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M.E. Orazem and J. Newman

June 1983

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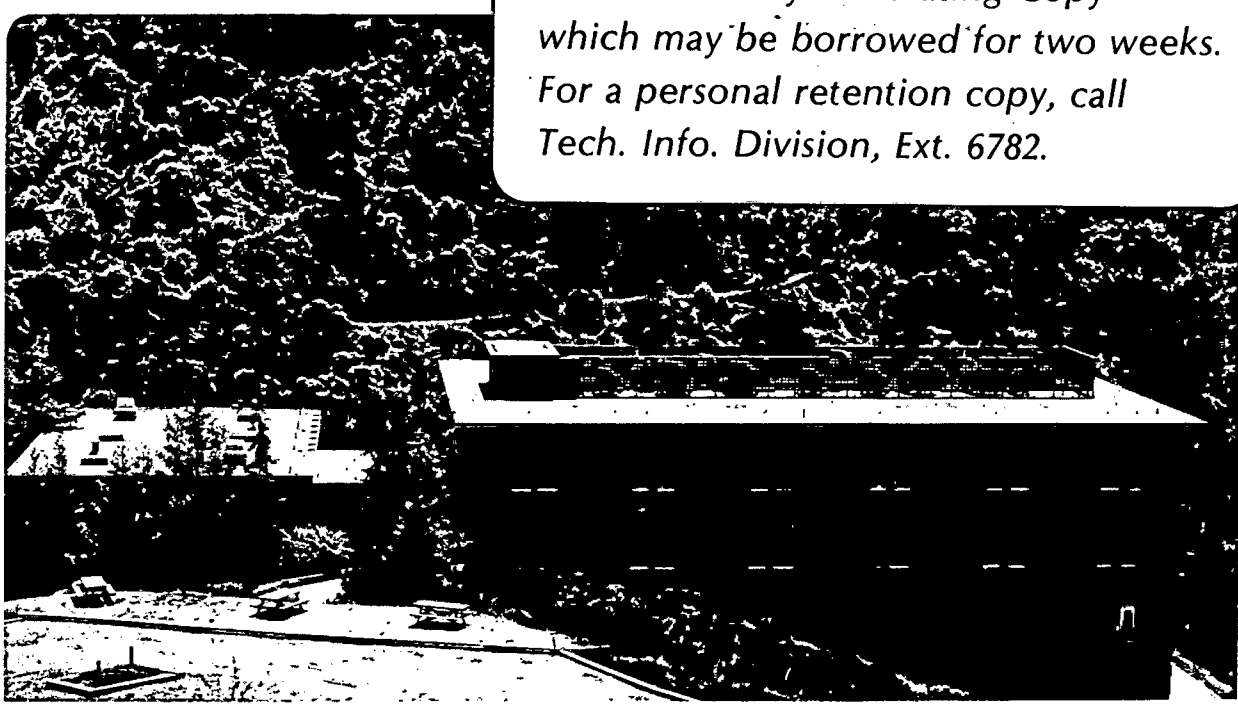

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Primary Current Distribution and Resistance of a Slotted-Electrode Cell

Mark E. Orazem and John Newman

Materials and Molecular Research Division, Lawrence Berkeley Laboratory, and Department of Chemical Engineering, University of California, Berkeley, California 94720

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ABSTRACT

The primary current distribution and the resistance of a cell containing a slotted electrode were calculated using numerical methods coupled with the Schwarz-Christoffel transformation. Results are presented and compared to asymptotic solutions. An approximate analytic expression for the cell resistance is presented.

Key Words: Electrolyte, Potential

Primary current and potential distributions apply when the surface overpotential can be neglected and the solution adjacent to the electrode can be taken to be an equipotential surface. Calculation of a primary current distribution and resistance represents a first step toward analyzing and optimizing an electrochemical system. The cell resistance calculated can be coupled with calculations including mass-transfer and kinetic effects to optimize approximately a given cell configuration. The objective of this work is to calculate the primary current distribution and resistance of a cell containing a slotted electrode.

1. INTRODUCTION

Calculation of the primary current and potential distributions involves solution of Laplace's equation, $\nabla^2\Phi = 0$, which is not trivial, even for relatively simple geometries. The method of images,[1] separation of variables,[2] and superposition[3,4] have been used to solve Laplace's equation for a number of systems. A review of analytic solutions has been presented by Fleck.[5]

The Schwarz-Christoffel transformation[6-8] is a powerful tool for the solution of Laplace's equation in systems with planar boundaries. This method was used by Moulton[9] to derive the current distribution for two electrodes placed arbitrarily on the boundary of a rectangle. Hine *et al.*[10] used this method to describe the primary current distribution for two plane electrodes of infinite length and finite width confined between two infinite insulating planes, perpendicular to but not touching the electrodes. Wagner[11] presented the primary and secondary current distribution for a two-dimensional slot in a planar electrode. Newman[12] has presented the primary current distribution for two plane electrodes opposite each other in

the walls of a flow channel. These solutions made use of the Schwarz-Christoffel transformation.

Application of the Schwarz-Christoffel transformation is generally limited by the ability to generate solutions to the resulting integrals. Analytic solutions allow calculation of the primary current and potential distribution throughout the cell but are possible for a limited number of system geometries. Numerical evaluation of these integrals allows calculation of both the primary current distribution along the electrodes and the cell resistance.

2. CELL GEOMETRY

A cell geometry is presented in Figure 1 which may be well suited for photoelectrochemical applications. This cell contains a slotted semiconductor with the semiconductor-electrolyte interface open to illumination. A glass cover plate protects the cell. Sunlight passes through the cover plate and the electrolyte to illuminate the semiconductor surface. Electrical current passes between the electrolyte and the counterelectrode through the slots of the semiconductor. This configuration has the advantages that no shadows are cast upon the semiconductor, reaction products can be separated, absorption of light by the electrolyte can be minimized, and an enhanced-surface-area counterelectrode (perhaps a porous electrode) can be used.

The slotted electrode cell can be sectioned and, under the assumption that the cell width W is large as compared to the spacing between slots, has the electrochemical characteristics of the two-dimensional cell presented in Figure 2a. The electrodes are represented by AB and EF, and all other boundaries of the cell are considered to be insulators. The coordinate

