \geq \varphi_2$, the film slips from the anode, the potential falls until $\varphi_1 < \varphi_a < \varphi_2$, and a film is again formed. The anode is polished (curve 3).

4. When $\underline{i} > i_3$, the anode potential rapidly reaches the value $\varphi_a > \varphi_1$, the anode is covered with an oxide film, and then the potential jumps to the value $\varphi_a \geq \varphi_2$. The liberation of oxygen begins and despite the removal of the film, the potential no longer falls (curve 4).

This behavior of the electrode may be explained by a scheme similar to the hypothesis in the work of A. L. L'vov.

During the anode polarization of a copper electrode in H_3PO_4 solution, the following process begins:

$$Cu - 2e \xrightarrow{v_1} Cu^{2+}.$$

If the rate of diffusion of copper ions from the layer adjacent to the anode v_D equals the rate v_1 or becomes equal to it with time, the anode is rapidly stabilized as a stationary state is established. Electrochemical etching occurs. This evidently occurs when $\underline{i} < i_1$.

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* i_1, i_2, i_3, φ_1, and φ_2 depend on the H_3PO_4 concentration and the temperature.

DISCUSSION

If v_1 is so much greater than v_D that they can only become equal when there is a considerable concentration of copper ions in the layer adjacent to the anode, then the latter is enriched in Cu^{2+} ions and this retards process 1. The anode potential increases and reaches the value $\varphi_a \ge \varphi_1$, when the following process begins:

$$H_2O - e \xrightarrow{v_2} O^- + 2H^+.$$

Singly charged atomic oxygen ions are adsorbed by the electrode. This makes the following process possible:

$$Cu + O^- - e \xrightarrow{v_3} CuO.$$

Process 3 obviously occurs primarily and at the highest rate on the most active sections of the anode surface, i.e., on protuberances, peaks, and ridges causing roughness. This leads to smoothing of the anode surface.

The oxide formed as a result of process 3 dissolves in the phosphoric acid and in the molecular form, this may be written as follows:

$$CuO + H_3PO_4 \xrightarrow{v_4} CuHPO_4 + H_2O.$$

An acid phosphate is formed, as was demonstrated in the work of G. S. Vozhdvizhenskii. The subsequent behavior of the anode depends on the ratio of the rates v_3 and v_4. If $v_3 \le v_4$, then the anode potential is stabilized on reaching the value $\varphi_a > \varphi_1$, as indicated above. No oxide film is formed and polishing occurs. This occurs when $i_1 \le i < i_2$.

If $v_3 > v_4$, then the electrode is covered with an oxide film. The oxide film retards process 3 and this leads to passivation of the anode by singly charged atomic oxygen ions and the potential increases to the value $\varphi_a \ge \varphi_2$, when the following process is possible:

$$O^- - e \rightarrow O \rightarrow \frac{1}{2} O_2.$$

Oxygen strips the film from the oxide surface. Now the behavior of the anode will depend on the ratio of the rates v_2 and v_3. If $v_2 < v_3$, then after removal of the oxide film, the anode potential falls to the value $\varphi_1 \le \varphi_a < \varphi_2$, and there is again formation of the oxide film. This ratio of v_2 and v_3 evidently occurs when $i_2 \le i < i_3$.

If after removal of the film, $v_2 > v_3$, then depassivation does not occur, the potential does not fall, and gas evolution does not cease. This is observed when $i > i_3$.

As we showed previously, the proposed scheme for the process makes it possible to derive the following relation between the current density and the copper anode potential during electrolytic polishing:

$$\varphi_a = a + b \lg i.$$

We found an analogous relation experimentally.

From what has been stated it follows that electrolytic polishing is caused by a process of a specific chemical nature. The enrichment of the layer adjacent to the anode in anode solution products reduces to the creation of the necessary anode potential for this process to occur. The high activity of protuberances and peaks guarantees that this specific process will occur at the highest rate on them, which leads to smoothing of the surface. Thus, the discovery of the chemistry of electrolytic polishing makes it possible to eliminate the difference of opinion on the mechanism of this process.

All this confirms the accuracy of the ideas on the liberation of oxygen on an anode developed in the work of A. I. Krasil'shchikov and again confirms the importance of electrochemical kinetics in the thorough understanding and complete elucidation of technical electrolysis processes.