Primary Current Distribution and Resistance of a Slotted-Electrode Cell

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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.

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 equilibrium potential 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.

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.

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 \( z = 0 \). 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 Fig. 2b by

\[ z = \int_{t_0}^{t} \frac{(a^2 s - t^2)^{1/2}}{(b^2 - t^2)^{3/2}(c^2 - t^2)^{3/2}(d^2 - t^2)^{1/2}} \, dt \]  

Cell Geometry

A cell geometry is presented in Fig. 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 flows from the semiconductor to 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 \( W \) (in the direction perpendicular to the plane of the paper in Fig. 1b) is large as compared to the spacing between slots, has the electrochemical characteristics of the two-dimensional cell presented in Fig. 2a. Here, the cell has been turned from Fig. 1b so that illumination now comes from the right in Fig. 2a; the semiconductor electrode is represented by \( AB \), the counterelectrode by \( EF \), and all other boundaries of the cell are considered to be insulators. The lines \( DE \) and \( BC \) and \( FG \) represent two planes of symmetry in the cell in Fig. 1b; one plane bisects the semiconductor electrode, and the other bisects the slot.

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

Fig. 1. Schematic diagram of the slatted-semiconductor photovoltaic cell
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 \( z = 0 \), 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
\[
\frac{dz_r}{dt_1} \bigg|_{ab} = jf(t_r) \quad [2a]
\]
where
\[
f(t_r) = \frac{(a^2 - t_r)^{1/2}}{(b^2 - t_r)^{1/2}(b^2 - t_r)(c + t_r)(d^2 - t_r)^{1/2}} \quad [2b]
\]
These equations will be used to calculate the derivative of the potential at the electrodes; \( z \) is the direction normal to the electrode in the \( z \) plane, and \( t_1 \) is the direction normal to the electrode in the \( t \) plane.

The variable \( \chi \) (see Fig. 2c) is related to the \( t \) plane by the Schwarz-Christoffel transformation
\[
\chi = \int_t^\infty \frac{1}{(t - a)(b - t)^{(c - t)(-c - d)}(-t - d)} dt \quad [3]
\]
Along the electrode \( ab \), Eq. [3] can be expressed as
\[
\frac{d\chi_r}{dt_1} \bigg|_{ab} = g(t_r) \quad [4a]
\]
where
\[
g(t_r) = \frac{1}{(t_r - a)(b - t_r)(c + t_r)(d + t_r)^2} \quad [4b]
\]
Equations [2] and [4] are also valid at the electrode \( EF \) \((-c -d\). The variable \( \chi_l \) is normal to the electrode in \( \chi \) space, and \( t_1 \) is, as above, normal to the electrode in \( t \) space.

The potential in the \( \chi \) system is
\[
\Phi = \frac{\chi_r}{\chi_{r,\text{max}}} V \quad [5]
\]
where \( V \) is the cell potential difference and \( \chi_{r,\text{max}} \) is the separation between electrodes in \( \chi \) space. The current density is related to the potential derivative at the electrodes. In the \( \chi \) system, this derivative is given by
\[
\frac{\partial \Phi}{\partial \chi_r} \bigg|_{c-d} = \frac{1}{\chi_{r,\text{max}}} V \quad [6]
\]
The potential derivative at the electrode \( ab \) in the \( t \) system is
\[
\frac{\partial \Phi}{\partial t_1} \bigg|_{ab} = \frac{\partial \Phi}{\partial \chi_r} \bigg|_{ab} \frac{\partial \chi_r}{\partial t_1} \bigg|_{ab} \quad [7]
\]
and the potential derivative in the \( z \) system is given by
\[
\frac{\partial \Phi}{\partial z_r} \bigg|_{ab} = \frac{g(t_r)}{f(t_r)} \frac{V}{\chi_{r,\text{max}}} \quad [9a]
\]
and
\[
\frac{\partial \Phi}{\partial z_r} \bigg|_{c-d} = \frac{g(t_r)}{f(t_r)} \frac{V}{\chi_{r,\text{max}}} \quad [9b]
\]
respectively.