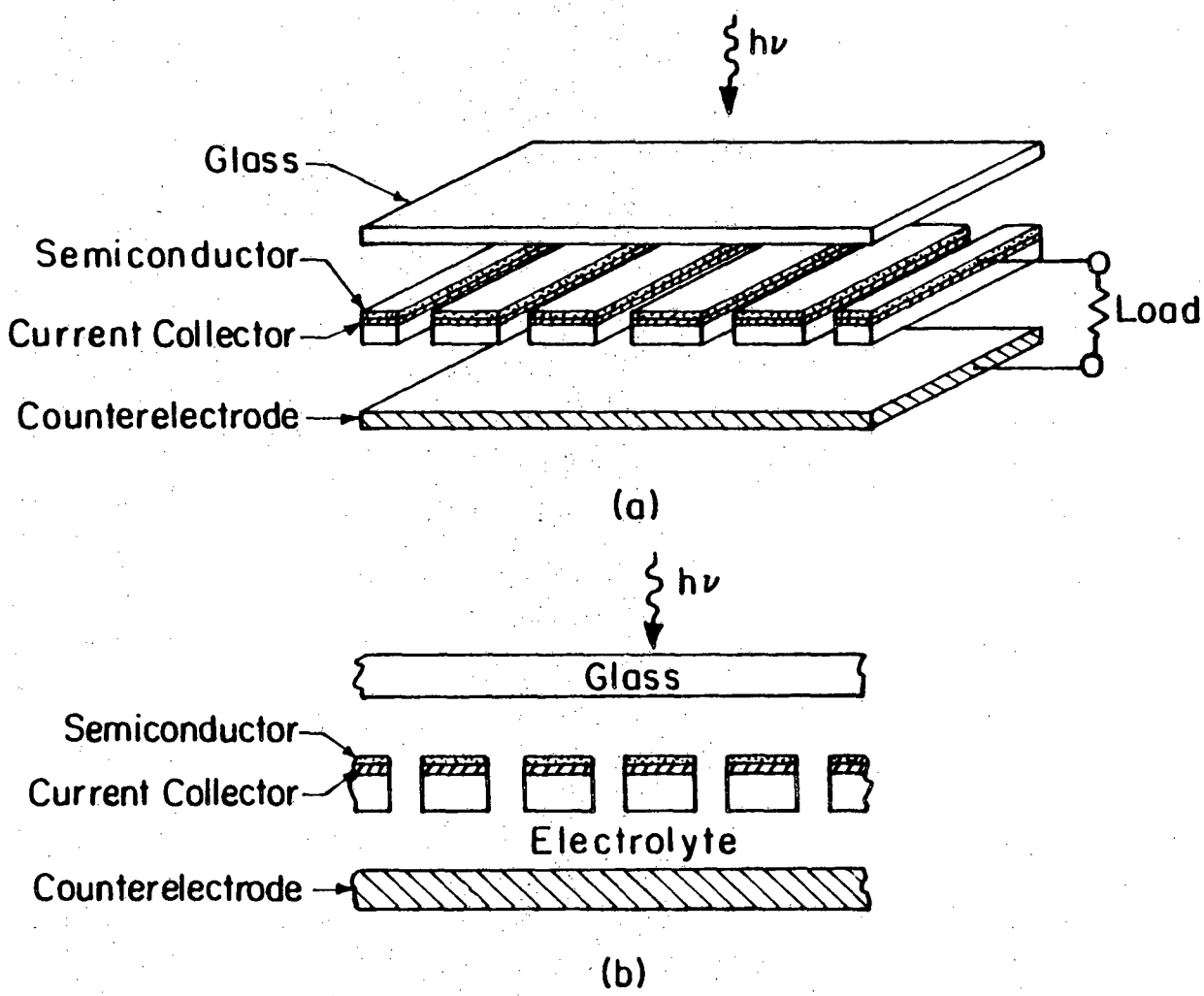

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Figure 1. Schematic diagram of the slotted-semiconductor photovoltaic cell.

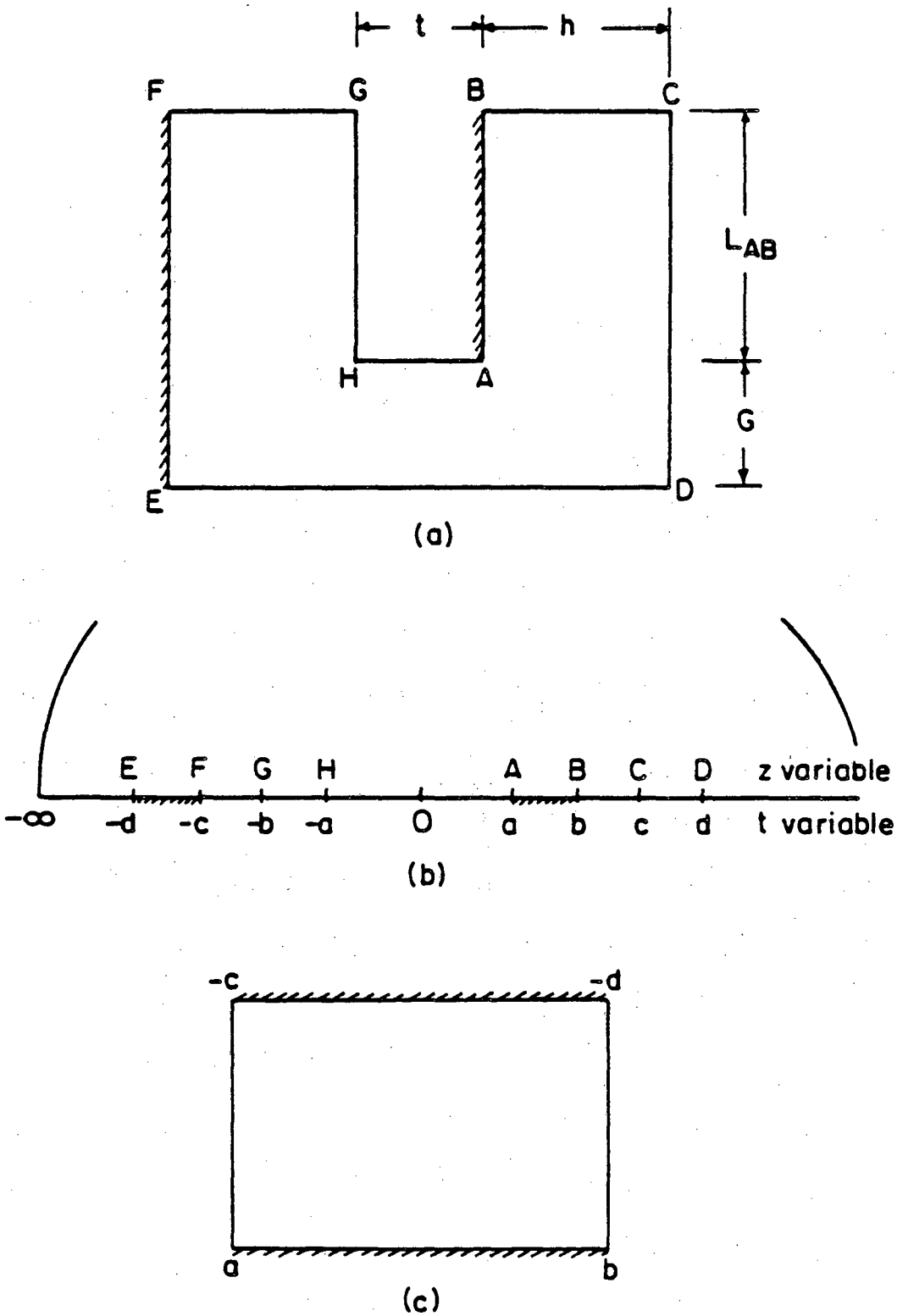

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Figure 2. Schematic diagram of the sectioned cell with coordinate systems;
a) $z = z_r + i\, z_i$
b) $t = t_r + i\, t_i$, and
c) $\chi = \chi_r + i\, \chi_i$.

system of Figure 2a is transformed through an intermediate half-plane t (see Figure 2b) to a coordinate system (Figure 2c) in which Laplace's equation can be solved easily.

3. THEORETICAL DEVELOPMENT

The primary current distribution along the electrodes and the cell resistance can be calculated through application of the Schwarz-Christoffel transformation. Complex coordinate systems are used, thus

$$z = z_r + j\, z_i \,.$$

The cell was assumed to be symmetric about $z_r = 0$. The approach presented below, however, could be easily extended to relax this assumption.

The z-coordinate system is related to the t-coordinate system of Figure 2b by

$$z = \int_0^t \frac{(a^2-t^2)^{1/2}}{(b^2-t^2)^{1/2}(c^2-t^2)^{1/2}(d^2-t^2)^{1/2}}\, dt \,, \tag{1}$$

where a, b, c, and d are the values of t corresponding to z values of A, B, C, and D, respectively. Through the assumption of symmetry about $z_r = 0$, the values $-a$, $-b$, $-c$, and $-d$ correspond to z values of H, G, F, and E, respectively. The electrodes AB and EF correspond to ab and $-c\,-d$ in the t-plane. Along the electrode AB (ab) this transformation can be expressed by

$$\left.\frac{dz_r}{dt_i}\right|_{ab} = j\, f(t_r) \,, \tag{2a}$$

where

$$f(t_r) = \frac{(a^2-t_r^2)^{1/2}}{(b^2-t_r^2)^{1/2}(c^2-t_r^2)^{1/2}(d^2-t_r^2)^{1/2}} \tag{2b}$$

These equations will be used to calculate the derivative of the potential at the electrodes; z_r is the direction normal to the electrode in the z-plane,

and t_i is the direction normal to the electrode in the t-plane.

