Diffusion-Controlled Chronoamperometry at a Disk Electrode

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An accurate formula exists for describing the decay of the current following the imposition of extreme concentration polarization on a disk electrode under diffusion-controlled conditions. It has been amply validated by diverse simulations and is presented here in a more compact form than hitherto. The formula finds application beyond the realm of potential-step chronoamperometry.

Inlaid disk electrodes enjoy great popularity due to their ease of construction and the benefits derived from their use as microelectrodes.[1] However, *exact* equations describing the faradaic current response to the simplest voltammetric experiment (the sudden imposition of a constant applied potential, large enough to make concentration polarization the only significant source of overvoltage, under diffusion-controlled conditions) are known only in the limits of zero and infinite time. The Cottrell equation[2] addresses the zero-time limit

$$I(t \to 0) = nFc^b R^2 \sqrt{\pi D / t} \qquad (1)$$

whereas in the long time limit, the Saito equation,[3]

$$I(t \to \infty) = 4nFc^b DR \qquad (2)$$

describing the steady-state current, is valid. In these equations, n is the number of electrons transferred (positive for an oxidation), F is Faraday's constant, and R is the radius of the inlaid disk. D and c^b are respectively the diffusivity (diffusion coefficient) and bulk concentration of the reactant species.

For the disk electrode problem, there have been many attempts to formulate approximate solutions[4−7] and to simulate[4,8] the diffusion-controlled current between the two time limits. The authors of several of these publications include empirical equations based on simulations, approximate solutions, or both. In striving to find an approximate formula, the greatest difficulty arises in bridging the gap[9] between power series expansions and asymptotic expansions at times in the vicinity of R^2/D. Simulations do not have particular difficulty at the changeover point, but the need to encompass large ranges of time and of two-dimensional space brings other problems to simulators. Some attempts using tabulated simulation data[10] have been used, but this information is not readily accessible in general. Moreover, having a formula, albeit with many terms, is more useful than a solution in the form of a table or graph.

In 1982, Shoup and Szabo derived the equation[4]

$$\frac{I(t)}{n\pi Fc^b DR} = 1 + \frac{R}{\sqrt{\pi Dt}} + \left(\frac{4}{\pi} - 1\right) \exp\left\{\frac{-0.39115R}{\sqrt{Dt}}\right\} \qquad (3)$$

where the number 0.39115 is an empirical fitting parameter. A recent publication[11] has stated "the most accurate and convenient theoretical equation at a disk electrode is the Shoup−Szabo equation". The convenience of this expression is unquestioned but because a considerably more accurate solution does exist, we take issue with the assertion that eq 3 is the most accurate relationship in the literature for describing diffusion-controlled chronoamperometry at an inlaid-disk electrode. The superior formula[12,13] is in the form of a bipartite expression where, for times less than $1.281R^2/D$

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$$\frac{I(t)}{n\pi Fc^b DR} = \frac{R}{\sqrt{\pi Dt}} + 1 + \frac{1}{2R}\sqrt{\frac{Dt}{\pi}} - \frac{0.12003\,Dt}{R^2} + \frac{0.013273\,(Dt)^{3/2}}{R^3} \quad (4)$$

whereas for times greater than $1.281R^2/D$

$$\frac{I(t)}{n\pi Fc^b DR} = \frac{4}{\pi} + \frac{8R}{\sqrt{\pi^5 Dt}} + \frac{0.0089542R^3}{(Dt)^{3/2}} - \frac{0.00025664R^5}{(Dt)^{5/2}} - \frac{0.00022312R^7}{(Dt)^{7/2}} + \frac{0.000027628R^9}{(Dt)^{9/2}} \quad (5)$$

Though the decimal numbers in eq 4 are fitting parameters, akin to that adopted by Shoup and Szabo, this is not the case for the corresponding numbers in eq 5, which are known precisely.[5,6] In the difficult "gap" region, eqs 4 and 5 are based on the Cope–Tallman method,[14] which relies on a numerical Laplace inversion and is quite distinct from other methods.

Its agreement, to within better than 0.02%, with a number of diverse digital simulations[15-17] vouches for the accuracy of the eq 4 + eq 5 combination. The numerical comparison of these various approaches has been clearly made in two recent publications.[16,17] Indeed, a comparison of the relative agreement between eq 3, eqs 4 and 5, and a few different simulation methods is discussed and clearly demonstrated in the literature.[17]

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There is measure of gratuitous precision in formulas 4 and 5, which makes them appear more complicated than, in fact, they are. Accordingly, we have simplified these equations, while retaining their inherent accuracy, in producing the more user-friendly version

$$\frac{I(t)}{n\pi Fc^b DR} =
\begin{cases}
\dfrac{1}{\sqrt{\pi\theta}} + 1 + \sqrt{\dfrac{\theta}{4\pi}} - \dfrac{3\theta}{25} + \dfrac{3\theta^{3/2}}{226} & \theta \leq 1.281 \\[2ex]
\dfrac{4}{\pi} + \dfrac{8}{\sqrt{\pi^5\theta}} + \dfrac{25\theta^{-3/2}}{2792} - \dfrac{\theta^{-5/2}}{3880} - \dfrac{\theta^{-7/2}}{4500} & \theta \geq 1.281
\end{cases} \quad (6)$$

where $\theta = Dt/R^2$. Numerical comparisons of eqs 4 and 5 with eq 6 reveal that the average deviation for $0 < \theta \leq 50$ is on the order of 0.4 ppm. The maximum difference is 24 ppm, and this occurs at $\theta = 1.281$, so very little accuracy has been lost due to this useful simplification.

Of course, with c^b augmented by a potential-dependent factor, the equations of this note apply equally to steps to other potentials, provided that the electron transfer is simple and rapid with the uncompensated resistance being negligible. However, the utility of relationships 4 + 5 (or its more convenient equivalent, eq 6) transcends its application to potential-step experiments. We have demonstrated[18] how it may be used in the context of convolutive modeling to predict the current resulting from any potential perturbation (for example, cyclic voltammetry) at a disk electrode, when the reaction is reversible. Moreover, controlled-current experiments were also shown to be equally amenable to the treatment.