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Potential Distribution in Axisymmetric Mercury-Pool

Electrolysis Cells at the Limiting Current

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Uniformity of potential at the working electrode has become an important criterion in the design of cells for controlled-potential electrolysis and coulometry. Deviations of the actual electrode potential from the desired control potential may cause significant errors in coulometry (1-4) and unwanted product distributions in electroorganic syntheses (4-7).

Because excursions of the working electrode potential are minimized, the preferred configuration of a mercury-pool type cell is the axisymmetric arrangement in which the counter-electrode separator is placed concentrically above the pool. When the separator is parallel to the pool, and of nearly the same diameter, a virtually uniform potential distribution should be achieved, and has been experimentally realized

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in several instances (1,7-10). Use of a large-diameter separator, however, complicates the placement of the other cell components and renders the design of an efficient cell more difficult. For cells whose separators are significantly smaller in diameter than the working electrode, (see, for example, Refs. 6, 10-13) a means for estimating the possible electrode potential deviations would be useful.

Stouffer and Richardson (14) considered the boundary-value problem represented by this configuration, and derived an equation (given in Ref. 2) for the potential difference arising at the working electrode under worst-case conditions, i.e., when the cell is operating at the limiting current and a uniform current density prevails at the working electrode. The somewhat unwieldy form of the Stouffer-Richardson equation and our recent need for a numerical evaluation of this potential distribution have prompted us to reexamine this problem.

The basic problem is formulated for the geometry shown in Figure 1, where the working electrode is assumed to be a uniform-current disk of radius r_w at the bottom of a cylindrical cell, and the counter electrode separator is taken to be a uniform-current disk of radius r_c placed concentrically at the solution level, i.e., in an insulating plane. This model does not take into account the typical experimental conditions of nonuniform mass transport at the working electrode, curvature of the mercury pool at its periphery, and deviations of the counter-electrode separator from the assumed uniform current source, but these characteristics are expected to be of secondary influence on the potential distribution.

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Figure 1. Axisymmetric cylindrical cell.

By the method of separation of variables (15), the appropriate solution of Laplace's equation is

$$\phi = \frac{iz}{\kappa} + \frac{ir_w}{\kappa} \sum_{n=1}^{\infty} c_n \cosh(\lambda_n \frac{z}{r_w}) J_0(\lambda_n \frac{r}{r_w}) \quad [1]$$

where ϕ is the potential, i is the current density at the working electrode, κ is the solution conductivity, J_0 is the Bessel function of the first kind of order zero, and λ_n is one of a sequence of eigenvalues. The first term on the right represents a uniform current density i on the working electrode. Each of the terms in the sum is a solution of Laplace's equation having zero current density on the working electrode and also on the cylindrical wall of the cell. This latter condition is assured by choosing the eigenvalues λ_n so that the derivative of $J_0(x)$ is zero at $x = \lambda_n$. Since the derivative of $J_0(x)$ is $-J_1(x)$, the Bessel function of the first kind of order one, this means that the eigenvalues λ_n are the zeros of J_1 . These are tabulated along with the values of $J_0(\lambda_n)$ in reference 16.

The coefficients c_n can then be chosen to yield the specified current-density distribution at the top of the cell: a uniform current density for $r < r_c$ and a zero current density elsewhere. Equation 1 is differentiated with respect to z , and then z is set equal to h , the height of the cell. Multiplication by $r J_0(\lambda_n r/r_w)$ and integration from $r = 0$ to $r = r_w$ give for the coefficients

$$c_n = \frac{2 \frac{r_w}{r_c} J_1(\lambda_n \frac{r_c}{r_w})}{\lambda_n^2 [J_0(\lambda_n)]^2 \sinh(\lambda_n h/r_w)} \quad [2]$$

The expression for the potential distribution at the pool then is:

$$\Phi_o = \frac{2I}{\pi \kappa r_w} \sum_{n=1}^{\infty} \frac{\frac{r_w}{r_c} J_1(\lambda_n \frac{r_c}{r_w}) [J_o(\lambda_n \frac{r}{r_w})]}{\lambda_n^2 [J_o(\lambda_n)]^2 \sinh(\lambda_n h/r_w)} \quad [3]$$

where I is the total cell current. Numerical evaluation of this equation for a range of typical cell parameters yields the curves shown in Figs. 2 and 3. The working electrode potential is most cathodic for a reduction process and most anodic for an oxidation process at the center of the cell.