The variable χ (see Figure 2c) is related to the t-plane by the Schwarz-Christoffel transformation;

$$\chi = \int_a^t \frac{1}{(t-a)^{1/2}(b-t)^{1/2}(-c-t)^{1/2}(-d-t)^{1/2}}\, dt \,. \tag{3}$$

Along the electrode ab equation (3) can be expressed as

$$\left.\frac{d\chi_i}{dt_i}\right|_{ab} = g(t_r)\,, \tag{4a}$$

where

$$g(t_r) = \frac{1}{(t_r-a)^{1/2}(b-t_r)^{1/2}(c+t_r)^{1/2}(d+t_r)^{1/2}} \,. \tag{4c}$$

Equations (2) and (4) are also valid at the electrode EF $(-c-d)$. The variable χ_i is normal to the electrode in χ-space, and t_i is, as above, normal to the electrode in t-space.

The potential in the χ-system is

$$\Phi = \frac{\chi_i}{\chi_{i,max}} V \tag{5}$$

where V is the cell potential difference and $\chi_{i,max}$ is the separation between electrodes in χ-space. The current density is related to the potential derivative at the electrodes. In the χ system this derivative is given by

$$\left.\frac{\partial\Phi}{\partial\chi_i}\right|_{-c-d} = \left.\frac{\partial\Phi}{\partial\chi_i}\right|_{ab} = \frac{1}{\chi_{i,max}} V \,. \tag{6}$$

The potential derivative at the electrode ab in the t-system is

$$\left.\frac{\partial\Phi}{\partial t_i}\right|_{ab} = \left.\frac{\partial\Phi}{\partial\chi_i}\right|_{ab} \left.\frac{\partial\chi_i}{\partial t_i}\right|_{ab} \,, \tag{7}$$

and the potential derivative in the z system is given by

$$\left.\frac{\partial\Phi}{\partial z_r}\right|_{ab} = \left.\frac{\partial\Phi}{\partial t_i}\right|_{ab} \left.\frac{\partial t_i}{\partial z_r}\right|_{ab} \,. \tag{8}$$

Substitution of equations (2a), (4a), (6), and (7) into equation (8) and similar

manipulations for the $-c-d$ electrode yield the potential derivative along the electrodes ab and $-c-d$ in the original z-coordinate system as functions of t_r;

$$\left.\frac{\partial \Phi}{\partial z_r}\right|_{ab} = \frac{g(t_r)}{f(t_r)} \frac{V}{\chi_{i,max}}, \tag{9a}$$

and

$$\left.\frac{\partial \Phi}{\partial z_r}\right|_{-c-d} = \frac{g(t_r)}{f(t_r)} \frac{V}{\chi_{i,max}}, \tag{9b}$$

respectively.

The current distribution along the electrode AB is therefore given by

$$\frac{i(z_i)}{i_{avg}} = \frac{g(t_r)}{f(t_r) \int_A^B \frac{g(t_r)}{f(t_r)} dz_i}. \tag{10}$$

A similar expression results for the electrode EF. The primary cell resistance is

$$W\kappa R = \frac{\chi_{i,max}}{\int_A^B \frac{g(t_r)}{f(t_r)} dz_i}. \tag{11}$$

The primary current distribution and the cell resistance for this system are functions of only three geometric ratios and were obtained numerically. Values of A, B, C, and D in the z-plane corresponding to a, b, c, and d in the t-plane were obtained through numerical integration of equation (1).[13] The value of $\chi_{i,max}$ was obtained through numerical integration of equation (3) between the limits of a and $-d$. The values of t_r corresponding to given values of z were calculated through numerical integration of equation (1) and were used to calculate the values of $f(t_r)$ and $g(t_r)$.

4. RESULTS

The calculated primary current distribution is presented below and compared to current distributions obtained from asymptotic solutions of Laplace's equation. The result most useful for cell design, however, is the cell resistance, presented in section 4.2.

4.1. Primary Current Distribution

The primary current distributions on the *AB* and *EF* electrodes are presented in Figures 3 and 4. This distribution is characterized by three geometric ratios, chosen here to be $t/G=0.25$, $h/G=1$, and $L/h=2.5$, where L is the length of the *AB* electrode, t is the thickness of the protruding electrode assembly, G is the gap between the front edge of the *AB* electrode and the insulating wall, and h is the separation between the lines *AB* and *CD* (and, by symmetry, *EF* and *GH*) (see Figure 2). The current distributions of the two electrodes have been superimposed. The current density is infinite at A and is finite at B, E, and F.

Asymptotic forms of the current distribution can be derived and compared to the calculated current distribution. The current distribution close to the edge of an electrode adjoining an insulator with an angle α is

$$\frac{i(z_i)}{i_{avg}} = const\ \frac{\pi}{2\alpha}(Q-z_i)^{\frac{\pi}{2\alpha}-1}, \tag{12}$$

where Q is the point of intersection of the electrode and insulator. At A, where α is $3\pi/2$, the current density is proportional to $(A-z_i)^{-2/3}$, and at B, E, and F the current density is independent of $(Q-z_i)$. The current density is seen in Figures 3 and 4 to approach a constant value at both edges of the *EF* electrode and at the far edge of the *AB* electrode. The current distribution along the *AB* electrode is presented in a log-log format in

