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Ohmic Potential Measured by Interrupter Techniques

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Interruption of the current is frequently used to assess the magnitude of the ohmic potential drop which is included in the measurement of electrode potentials during the passage of current. The value so measured corresponds to the primary current distribution in the electrode system being studied.

When the current is interrupted, the double-layer capacity is left charged at the value prevailing locally. This double-layer capacity may then be discharged by means of a faradaic reaction. The time constant for this decay of charge may be approximated by

$$\tau_1 = RTC/Fi_o \quad . \tag{1}$$

For an exchange current density i_o of 1 mA/cm^2 and a double-layer capacity C of 20 μF/cm^2, this equation yields τ_1 = 0.51 msec at 25°C. The electrode potential may subsequently shift by decay of the concentration overpotential.

Immediately after the current is interrupted, the current density is not necessarily zero everywhere. If the double layer was nonuniformly charged, current will flow through the solution from one part of the double layer to another in an attempt to make the state of charge uniform. A characteristic time for this process is

$$\tau_2 = r_o C/\kappa \quad , \tag{2}$$

where r_o is a length characteristic of the electrode. The value $\tau_2 = 0.5$ msec is obtained for $r_o = 0.25$ cm, $C = 20\ \mu F/cm^2$, and a solution conductivity of 0.01 mho/cm. For an ideally polarizable electrode, this process will take precedence over decay by a faradaic reaction and in at least one case obscured observation of double-layer relaxation at such an electrode.[1,2]

Let us ignore for the moment the concentration overpotential. A nonuniformly charged double layer is associated with a nonuniform ohmic potential drop during the passage of current. In such a case, what ohmic potential drop is measured by an interrupter technique? It must be some average value which does not prevail everywhere on the electrode. Since, upon interruption, the double-layer capacity remains charged, the potential just outside the double layer (relative to the reference electrode) changes by a uniform amount over the entire surface of the electrode. Hence, independent of the current-density distribution prevailing before interruption, the current density <u>changes</u> by amounts which correspond to a primary distribution, and the observed ohmic drop measured by the interruption corresponds to this distribution. (Here the thickness of the double layer is taken to be small compared to the size of the electrode, a condition which is unlikely to be violated. This allows the double layer to be treated as part of the boundary, being characterized locally by its surface charge density and faradaic current density.)

A rotating disk electrode can be used to illustrate this general conclusion. The current and potential distributions have been worked out under steady conditions,[3] and the frequency dispersion in capacity measurements has recently been treated[4] for a disk electrode embedded in a large insulating plane. The potential Φ_o just outside the double layer can be represented by a series in Legendre polynomials

$$\frac{ZF}{RT}\Phi_o = \sum_{n=0}^{\infty} B_n P_{2n}(\eta) \quad , \tag{3}$$

where $\eta = \sqrt{1 - (r/r_o)^2}$. (To be consistent with reference 3, the coefficient ZF/RT has been introduced; it will cancel out shortly.) By means of the orthogonal property of the Legendre polynomials, the coefficients B_n can be expressed as

$$B_n = (4n+1)\frac{ZF}{RT}\int_o^1 \Phi_o(\eta)P_{2n}(\eta)d\eta \quad . \tag{4}$$

In particular, the first coefficient B_o can be related to the <u>total</u> current flowing to the disk

$$B_o = \frac{ZF}{RT}\int_o^1 \Phi_o(\eta)d\eta = \frac{ZF}{RT}\frac{I}{4r_o\kappa} \quad . \tag{5}$$

Let quantities after interruption be denoted by primes. Then, since the double-layer charge does not change instantaneously on interruption,

$$\Phi'_o = \Phi_o - \Delta\Phi \quad ,$$

where $\Delta\Phi$ is constant over the disk and represents the ohmic drop measured by the interrupter technique. The value of B'_o must be zero since the total current is now zero. Hence,

$$B'_o = 0 = \frac{ZF}{RT}\int_o^1 (\Phi_o - \Delta\Phi)d\eta = \frac{ZF}{RT}\left(\frac{I}{4r_o\kappa} - \Delta\Phi\right) \quad . \tag{6}$$

Thus $\Delta\Phi = I/4r_o\kappa$. The change in potential and the resistance $\Delta\Phi/I$ measured by the interrupter technique correspond to the primary current distribution.[5] Suitable allowance can be made for the position of the reference electrode probe,[5] and the conclusion also remains valid for other electrode geometries. (Except for B_o, the other B_n's will not change at the instant of interruption, that is, $B'_n = B_n$ for n = 1, 2,...)

It may be noted that the current distribution will approximate the primary distribution when the concentration and surface overpotentials are small compared to the ohmic drop. In this case, the interrupter may yield the desired value of the ohmic drop. On the other hand, when the current distribution is more nearly uniform, the ohmic drop will not be large compared to the overpotential, and the interrupter may still yield results of satisfactory accuracy.

Of course, the value measured by current interruption will correspond to the ohmic potential drop to some point on the electrode surface. On the basis of figure 1 of reference 3, one can estimate that this point will be about 80 percent of the way from the center to

edge of the disk. At this point the current density will be approximately equal to the average current density, and errors associated with the non-uniform current density and potential distributions at the disk will largely cancel if one associates the average current density with the ohmic drop measured by the interrupter technique.

The concentration overpotential will complicate the picture slightly. With an excess of supporting electrolyte, conductivity variations probably make a negligible contribution to the ohmic drop. For discharge of an ion from a binary electrolyte, this contribution is larger but can be estimated separately. The observed ohmic drop would not correspond exactly to the primary resistance in this case.

McIntyre and Peck[6] recently perfected a short-time interrupter for use under potentiostatic conditions. For a rotating disk electrode, the ohmic resistance was observed to be independent of current. This should be expected in view of the analysis presented here. It would be desirable to compare their value with one estimated from the disk radius and the solution conductivity, with due allowance for the placement of the reference electrode and the size of the insulating disk in which the electrode was embedded.

Acknowledgment

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