

THE MEANING OF CURRENT DENSITY

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The question has been raised by Tommasi as to the exact meaning of current density. There is perhaps not much doubt in the minds of most electrochemists that the term, current density, as applied to any particular electrode, means the amount of current flowing through unit surface area of that electrode, or the quotient obtained by dividing the amperage of the current passing by the surface area of the electrode. Ordinarily, one deems this method of specification quite sufficient. In the following paragraphs it is intended to show that the consideration of these two factors alone is not sufficient, except under certain circumstances, to convey an exact idea of current density.

The usual way in which current density is defined is decidedly loose; this makes it impossible to reproduce conditions of electrolysis with accuracy and certainty. The success with which such conditions have been repeated heretofore has been due to a fortunate set of circumstances, tending to regulate and equalize conditions, rather than to any definiteness on the part of the author describing the conditions. It is with the hope that electrochemists may be induced to give in greater detail the size and shape, construction and position of the electrodes when these items tend to influence current density, that these lines are written.

The paths of the electric current through an electrolytic cell, its concentration on certain parts of, and its distribution over, the electrode surface are determined, in agreement with Ohm's and Kirchhoff's laws, by the resistance which it encounters. This resistance is found (1) in the substance of the electrode itself, (2) in the surface of contact between the electrodes and the electrolytic bath, in which region polarization occurs and energy-consuming reactions take place, such as the deposition of a metal, and (3), in the bath itself. The resistance there is due to the friction which the solvent offers

to the passage of the migrating and current-bearing ions.

The resistance within the electrode may be considered constant for that electrode. In cases where the electrode is of considerable bulk or thickness, as, for example, in the case of the anode used in the electrochemical purification of copper in the multiple system, the resistance within it may easily become entirely negligible.

At the point where the current passes from the metallic portion of its circuit to the liquid portion, the resistance varies with the nature and concentration of the electrolyte, with the sort of reaction which there takes place and with the kind of products which are there produced. The resistance due to the nature of the electrolyte is measured in terms of decomposition voltage and rarely exceeds that which is represented by 2.5 volts.

The concentration of the electrolyte operates to influence resistance at the electrode surface by determining the supply of ions. With a more concentrated solution as the bath, the number of ions in proximity to the electrode is increased and the chances for the impoverishment of ions are lessened. With impoverishment of ions resistance increases.

The influence of the nature of the electrode reactions on resistance is again largely a matter of decomposition voltage. The products of the electrode reactions produce this effect through forming coatings on the electrodes which are more or less impenetrable to the current. The increase in resistance due to the phenomenon usually designated as polarization is caused by gas films which more or less effectually intercept the passage of the current. They separate the electrode from the electrolytic bath. In the "electrolytic forge" this film becomes so thick and its resistance so high that an arc is formed between the solution and the electrode.

The resistance within the electrolytic bath itself varies directly as the distance apart of the electrodes and with the concentration and the temperature of the bath. With a rise in temperature the mobility of the liquid of the bath is enhanced; it therefore presents less friction to the passage of the

ions. Where the distance between the poles is great the resistance of the bath may be so increased that that from the other sources mentioned may become relatively insignificant.

The effect which the resistance in the different portions of the circuit, as outlined above, exert on the direction of the flow of current will be seen when we consider the case where the anode is a point and the cathode a plate.

The electric current does not always flow through an electrolytic bath in straight lines; it is able to pass around obstructions, where, by so doing, energy is conserved. Thus the current flows through the substance of, or through the interstices in, a diaphragm of the porous, conducting type, depending on whether the resistance in the circuitous path through the pores of the diaphragm offer a greater resistance than the ohmic resistance of the substance of the diaphragm itself, plus that produced by the necessity of decomposing the electrolyte at the two faces of the diaphragm. But it stands to reason that the current does flow in straight lines when it can do so.