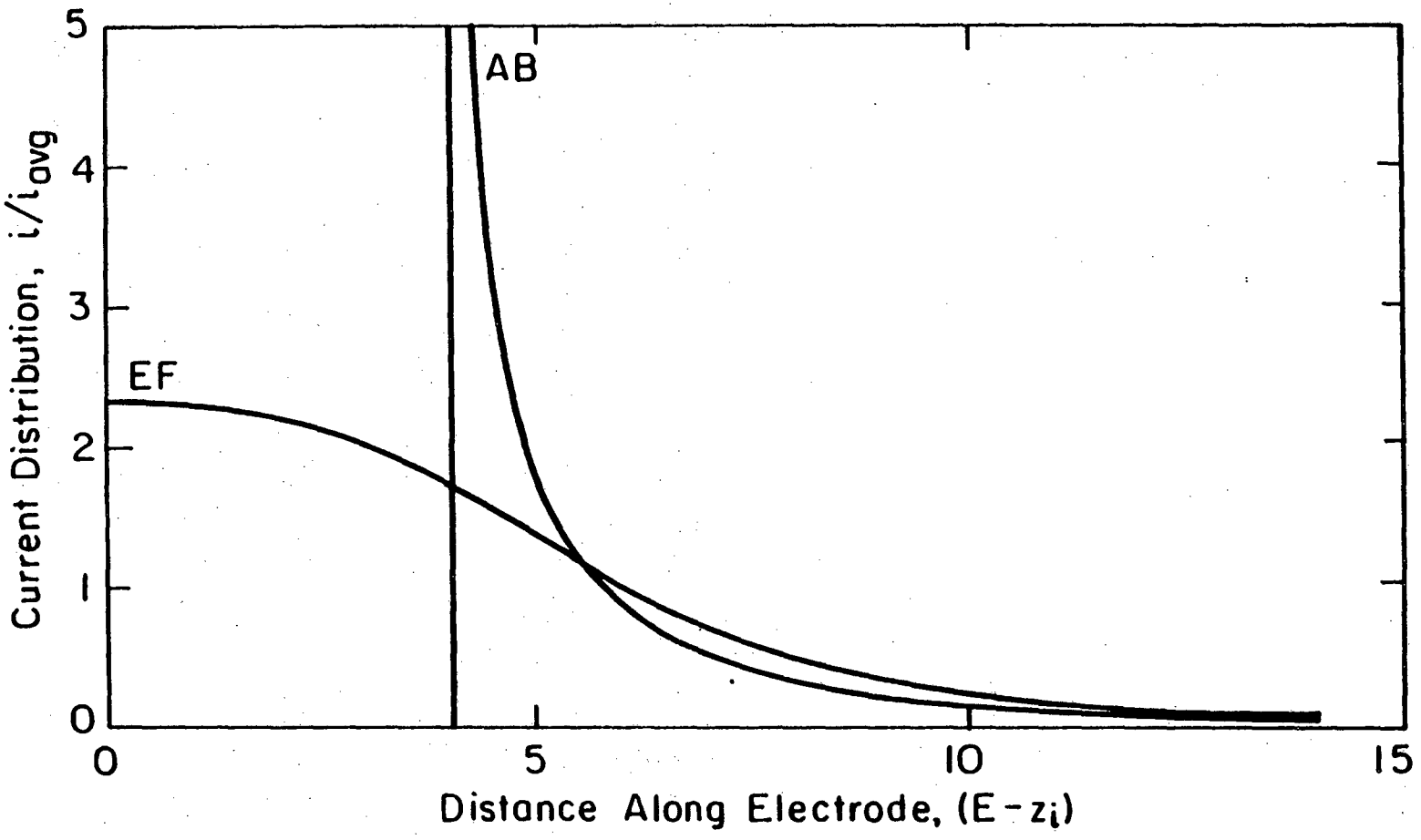

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Figure 3. Current distribution along the AB and EF electrodes for L/h = 2.5, t/G = 0.25, and h/G = 1.

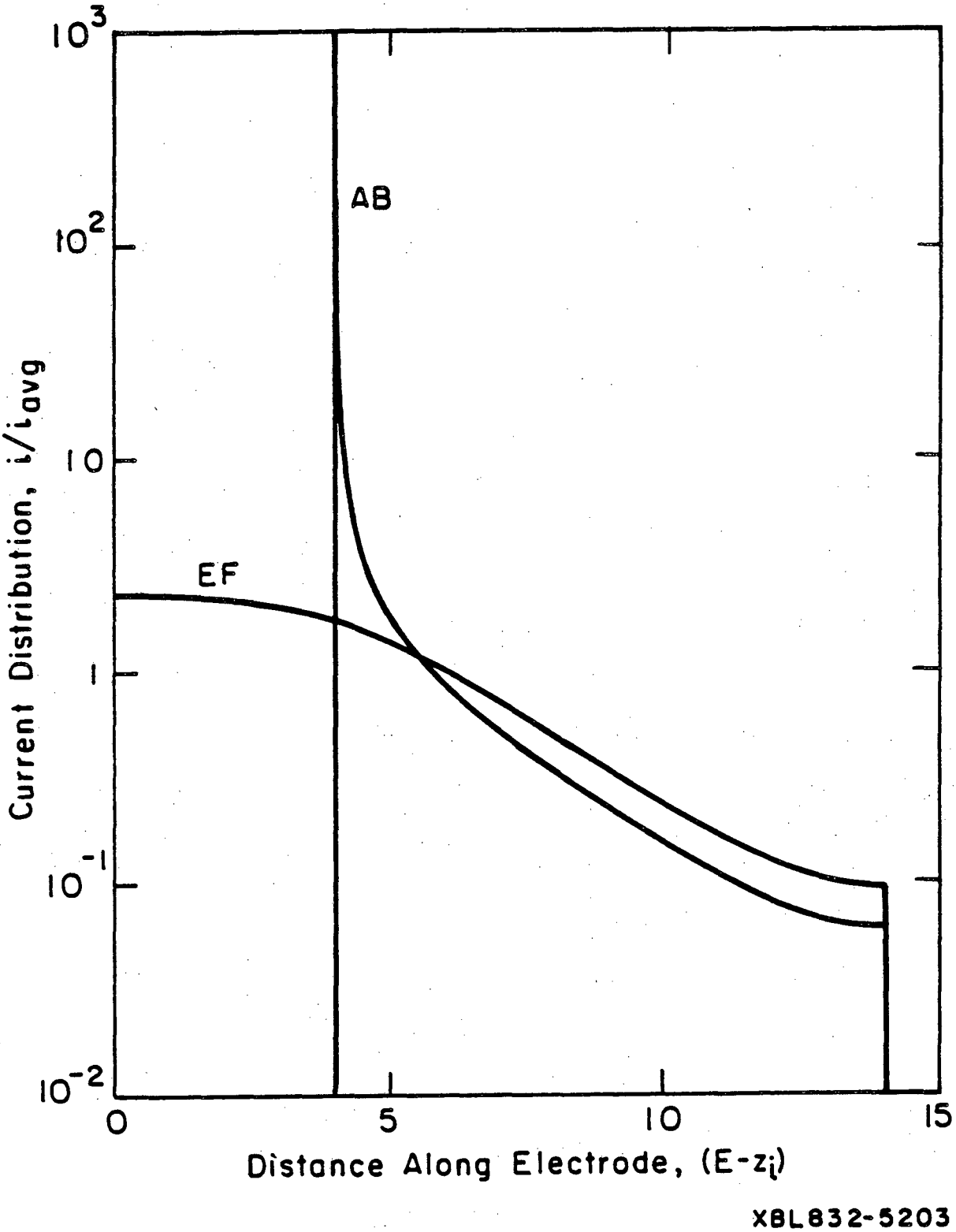

Figure 4. Current distribution along the AB and EF electrodes for L/h = 2.5, t/G = 0.25, and h/G = 1.

Figure 5. The behavior close to the edge is emphasized, and the expected -2/3 power dependence on $(A - z_i)$ is observed.

Far from the gap, the asymptotic form for the current distribution is

$$\frac{i(z_i)}{i_{avg}} = const\ \nu \cosh[\nu\ (z_i - z_{i,max})]\ , \tag{13}$$

where

$$\nu = \frac{\pi}{2h}\ .$$

The calculated current distributions for the AB and the EF electrodes are presented along with equation (13) in Figures 6 and 7, respectively. The constant was obtained by matching the asymptotic solution at $z_{i,max}$ to the calculated current distribution. The calculated current distributions match the asymptotic solutions in the region far from the gap.

4.2. Primary Cell Resistance

The primary cell resistance can be expressed as a dimensionless group $W\kappa R$. The dimensionless primary cell resistance for this system is a function of three geometric ratios, as described in the previous section. In the limit that the thickness t approaches zero, the resistance approaches a value that is independent of t/G. The cell resistance can therefore be expressed as the sum of the resistance for t/G equal to 0, $W\kappa R_0$, and a dimensionless correction term, Δ.

$$W\kappa R = W\kappa R_0 + \Delta\ . \tag{14}$$

The resistance $W\kappa R_0$ is presented in Figure 8 as a function of L/h with h/G as a parameter. For all values of h/G, the dimensionless resistance in Figure 8 approaches a constant value as L/h becomes greater than 2. The additional electrode length is relatively inaccessible and does not contribute much to current flow (see Figures 3 and 4). For all values of h/G and with