Important in many design calculations would be the maximum potential difference, $\Delta\Phi_{\max}$, between the center of the cell and its periphery. Figure 4 shows how this quantity varies with I , h/r_w , and r_c/r_w , as well as the overall cell size as represented by r_w . Figure 5 emphasizes the effect of changing the size of the counter-electrode separator and provides a means for interpolating on Figure 4. These figures demonstrate that one must increase the size of the counter-electrode separator considerably in order to obtain appreciable improvement over the potential distribution for $r_c = 0$. Changes in h affect the potential distribution more profoundly, and this design parameter can be adjusted to render $\Delta\Phi_{\max}$ negligible. However, increasing h for this geometry also would increase the volume of the solution and hence the time of the electrolysis, unless the rate of stirring were also increased.

The order of magnitude of expected potential gradients is indicated by numerical evaluation of a typical case. For a cell in which $r_w = h = 3$ cm, $r_c = 1$ cm, and $I = 100$ mA, $\Delta\Phi_{\max}$ would be 200 mV for a 0.1 M solution of tetrabutylammonium perchlorate in DMF ($\kappa \approx 0.0045 \text{ ohm}^{-1} \text{ cm}^{-1}$)

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Figure 2. Potential distribution at the pool for the limiting current, with $r_c/r_w = 0.3$. The lowest curve also appears on figure 3 with an expanded scale.

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Figure 3. Potential distribution at the pool for the limiting current, with $h = r_w$.

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Figure 4. Maximum potential difference in the solution adjacent to an electrode with a uniform current density, as it depends on the distance from the counter electrode.

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Figure 5. Maximum potential difference, normalized with the value for a small counter electrode, showing the dependence on the size of the counter electrode.

and 4 mV for 0.5 M H_2SO_4 ($\kappa \approx 0.2 \text{ ohm}^{-1} \text{cm}^{-1}$).

The dashed line on Figure 4 indicates the potential variation for the two-dimensional rectangular geometry of Figure 6, in which the counter-electrode separator is regarded as being a line at the upper edge of the cell. This configuration is thus a two-dimensional analogue of the axisymmetric geometry for $r_c = 0$.

Placement of the Reference Electrode

The position of the reference electrode probe within the controlled-potential electrolysis cell can be chosen on the basis of the known potential distribution at the working electrode, and the specific purpose of the electrolysis. In most analytical coulometry and separations, the optimum location for the probe is the center of the cell, because exceeding the desired control potential may cause the co-electrolysis of interferences or the supporting electrolyte (2). This configuration also ensures that the cell transfer function will have a minimum phase shift, which facilitates attaining good control system response (10). The probe should of course also be placed close to the working electrode to minimize the uncompensated resistance.

On the other hand, when controlled-potential electrolyses are utilized for the elucidation of electrode reaction pathways via coulometry and the analysis of current-time curves, or the technique is used as a tool for organic synthesis, it would usually be desirable to minimize the maximum difference between the actual electrode potential and the control potential. Such potential control in the axisymmetric cell could be

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Figure 6. Two-dimensional cell with counter-electrode separator reduced to a line at the upper edge of the cell.

established by positioning the reference electrode probe off-center, at an appropriate location selected on the basis of the known potential gradient. The actual electrode potential would then deviate both above and below the nominal control potential. This configuration would result in increased phase shift in the cell transfer function, but in most cases this could be neutralized by adjustment of the phase compensation in the potentiostat.

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NOMENCLATURE

c_n	coefficient in series for potential
h	height of cell solution and counter electrode separator, cm
i	normal current density at working electrode surface, amp/cm ²
I	total cell current, amp
$J_0(x), J_1(x)$	Bessel functions of the first kind of order zero and one, respectively
l	length of rectangular cell, cm
n	index
r	radial position coordinate
r_c	radius of counter electrode separator, cm
r_w	radius of working electrode and cell, cm
x	argument of Bessel function
z	normal distance from working electrode surface, cm
κ	solution conductivity, ohm ⁻¹ cm ⁻¹
λ_n	zeroes of $J_1(x)$
ϕ	potential, volts
ϕ_o	potential of solution adjacent to working electrode surface; the "working electrode potential"; volts
$\Delta\phi_{\max}$	maximum potential difference at the working electrode, between the center of the cell and its periphery, volts

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