The current distribution along the electrode \( AB \) is therefore given by
\[
\frac{i(z_r)}{i_{avg}} = \frac{g(t_r)}{f(t_r)} \int_0^\infty \frac{g(t_r)}{f(t_r)} dz, \quad [10]
\]
A similar expression results for the electrode \( EF \). The dimensionless primary cell resistance is
\[
\frac{W_{R}}{R} = \frac{\chi_{r,\text{max}}}{\int_0^\infty f(t_r) \int_0^\infty g(t_r) dz} \quad [11]
\]
where \( R \) is the actual cell resistance. 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 Eq. [1] (13). The value of \( \chi_{r,\text{max}} \) was obtained through numerical integration of Eq. [3] between the limits of \( a \) and \(-d\). The values of \( t_1 \) corresponding to given values of \( z \) were calculated from asymptotic solutions of Laplace’s equation. The result most useful for cell design, however, is the cell resistance.

**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.

**Primary current distribution.** The primary current distributions on the \( AB \) and \( EF \) electrodes are presented in Fig. 3. 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 Fig. 2a). 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 distribu-
The calculated current distributions for the $AB$ and the $EF$ electrodes presented in Fig. 3 show agreement with this form for values of $E - z_i$ greater than about 7.5. The curves have the same shape in this region but are displaced vertically, attesting to the need for a different coefficient (“const.”) for the two electrodes.

**Primary cell resistance.**—The primary cell resistance $R$ can be expressed in terms of a dimensionless group $WkR$. 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, $WkR_0$, and a dimensionless correction term $\Delta$.

\[
WkR = WkR_0 + \Delta
\]  

The resistance $WkR_0$ is presented in Fig. 5 as a function of $L/h$ with $h/G$ as a parameter. For all values of $h/G$, the dimensionless resistance in Fig. 5 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 Fig. 3). For all values of $h/G$, the resistance approaches infinity as $L/h \rightarrow 1$ (or $L/h > 1$) as $L/h$ approaches infinity. The resistance increases with $h$ at constant $L$ and $G$ because the distance between the electrodes $AB$ and $EF$ increases.

The correction term $\Delta$ can be considered to be the additional resistance due to a finite (nonzero) electrode thickness $t$. $\Delta$ is presented in Fig. 6 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 Fig. 6 for $L/h > 1$ and by the lower line in Fig. 6 for $L/h < 0.01$. The slope of $t/G > 0.5$ 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 Fig. 5 and 6 with Eq. [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 Eq. [11]. The correction term for a finite electrode thickness can be expressed by

\[
\Delta = t/G + \Delta,
\]  

The resistance of the cell with a zero electrode thickness is given by
Fig. 6. Dimensionless correction to the cell resistance as a function of \( t/G \) with \( L/h \) as a parameter.

\[
W_R = \frac{1}{\pi} \ln \left[ \frac{16}{(1 - e^{-x})} \right] - (32 - e^x) + \Delta_\alpha \tag{16}
\]

where

\[
b/c = \tanh \left\{ \frac{\pi}{2} \left[ \frac{(1 + \frac{c}{b})}{L} \right]^{\frac{1}{2}} + \left( \frac{L}{h} \right)^{0.5} \right\} \tag{17}
\]

\[
\left( 1 - \frac{c}{d} \right) = \frac{\sinh^2 \left( \frac{x}{2} \right)}{\cosh(x)} \tag{18a}
\]

and

\[
x = \frac{4 \cos \left( \frac{\pi}{2} \frac{L}{L + G} \right) e^{-\frac{\pi}{2} \frac{h}{L + G}}} {\cosh \left( 0.3 \frac{\pi}{2} \frac{L}{h} \right)} + \frac{\pi}{2} \frac{G}{h} \cosh^2 \left( 1.2 \frac{\pi}{2} \frac{h}{L + G} \right) \tag{18b}
\]

Fig. 7. Dimensionless correction to Eq. [16] for a resistance of a cell with \( t/G = 0 \).

The term \( \Delta_\alpha \) in Eq. [16] is presented in Fig. 7 as a function of \( L/h \). This term amounts to less than 5% and approaches a constant value as \( L/h \) approaches infinity and as \( L/h \) approaches zero. The term \( \Delta_b \) in Eq. [15] is presented in Fig. 8.

The effect of the cell resistance in the photoelectrochemical cell proposed in the "Cell Geometry" section 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 Eq. [14], [15], and [16] as

\[
WKR = W_R + \Delta_b + t/G + \Delta_\alpha \tag{19}
\]

\[
WKR = 2.9891 + 0.0148 + 20. + 0.2
\]

The error in neglecting the correction terms, \( \Delta_\alpha \) and \( \Delta_b \), is 0.93%.