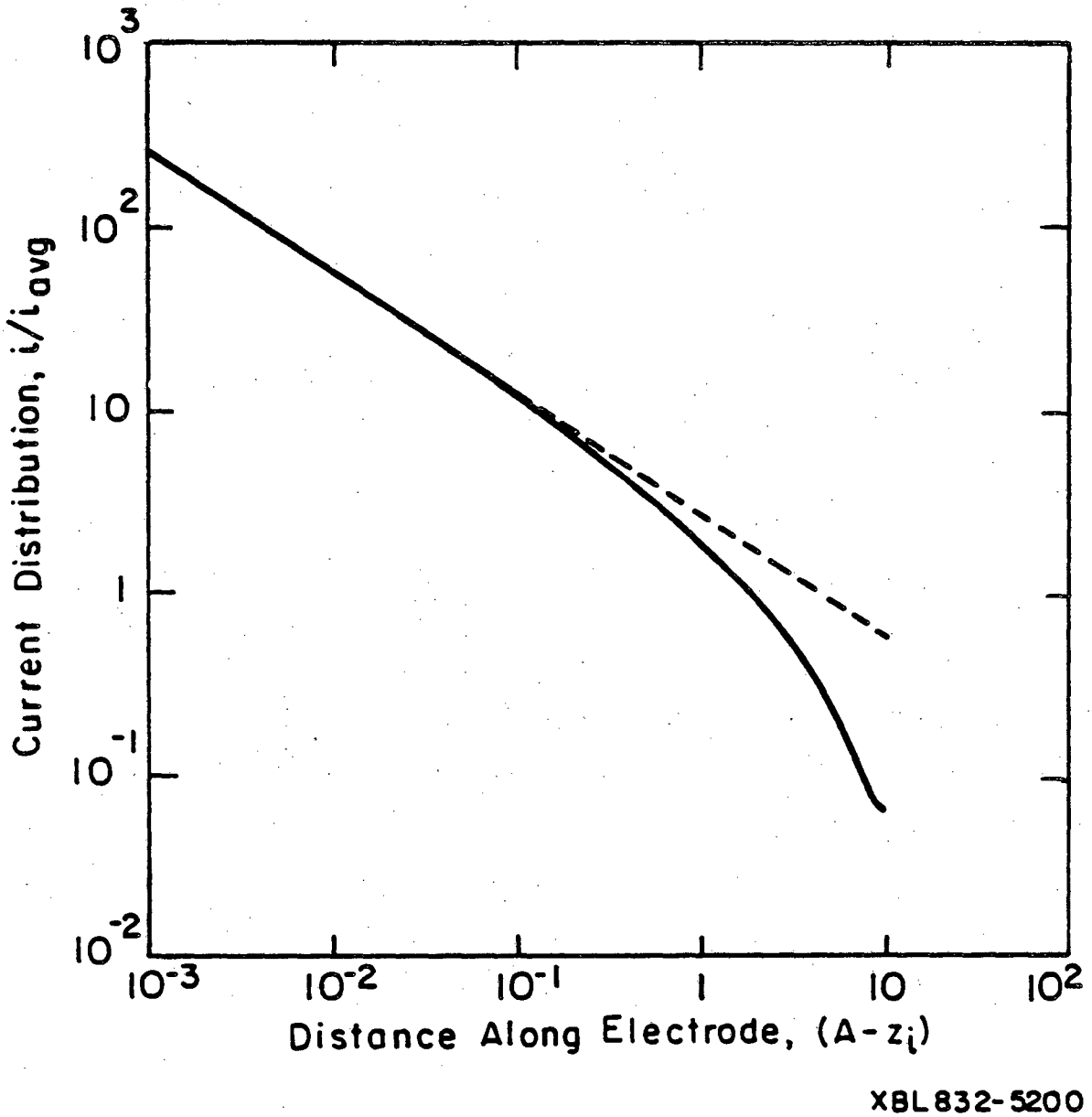

Figure 5. Current distribution along the AB electrode compared to the asymptotic solution for L/h = 2.5, t/G = 0.25, and h/G = 1.

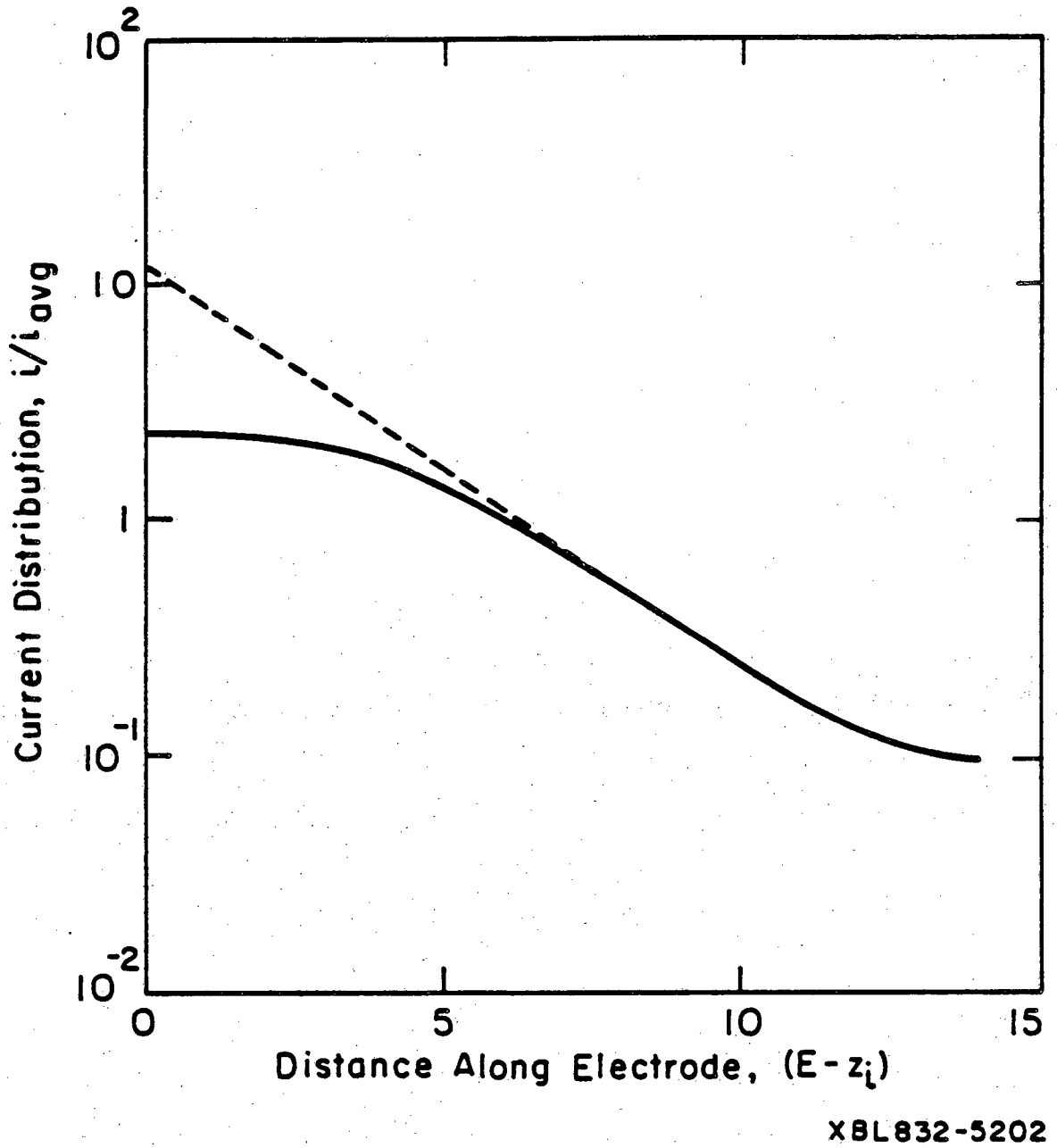

Figure 6. Current distribution along the EF electrode compared to the asymptotic solution for L/h = 2.5, t/G = 0.25, and h/G = 1.

