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On the Resistance to Electrodes at Nonuniform Potential

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Nanis and Kesselman\(^1\) have recently raised the question of the definition of the resistance in electrode configurations where the primary potential distribution does not prevail and where, instead, surface and concentration overpotentials must exist. They have given a valid justification for defining the resistance as an average potential over the surface of the disk, divided by the total current to the disk.

As Wagner\(^2\) has stated, the term electrical resistance is confusing in situations where the potential varies along the boundary of the electrolytic solution. The potential of the electrode is uniform. The ohmic potential drop, the surface overpotential, and the concentration overpotential vary with position on the electrode in such a way that their sum is uniform. There should be no ambiguity if these variations are described in detail.

In such a situation, Newman\(^3\) emphasized the ohmic potential drop and the current density to the center of a disk electrode. Thus, the current-potential curve was calculated by adding the ohmic potential drop, and concentration and surface overpotentials at this point. The same overall curve would be obtained by performing the addition at the edge of the disk or at any point between the center and the edge. Emphasis was placed
on the center of the disk in part because the concentration and surface overpotentials at that point are easily computed from the local current density.

This ohmic potential drop is not, of course, directly comparable to the average resistance. In order to use the average resistance, one would first need to know at what point on the electrode the ohmic potential drop is given by the average resistance. At this point he would then need to know the local current density and the local surface concentration in order to calculate the concentration and surface overpotentials.

Newman has used a simple equivalent circuit to describe the impedance of a disk electrode system in frequency dispersion in capacity measurements. The low-frequency limit, when the interfacial impedance is purely capacitive, coincides with Nanis and Kesselman's result for uniform current density, \( 4r_0 K R_{\text{eff}} = 1.08076 \). When faradaic reactions are involved, the value of the effective resistance in the equivalent circuit is different because it includes the impedance of the interface. Thus, the entire electrode system is used to define the effective impedance in this case.

In a later paper, Newman points out that, for the secondary distribution on a disk electrode, one can estimate the ohmic potential drop from the total current and the resistance for the primary potential distribution. The surface overpotential obtained by subtracting this ohmic potential from the electrode potential can be associated, with little error, with the average current density.
References


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