Conclusions

The primary resistance of a slotted-electrode cell was obtained by numerical integration coupled with the Schwarz-Christoffel transformation. An approximate analytic expression is also presented for the cell resistance. The slotted-electrode cell design may be well suited for photoelectrochemical devices for solar energy conversion. For optimal solar cell designs, the cell resistance can be expressed as the sum of \( W_K R \) (given by Eq. [16]) and the simple parallel-plate term \( t/G \).

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LIST OF SYMBOLS

- \( G \): 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/cm²)
- \( L \): half-length of \( AB \) electrode (cm)
- \( R \): cell resistance (Ω)
- \( t \): thickness of \( AB \) electrode assembly (cm)
- \( V \): cell potential (V)
- \( W \): cell width in direction with no variations (cm)
Effect of the Ru\textsuperscript{3+} Surface Treatment

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ABSTRACT

We present a method for obtaining the photodissolution kinetics of n-GaAs in 1M KOH. It is based upon the simultaneous measurement of photocurrent and impedance. It is shown that an accurate determination of the band bending is absolutely necessary to obtain the actual kinetic constants. In fact, the semiconductor bandedges shift toward positive potentials when illumination is increased. In addition, a potential-dependent surface charge variation is responsible for another voltage drop in the Helmholtz layer which modifies the band bending. This is shown by the surface-state capacitance $C_{s}(V)$, which presents sharp variations in applied potential. According to the current expression, $J_{cor~} = k_{cor} p^{2}$, a value of $k_{cor} = 5.7 \times 10^{-27}$ mA cm$^{-4}$ is found to be independent of the photon flux, the surface orientation, and the ruthenium treatment. This value is used to estimate the stabilization coefficient $s$ of the n-GaAs/1M (Se$^{2-}$/Se$_{2}^{2-}$) + 1M KOH junction. A value of $s$ close to 1% is found. We then discuss the ruthenium treatment in selenide solution, where energetic conditions for charge transfer are changed through surface-charge modifications. Our calculations show an improvement of both cell performances and stability, as expected, when the electrode is Ru treated. Moreover, the effect of Ru$^{3+}$ cations upon the impedance data suggests that the flatband potential shift is linked to chemical surface modifications, prior to corrosion. This is confirmed by the fact that $k_{cor}$ is not photon-flux dependent. Finally, we examine whether the bonds (GaAs) with one electron might be responsible for the bandedge shift and the $C_{ss}(V)$ behavior of the n-GaAs/1M KOH junction. The case of the Se$^{2-}$ stabilized junction is also discussed.

For many years, the photocorrosion process at illuminated n-type III-V semiconductor electrodes in contact with aqueous electrolytes has been extensively studied in view of possible photoelectrochemical (PEC) application for solar energy conversion. A number of articles deal with the corrosion mechanism itself (1, 2) or with the competition between the photocorrosion of the semiconductor and the oxidation of a redox couple in solution (3-5). Until now, very little, to our knowledge, has been done to estimate the photocorrosion kinetic constants (6, 7).

At first, it was stated that for all n-type semiconductor electrodes, except Ge, holes are entirely responsible for the photocorrosion reaction (1). For example, for GaAs, six charges per molecule of GaAs are consumed. It is shown also for III-V semiconductors that the stabilization coefficient, defined as the fraction of the photocurrent associated with the oxidation of the redox couple over the total photocurrent, is light-intensity dependent (3, 4). This very important result led workers to study the different mechanisms for explaining the competition between the semiconductor and redox couple photo-oxidations (1-5). These studies show that the corrosion process can be described by a two-step reaction, each one involving a hole. The first one is rate limiting while the second one is considered as very fast. Cardon et al. (3) developed a very general kinetic scheme assuming the first corrosion step can be reversible or not, the transfer upon the redox couple: direct or indirect, and the intermediates mobile or motionless. These assumptions lead, for III-V semiconductors, to $s = f(y/j)$ or $s = f(y/j^{2})$ relationships, where $y$ is the redox concentration and $j$ the total photocurrent. Unfortunately, it seems difficult to connect unambiguously experimental facts to these resulting equations. If a mechanism may be deduced from such equations, the number of parameters does not reasonably allow one to reach a kinetic constant for the corrosion. This quite extensive analysis was applied to n-GaP and n-InP electrodes (3). However, Frese and co-workers (4) and, more recently, Gerischer (5) presented very similar models for the corrosion-stabilization mechanism of n-GaAs and n-GaP, respectively.

In fact, all these models can be reduced to a mechanism that focuses on the breaking of a single surface bond, involving two electrons, as the one of Frese et al., although it is known that six holes are consumed per mole-