We now come to the question of how increased anodic dissolution promotes intergranular stress corrosion cracking. One might expect anodic dissolution to promote crack blunting. The simplest explanation seems to be that this is a case of active path dissolution or "stress-assisted intergranular corrosion." The corrodents, by delaying repassivation, keep the anodic process going within the grain boundary region until the zone of very high stress arrives at the next weak point. This could be a defect, dislocation, precipitate core, or strain-induced phase transformation, etc. Metal cracking then occurs, generating fresh metal surface which reinigorates the anodic dissolution reaction, continuing the process. This follows the observations of the Brookhaven workers (13) giving evidence for intermittent crack growth, sometimes at rates higher than can be accommodated by anodic dissolution only. Because the sides of the crack walls around the growing crack tip participate in the anodic process due to the repassivation of the corrodent, the actual current densities are lower than that required by Faraday's law for crack tip advancement.

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Calculation of the Electrical Resistance of a Compact Tension Specimen for Crack-Propagation Measurements

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ABSTRACT

The electrical resistance of a notched compact specimen for determination of plane-strain fracture toughness was calculated using numerical methods coupled with the Schwarz-Christoffel transformation. Experimental measurement of this resistance is commonly used to obtain the crack length in notched specimens subjected to stress corrosion and hydrogen embrittlement tests. The results presented here predict the shape of the calibration curve for this experiment and facilitate optimal design of notched specimens for sensitivity of the resistance measurements to crack length. The electrical resistance is shown to be most sensitive to crack length for specimens containing a small starter notch. Placement of the current input leads also influences the sensitivity of the specimen resistance to the crack length. An analytic interpolation formula is presented for the primary resistance as a function of cell dimensions that reproduces the calculated results to within 5%.

The plane-strain fracture toughness of metals can be determined through tensile loading of notched specimens that have been precracked in fatigue. Common methods for this test are described in the annual book of ASTM standards (1). Measurement of crack length is an important step in the test procedure. Electrical resistance measurements have been used to monitor crack lengths in the course of hydrogen embrittlement (2), precipitation (3), sustained load (4), fatigue crack growth (5, 6), and stress corrosion cracking experiments (7, 8). This method has the advantages that the crack length can be monitored continuously and that the specimen is not subjected to intermittent loading and unloading of tensile stress.

The objective of this work is the calculation of the electrical resistance of a compact tension fracture specimen as a function of crack length. This calculation can be used as an aid in the selection of specimen dimensions for optimal sensitivity of electrical resistance to crack length. The results presented here can also be applied to other electrical or electrochemical systems of similar shape for which primary current and potential distributions apply.

Primary current and potential distributions apply to systems for which the surface overpotential can be neglected and the phase adjacent to the electrode has a uniform potential. These assumptions are strictly valid for solid conductors in which the current is electronic. Calculation of the primary current and potential distributions involves solution of Laplace’s equation, $\nabla^2 \phi = 0$, which is not trivial, even for simple geometries. The method of images (9), separation of variables (10), and superposition (11, 12) have been used to solve Laplace’s equation for a number of systems. A review of analytic solutions has been presented by Fleck (13).

The Schwarz-Christoffel transformation (14-16) is a powerful tool for the solution of Laplace’s equation in systems with planar boundaries. This method was used by Mouton (17) to derive the current and potential distribution for two electrodes placed arbitrarily on the boundaries of a rectangle. Hine et al. (18) used this method to describe the primary current and potential 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 (19) presented the primary and secondary current distribution for a two-dimensional slot in a planar electrode. Newman (20) 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.

Theoretical calibration curves for fracture specimens have also been obtained through application of conformal

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mapping for a number of simple specimen geometries, such as center- and edge-cracked plates with various starter notch or crack configurations (21-23). These are reviewed by Halliday and Beever's (24), Aronson and Ritchie (25) and Ritchie and Bathe (26) have obtained numerical solutions of Laplace’s equation for the compact tension specimen considered here through application of finite element analysis. Some discrepancy was found between experimental and calculated crack lengths at long crack lengths. This discrepancy was attributed to the size of the finite-element mesh. Accurate use of finite-element solutions of Laplace’s equation for this system requires a large number of nodes due to the singularities observed at the electrode edges. This difficulty is alleviated by use of the Schwarz-Christoffel transformation.

Application of the Schwarz-Christoffel transformation is generally limited, however, by the difficulty of generating solutions to the resulting integrals. Analytic solutions allow calculation of the primary current and potential distributions 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. Orazem and Newman (27) have coupled application of the Schwarz-Christoffel transformation with numerical integration to calculate the primary resistance and current distribution for a cell containing a slotted electrode. A similar approach is taken here.

**Cell Geometry**

The geometry of a compact tension specimen for measurement of plane-strain fracture toughness is presented in Fig. 1. The ASTM standards for specimen design are included within the figure. These standards are modified for the study of crack growth in response to fatigue. The envelope of the starter notch is typically small; Hackett et al. (8) used a larger notch envelope to accommodate a reference electrode. Use of a large notch may require other adjustment of the cell dimensions, e.g., use of smaller loading pinholes or wider specimens. Under the ASTM standards, the test block must be sufficiently thick that edge effects do not influence the propagation of the crack as a plane. This requirement is consistent with analysis of the primary resistance of this system as being that of a two-dimensional specimen of the shape presented in Fig. 1 and of thickness W.

