

CCCLIX.—*Some Effects of the Uneven Distribution of Current Density over an Electrode.*

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IN the ordinary course of electrolysis, the current density is not evenly distributed over a rectangular electrode, but tends to concentrate at the corners and edges. (Possibly, this is related to the well-known tendency of an electric charge to escape from a point.) Thus, whenever film formation takes place at such an electrode, the film first forms at the lowest part of the electrode and travels up the metal in the form of a U of diminishing concavity. This is not due to a concentration gradient in the solution, for the phenomenon occurs however vigorously the liquid is stirred, and is independent of the direction of flow of liquid over the electrode. For the same reason, the inside of an anode (*i.e.*, the side facing the cathode) is more readily attacked than the outside. At a cathode, more metal is deposited on the inside than on the outer side, and the deposit is thicker at the corners and edges.

In experiments with the easily passivated metals, some curious effects were observed through this behaviour. Anodes of iron were often found to be passive on the inside and active on the outside, where no oxygen was evolved; or, at somewhat higher *C.D.*'s, the lower portion of the outside of the electrode became passive, leaving the upper portion active, with the characteristic U-shaped boundary of separation. In certain cases, a small active

area was left near the liquid line, where rapid corrosion took place (compare Evans, J., 1927, 1035; Hedges, J., 1926, 831). It may be necessary to consider this factor in the type of liquid-line corrosion which is characterised by the presence of passivating media. In other cases, the main electrode remained active, whilst just the corners and edges of the electrode became passive. The most striking effects were observed with anodes of cobalt, which readily became passive, with evolution of oxygen, in moderately concentrated solutions of sulphuric acid. In 50% (by vol.) sulphuric acid cobalt dissolves at low *C.D.*'s as a pink, cobaltous ion, but at higher *C.D.*'s it goes into solution as a green cobaltic compound. It was frequently observed that the inside of the electrode was dissolving to give a green solution, whilst the outside dissolved simultaneously to form a red solution.

An interesting conclusion may be drawn from these observations in connexion with Adler's theory (*Z. physikal. Chem.*, 1912, 80, 385) of the cause of the periodic anodic dissolution of passive metals, according to which the periodic phenomenon is to be traced to alternations of polarity in local elements composing the electrode. In the experiments described above, periodic phenomena were observed, but they did not consist of an alternation of the active and passive regions. The phenomena did not differ in any respect from those observed at higher *C.D.*'s, when the whole surface of the electrode became alternately active and passive. Moreover, electrodes have been observed which, although clearly differentiated into active and passive zones, did not dissolve periodically.

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