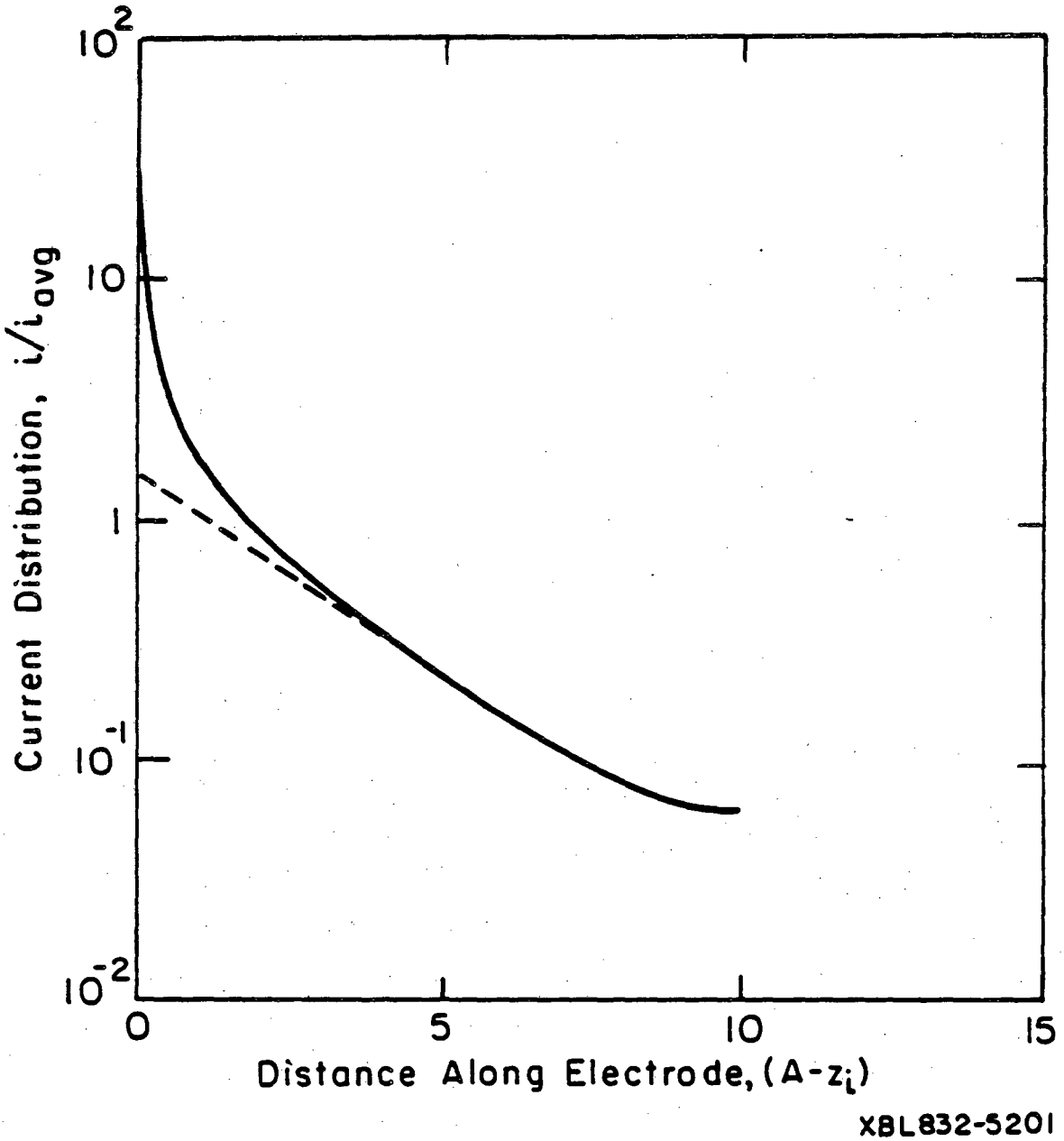

Figure 7. Current distribution along the AB electrode compared to the asymptotic solution for L/h = 2.5, t/G = 0.25, and h/G = 1.

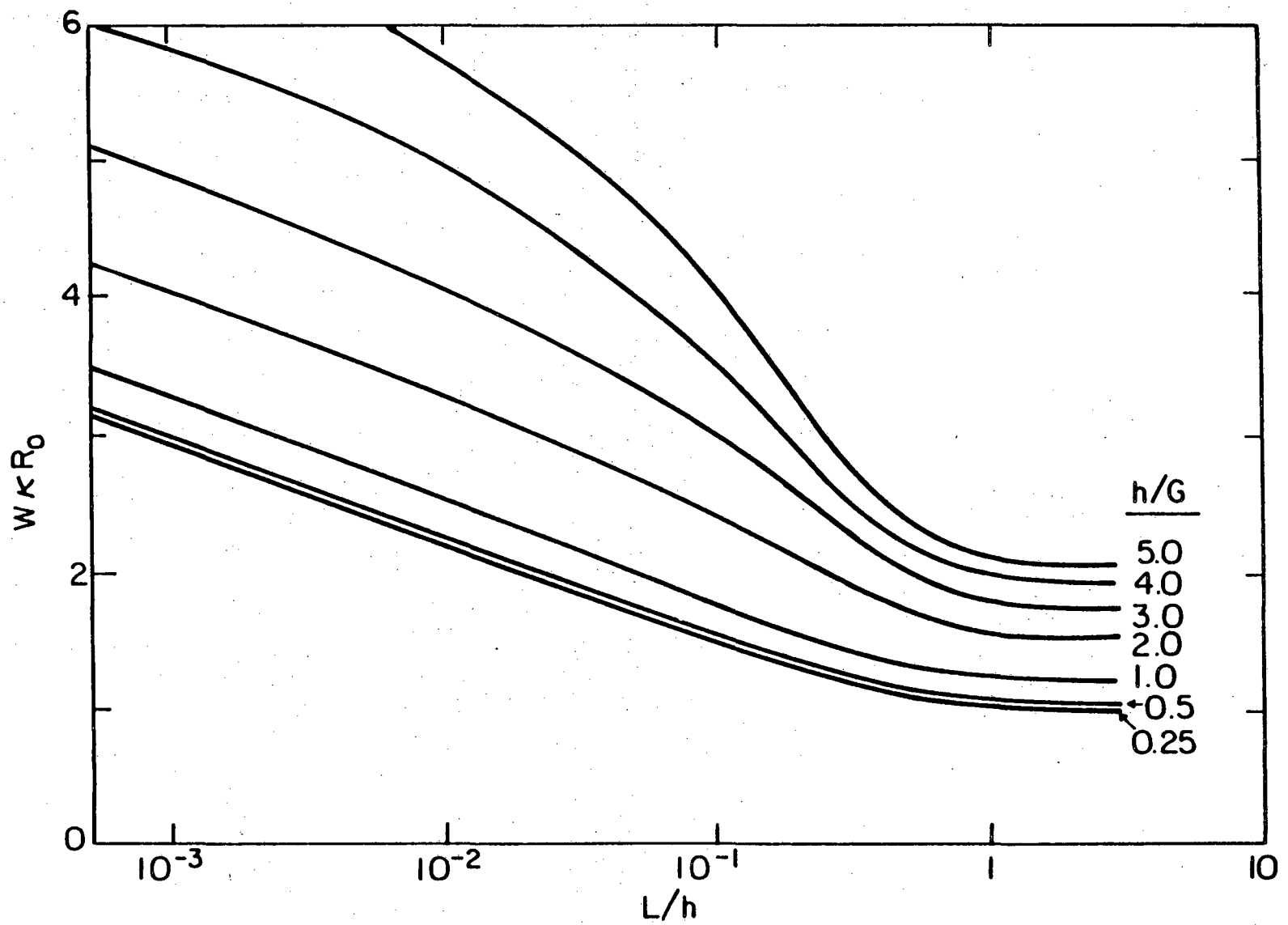

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Figure 8. Dimensionless cell resistance with t/G equal to zero as a function of L/h with h/G as a parameter.

sufficiently small values of L/h, the resistance approaches infinity with $\left[-\frac{1}{\pi}\ln(L/h)\right]$ as L/h approaches zero.

