THE NEUTRALIZATION OF METALLIC IONS AT MACRODISTANCES FROM THE CATHODE

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Electrolytic neutralization of metallic ions occurs at a phase interface. Pohl [1], S. A. Artsibyshev [2], and others, have shown that neutralization will also occur between the electrodes when metallic ions pass through solid electrolytes. Thus, copper ions are neutralized in KCl or $NaNO_3$ crystals by the countercurrent of electrons to form a characteristic "red cap" in the neighborhood of the anode. Spectral analysis proves this "red cap" to be a cloud of finely dispersed copper.

There is no mention in the literature of similar effects in liquid electrolytes. Nevertheless, an investigation of this problem would be of undoubted interest for both theoretical and applied electrochemistry. This fact has served as an impetus for the present work.

Results of observations on the neutralization of metallic ions at macrodistances from the cathode during electrolysis of aqueous $NaNO_3$ and KNO_3 solutions are outlined below.

These experiments were carried out in the following manner. A thin-walled glass capillary, 0.2-0.6 mm in internal diameter, was filled with a saturated solution of $NaNO_3$ or KNO_3. Copper electrodes of approximately this same diameter were introduced into the capillary and connected to the current source. The capillary was then placed on the platform of a microprojecter and projection made onto a screen so that the electrolysis could be observed and photographed. The distance between the ends of the electrodes was 0.4-1.0 mm. An opaque layer, convex toward the cathode, appeared in the space between the electrodes 30-50 seconds after the current (2-5 ma) was turned on.

Figure 1, shows a photograph of a layer of this kind which was formed during a 50 second electrolysis. The distance between the electrodes was approximately 1.0 mm in this case and the potential, 1.5 volts. The color of the layer was that of finely dispersed copper. The layer structure was diffused in the side toward the anode. Once this layer had appeared, it would continue to increase in depth for a certain time even after the current had been cut off, an effect which was obviously due to the aggregating of copper atoms into colloidal particles.

The distance from the cathode to the layer, the sharpness of the face of the layer which was turned toward the cathode, and the transparency of the electrolyte in the space between the electrode, all became constant if electrolysis was continued long enough. The depth of the layer increased by displacement of the one face toward the anode. The color of the electrolyte in the space between the layer and the anode gradually approached that which is characteristic of copper nitrate solutions. Anodic dissolution must have occurred here since an anode which had been repeatedly used took on the form of a sharp needle. The photograph clearly shows small bubbles of gas forming on the anode. The dimensions of these bubbles increased during passage of the current until the entire cross section of the capillary was finally filled by them. The current in the circuit then diminished sharply and observations were discontinued.

It is to be especially emphasized that no traces of gas evolution on the cathode surface were observed at any time during the experiment. The form and dimensions of the cathode also remained unaltered.

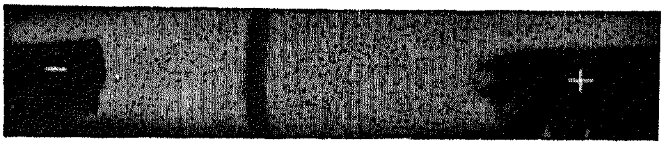

Fig. 1. A layer of finely dispersed copper which was formed in a capillary between copper electrodes during electrolysis of an aqueous $NaNO_3$ solution.

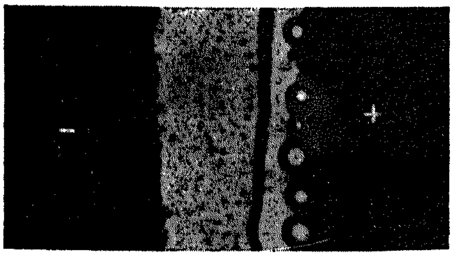

Fig. 2. A layer of finely dispersed copper which was formed in a plane-parallel cell during electrolysis of an aqueous $NaNO_3$ solution.

Fig. 3. Distortion of a layer of finely dispersed copper in a magnetic field.

The position of the layer relative to the electrodes clearly depended on the dimensions of the system and on the applied potential. It was definitely proven that an increase in the potential would force the layer to form nearer the anode, while a decrease in the potential would cause it to move toward the cathode. The layer formed in the immediate neighborhood of the cathode at potentials less than 0.8-0.9 volts and was approximately centered between the electrodes at 1.5-2.0 volts. It is still not clear what quantitative relation exists between the applied potential and the position of the layer. The fact that the position of the layer relative to the electrodes did depend on the applied potential can serve as indication that the mobilities of the current carriers to the right and left of the layer are functions of the applied field potential and that the mobility of the carrier in the cathode – layer region increases the more rapidly when the field strength is increased.

There were no essential changes in the observed effects when the copper cathode was replaced by a cathode of any other metal (Fe, Al, Ni, Pb, Sn, Ag). Only the minimum potential required for separating the layer from the cathode altered somewhat on passing from one metal to another.

Further experiments showed the formation of a layer in the space between the electrodes when Fe, Al, Pb, Sn and Ag anodes were used. In each of these cases, the configuration and structure of the layer was the same as that observed with copper. Layer formation was not observed with Pt, W, or Mo electrodes.

It was of interest to study the effect in a differently shaped cell. A cell was constructed for this purpose by sealing two cover glasses to a glass plate with BF-4 cement, setting the glasses at a distance of 10 mm from one another. Two copper electrodes, 0.1 mm thick, were sealed into the space between these glasses. The distance between the electrodes was 10 mm. The space between the electrodes was filled with the electrolyte and closed with a cover glass. A special device was used to project an enlarged view of this cell onto a screen so that the processes occurring in it could be observed.

Figure 2, gives the results of one such experiment. It is easily seen that ionic neutralization led to the formation of a layer of metal between the electrodes. This ionic neutralization occurred approximately 6-8 mm from the cathode. There were no visible changes in the cathode. Gas bubbles accumulated on the anode, just as in the earlier case. The development and growth of the layer and the coloration of the electrolyte proved to be the same here as in the capillaries. Layer formation at the approximate center of the space between the electrodes was observed at a potential of 6-8 volts.

A transport of negative charges to the developing layer is required for neutralization of the metallic ions. Various assumptions can be made as to the nature of the current carriers. The absence of a visible evolution of gas on the cathode suggests electrons as the current carriers in the space between the layer and the cathode. If such is the case, a magnetic field might be expected to have a pronounced effect on the layer configuration because of the bending which it would produce in the electron paths. We have not attempted a quantitative check of this supposition, since that might well serve as the subject of an independent study, but limited ourselves to a qualitative discussion of the problem. Observation was made of the effect of a magnetic field on the form of layer produced in the plane-parallel cell so set in the field of a fixed magnet that the field strength vector would stand at right angles to the surface of the electrolyte. A photograph of a layer which had been thus formed in a magnetic field is shown in Fig. 3. A comparison of Figs. 2 and 3, brings out the pronounced distortion which the magnetic field caused in this layer and thus confirms, to a certain degree, the assumption as to the nature of the current carriers in the region between the layer and the cathode. The magnetic field strength was not measured but it clearly did not exceed several hundred oersteds. Qualitative measurements on the Hall constant and the specific charge would be very desirable here.

LITERATURE CITED

[1] R. Pohl, Phys. Zs., 35, 107 (1934).

[2] S. A. Artsibyshev, Sov. Phys., 10, 58 (1936); 11, 636 (1937) [USSR].