The resistance presented by an electrolytic bath acts like ohmic resistance in that it varies directly with the length and inversely as the cross section of the liquid conductor. The length of the conductor is shortened when the path is straightened. We may then represent the paths of the current from anode to cathode as a number of straight lines drawn from the anode to different points on the cathode face. The shortest line is that drawn perpendicularly to the cathode face at a point directly opposite the anode. It is seen that the current would tend to flow in general along this one line from electrode to electrode and to enter the cathode at that point on its surface, directly opposite the anode. That the current is not confined to this spot, though it may be, and probably is, concentrated there, is a matter of observation and is no doubt due to the increase in resistance at the electrode surface with increase in current density. The augmented resistance may arise either from a more vigorous evolution of gas or from impoverishment of ions. The current

would then tend to flow to those regions where these impediments exist to a less extent. This scattering of the current is limited by the resistance of the electrolytic bath; this would become so great in the peripheral regions of the current's path that the electromotive force of the current would be expended in passing through the bath so that on arriving at the electrode surface, the current would find itself, so to speak, so depleted in electromotive force that it would not be able to overcome the counter electromotive of the electrolyte which it must decompose there. How soon this limit would be reached depends on the potential difference back of the current. At the same time, with increased potential difference, the current would be better able to overcome an increased resistance due to gas films or to impoverishment of ions. Thus the equilibrium between the two counteracting forces is not overthrown by changes in electromotive force. Or, different lines drawn from the point to the plate may be regarded as so many split circuits, to the flow of current through which Kirchhoff's law is applicable. The resistance in each circuit is equal to the resistance of the bath plus the decomposition voltage of the electrolyte. With the exclusion of all consideration of the effect of electrode films and ion depletion, by Kirchhoff's law it would be possible to calculate exactly the distribution of the current over the electrode surface.

The concentration of current at one point on the cathode face is greatly heightened when the two plates are brought into close proximity; like-wise, when the two are more widely separated the relative advantage, in point of resistance of the bath, of one line of travel over any other is greatly diminished. As the electrodes are brought closer together, then, the current tends to concentrate in one region, and as they are moved apart, it tends to distribute itself with equal intensity over the face of the electrode.

Passing to a case at the other extreme, where the electrodes are two plates of the same size, and are placed directly opposite to each other, with their faces in parallel planes and

with the current admitted equally to all portions of them, then we generally have a practically uniform current density on both. These are the ideal conditions, but they do not often obtain actually in practice. Frequently electrodes are plates of metallic foil and are so thin that they present considerable resistance to the passage of the current through them. With the current admitted only to their upper edge, as is nearly always the case, the path of least resistance through the cell is from the upper portion of the one electrode to the upper portion of the other, instead of through their entire lengths. This tendency is heightened where the anode is a soluble one, by the convection current of the heavier solution of that salt, which is the product of the corrosion, flowing downward over the face of the electrode. With a copper anode in a sulphate or nitrate bath a line of accentuated corrosion just beneath the top surface of the electrolytic bath is very noticeable.

The same considerations would apply in varying degree to cases between these two extreme ones, where the electrodes are of different size and shape. Likewise, varying the relative positions of the electrodes would have its effect on current density.

Usually in reckoning current intensity per unit area, one-quarter to one-third of the back of sheet electrodes is considered included in the active electrodes surface. The back of an electrode may be entirely inactive, depending on the distance such an electrode is placed from the walls of the containing vessel. The limiting case, of course, is that in which the electrode is placed *against* the sides of the containing vessel. All action on the back of the electrode would then be prohibited. How far from the cell walls the electrodes must be so that the distance is not a factor in determining the course of the current is hard to say, nor is it especially desirable to know so long as this distance is specified when current densities are recorded.

What then should be specified in describing current density? Certainly the size of the electrodes, not of one but

of both, should be given, and their distance apart, and their distance from the walls of the cell. Also, in cases where conditions of current density are of especial importance, mention should be made of the relative positions of the electrodes, whether parallel and opposite each other, and of the construction and thickness of them. In every case, of course the current strength must be specified.

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