The resistance correction term, Δ, can be considered to be the additional resistance due to a finite (non-zero) electrode thickness t. Δ is presented in Figure 9 as a function of t/G with L/h as a parameter. This term is independent of h/G and is only a very weak function of L/h. The correction term is given by the upper line in Figure 9 for $L/h>1$ and by the lower line in Figure 9 for $L/h<0.01$. The slope for $t/G>0.5$ has the value 1, as anticipated from the asymptotic solutions for t/G approaching infinity.

The cell resistance for a given configuration can be obtained from Figures 8 and 9 with equation (14). The cell resistance is smallest when the gap (G) is large, the height (h) is small, and the electrode length (L) is large. An approximate analytic expression for the cell resistance can be obtained by interpolation of asymptotic solutions to Equation (11). The correction term for a finite electrode thickness can be expressed by

$$\Delta = t/G + \Delta_1 . \tag{15}$$

The resistance of the cell with a zero electrode thickness is given by

$$W\kappa R_0 = \frac{1}{\pi}\ln\left[\frac{16(1+\frac{c}{b})}{(1-\frac{c}{d})} - (32 - e^{\pi})\right] + \Delta_0 , \tag{16}$$

where

$$\frac{b}{c} = \tanh\left\{\frac{\pi}{2}\left[\frac{(\frac{L}{G})^4}{(1+2\frac{L}{G})^2} + (\frac{L}{h})^4\right]^{0.25}\right\}, \tag{17}$$

$$(1-\frac{c}{d}) = 2\,\frac{\sinh^2(\frac{x}{2})}{\cosh(x)} , \tag{18a}$$

and

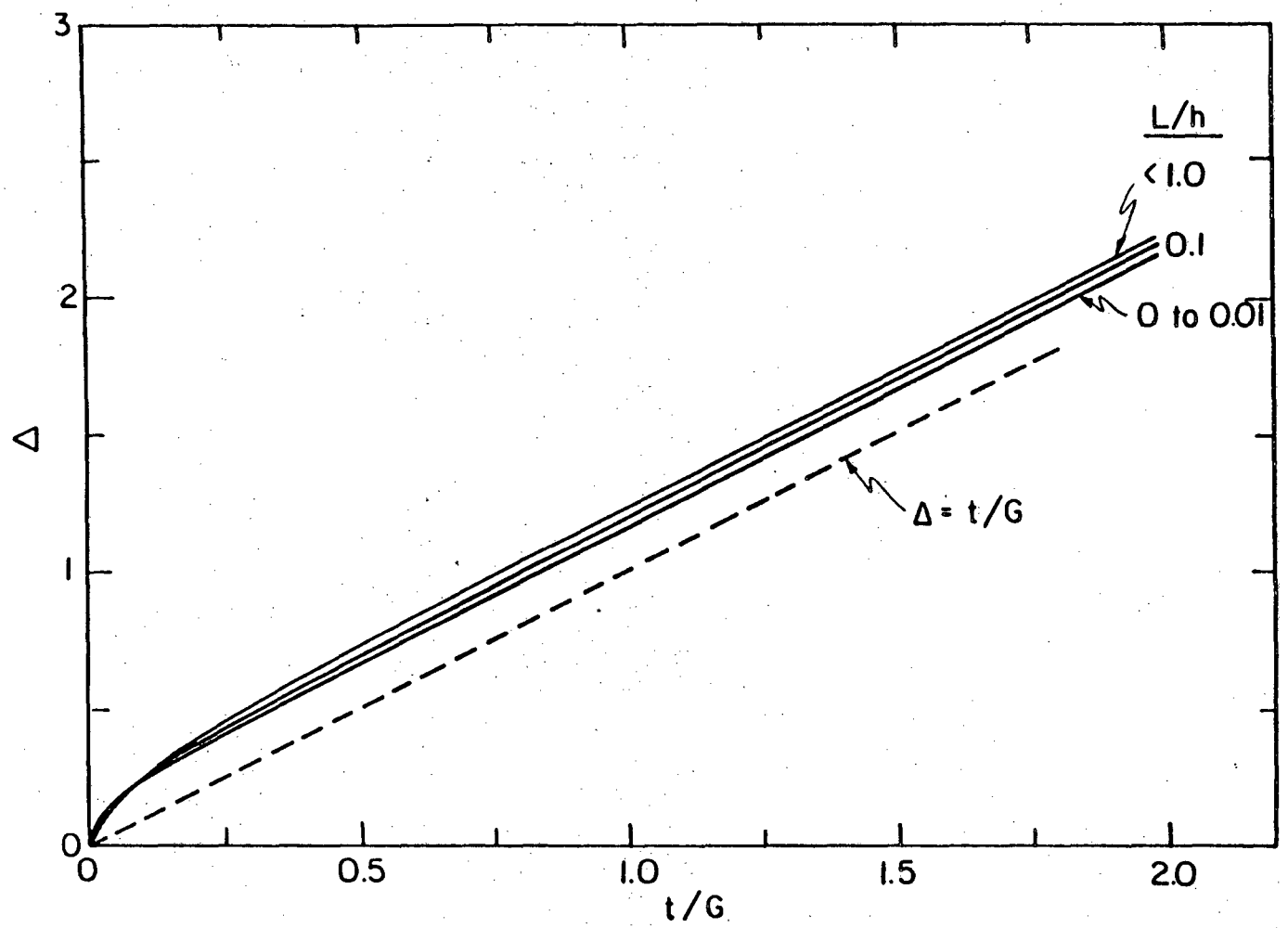

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Figure 9. Dimensionless correction to the cell resistance as a function of t/G with L/h as a parameter.

$$x = \frac{4\cos(\frac{\pi}{2}\frac{L}{L+G})\, e^{-\frac{\pi}{2}\frac{h}{L+G}}}{\cosh(0.3\,\frac{\pi}{2}\frac{L}{h})} + \frac{\frac{\pi}{2}\frac{G}{h}}{\cosh^2(1.2\,\frac{\pi}{2}\frac{h}{L+G})}. \tag{18b}$$

The term Δ_o in equation (16) is presented in Figure 10 as a function of L/h. This term amounts to less than five percent and approaches a constant value as L/h approaches infinity and as L/h approaches zero. The term Δ_1 in equation (15) is presented in Figure 11.

The effect of the cell resistance in the photoelectrochemical cell proposed in Section 2 must be balanced with the need for a large semiconductor area open to illumination. Optimal design of this cell requires a large number of narrow slots.[13,14] The resistance of such a cell with $h/G = 10$, $L/h = 0.5$, and $t/G = 20$, can be expressed in terms of equations (14), (15), and (16) as

$$\begin{aligned} W\kappa R &= W\kappa R_o + \Delta_0 + t/G + \Delta_1 \\ W\kappa R &= 2.9891 + 0.0148 + 20. + 0.2 \end{aligned} \tag{19}$$

The error in neglecting the correction terms, Δ_0 and Δ_1, is 0.93 percent.

5. CONCLUSIONS

Numerical integration was coupled with the Schwarz-Christoffel transformation to calculate primary current distributions and cell resistances. Primary current distributions and resistances were presented for a cell consisting of a slotted electrode over a solid electrode. An approximate analytic expression for the cell resistance was presented.

6. ACKNOWLEDGEMENT

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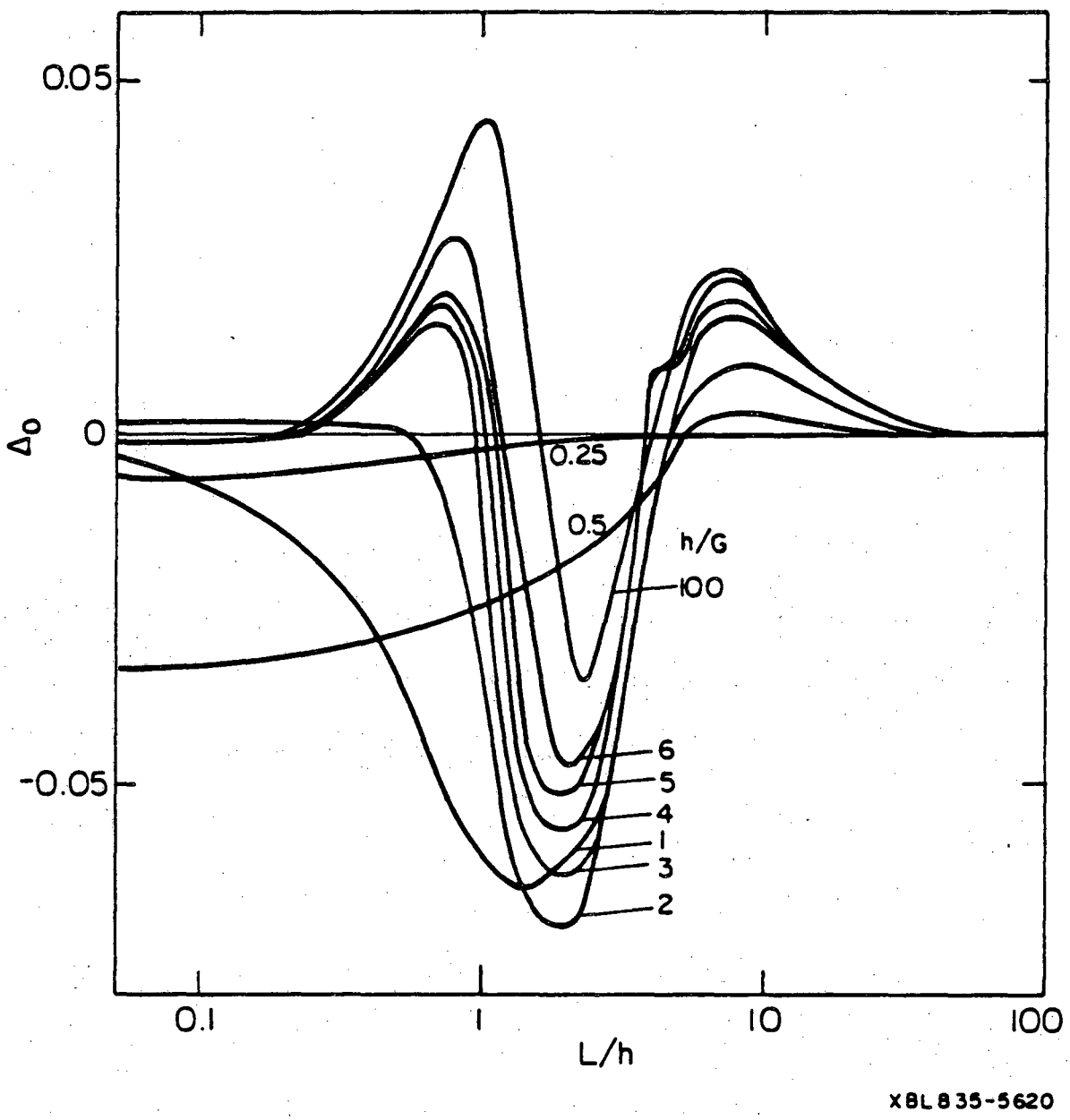

Figure 10. Dimensionless correction to equation (16) for the resistance of a cell with t/G = 0.

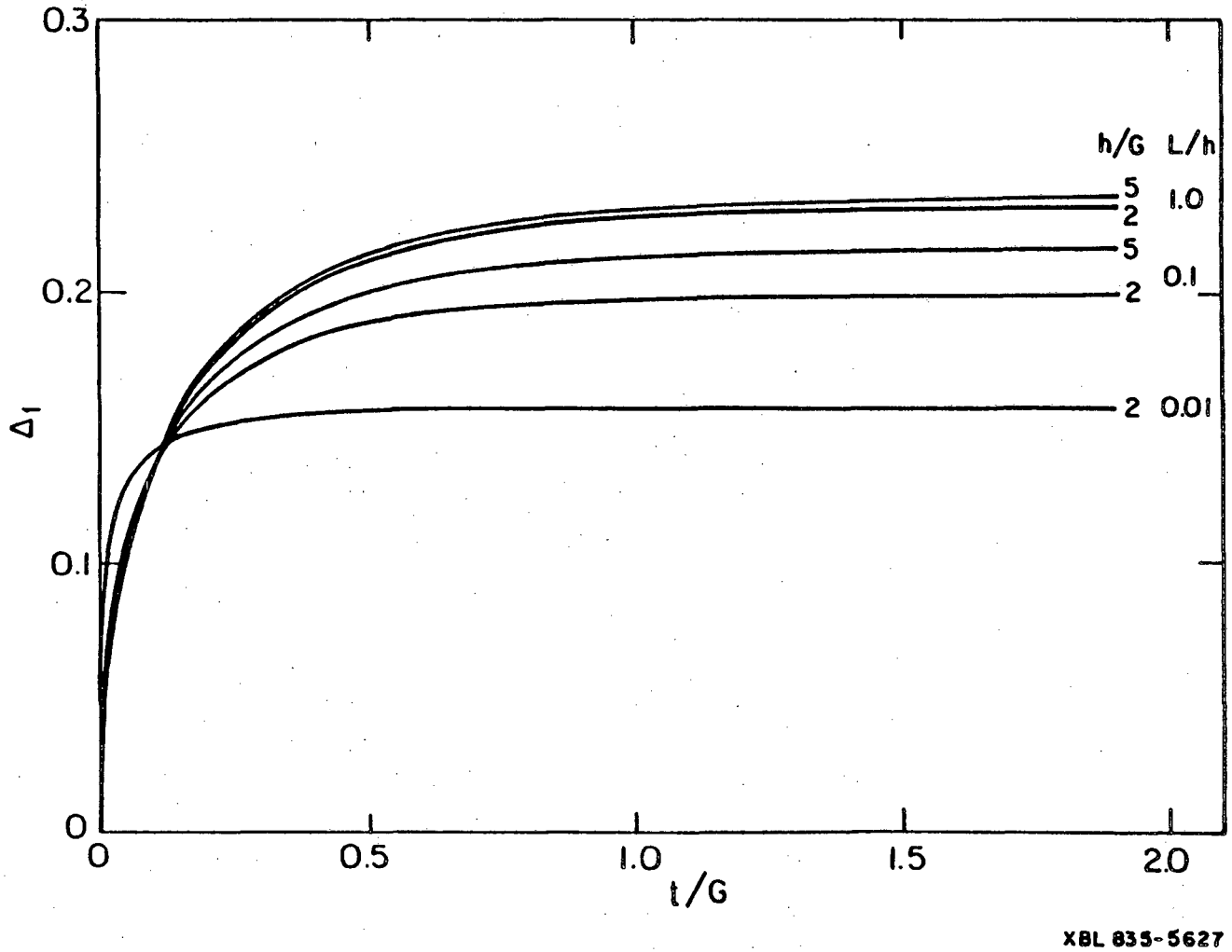

Figure 11. Dimensionless correction to equation (15) for the contribution of t/G to the cell resistance.

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7. NOTATION

8. Roman Characters

G	distance between edge of AB electrode and the center of the gap, cm
h	separation between electrode AB and cover plate CD, cm
i	current density, mA/cm^2
j	$\sqrt{-1}$
L	half length of AB electrode, cm
t	thickness of AB electrode assembly, cm
V	cell potential, V
W	cell width, cm

9. Greek Characters

α	angle at corner of electrode and insulating wall, radians
Δ	cell resistance correction associated with a finite value of t/G
Δ_0	error term in equation (16)
Δ_1	error term in equation (15)
κ	conductivity, mho/cm
ϕ	electrical potential, V

10. Subscripts

avg	average
i	imaginary
o	value with $t/G = 0$.
r	real

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