Under the assumption that electrodes for resistance measurement are placed directly opposite each other, the specimen may be bisected by a plane of symmetry represented by AC in Fig. 1. Thus the specimen will have twice the electrical resistance of the system presented in Fig. 2a, where constant potential surfaces are designated by RS and PQ and all other boundaries are considered to be insulating. The pinholes (see Fig. 1) were assumed to be filled by a close fitting pin with the conductivity of the test specimen. The specimen is placed in a complex coordinate system such that the line OA lies on the real-z axis. 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.

**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

$$z = z_0 + jz_1$$

The z coordinate system is related to the t coordinate system of Fig. 2b by

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

where a, b, c, d, and e are the values of t corresponding to z values of A, B, C, D, and E, respectively. The outside angle at D is represented by β such that βπ = 1/2 for a right-angle corner. The electrode PQ and CS correspond to pq and cs in the t plane.

The variable χ (see Fig. 2c) is related to the t variables by the Schwarz-Christoffel transformation

$$\chi = \int \frac{1}{(t - p)^{1/2}(q - t)^{1/2}(e - t)^{1/2}} dt$$

Solution of Laplace’s equation for the χ system yields the potential as a linear function of χ

$$\Phi = \frac{x_0}{x_{\text{max}}} V$$

where $x_{\text{max}}$ is the separation between electrodes cs and pq in the χ system, and V is the potential difference between the electrodes. The potential drop in the original cell of Fig. 1 is 2V. The current density is related to the potential derivative at the electrodes. The relationships among the potential derivatives at the electrodes in the χ, t, and z coordinate systems are developed in Appendix A. These relationships are the basis for a system of nonlinear integral equations that can be solved to obtain the current density along either electrode in the z coordinate system.

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Fig. 1. Notched specimen for determination of plane-strain fracture toughness.

Fig. 2. Schematic diagram of the sectioned cell with coordinates, a: $x = x_0 + jx_1$, b: $t = t_0 + jt_1$, c: $\chi = \chi_0 + j\chi_1$. 
The dimensionless primary resistance, \( WKR \), is obtained through integration of the current density. The numerical method used in this calculation is presented in Appendix B. The primary current distribution and the dimensionless resistance are functions only of geometric ratios.

**Results**

The methods outlined in Appendix B were used to calculate the primary current distribution and the primary resistance of the crack-propagation test block. The calculation of the primary current distribution was used primarily to check the calculations. The quantity of greatest interest for test block design is the primary resistance, presented in the Primary resistance section.

Current distribution.—The current distribution close to the edge of an electrode adjoining an insulator with an angle \( \alpha \) is

\[
\frac{i(z)}{i_{ave}} = \text{const.} \frac{\pi}{2\alpha} (Q - z) \cosh^{-1} \left[ \frac{z_j}{zh} \right] \quad [4]
\]

where \( Q \) is the point of intersection of the electrode and the insulator. The calculated current distribution shows the expected asymptotic behavior, being proportional to \( (Q - z)^{1/2} \) at \( P, Q, \) and \( S \), and approaching a finite value at \( C \).

Primary resistance.—The primary resistance of the cell can be expressed as the dimensionless group \( WKR \). The dimensionless primary resistance is a function of the angle \( \beta \), three geometric ratios associated with cell shape (e.g., \( Z_l/Z_h, Z_m/Z_h, \) and \( Z_c/Z_h \)), and three geometric ratios associated with electrode placement (e.g., \( Z_l/K_m, Z_m/K_h, \) and \( Z_c/K_h \)). In the limit of the starter envelope area approaching zero, the primary resistance approaches that of a rectangle with appropriately placed electrodes. The solution for this problem has been presented by Moulton (17) in terms of tabulated elliptic functions (29) as

\[
WKR_m = K(1 - m)K(m) \quad [5]
\]

where \( K(m) \) is the complete elliptic integral of the first kind with parameter \( m \). The parameter is obtained from the geometry of the rectangle by

\[
m = \frac{\sin(z_l/m) - \sin(z_m/m)}{\sin(z_m/m) - \sin(z_c/m)} \quad [6]
\]

where \( m \) is the parameter defined by \( K(1 - m)/K(m) = L/h, \) \( z_l \) is the location of point \( Q, z_m \) is the location of point \( P, \) and \( z_c \) is the location of point \( S \). Equation (16.23.1) in Ref. (29) was used to calculate values for the elliptic function \( m \).

The primary resistance of a rectangle is presented in Fig. 3 as a function of the dimensionless length of the electrode \( \xi = (z_l - z_o - z_c)/z_h \). This value represents a first approximation to the primary resistance of the notched specimen and includes the influence of electrode placement and crack length. The variable \( \xi \) approaches zero as the crack grows to bisect the block, and the primary resistance approaches infinity according to

\[
WKR \rightarrow -2\pi \ln(\xi) \quad [7]
\]

The greatest sensitivity of primary cell resistance to crack length is shown to be for values of \( \xi \) less than 0.5. Under the ASTM standards, the maximum value for \( \xi \) is 0.4. The range of values for \( \xi \) that are of greatest interest for crack-propagation experiments extends from 0.1 to 0.4. Under the restriction of the ASTM standards for the length of the starter crack envelope, this corresponds to values of dimensionless crack length \( z_l/z_c \) of 0 to 0.3. Placement of electrodes in a manner that increases the mean path for current flow \( (z_l/z_c \rightarrow \infty) \) also increases the sensitivity of resistance to crack length in the region of primary importance to crack-length measurements; this advantage is offset by the disadvantage that the resistance in this region no longer be represented by Eq. [7].

Primary resistance curves are presented in Fig. 4 for test blocks with finite crack envelope areas. The sensitivity of resistance measurements to crack length in the region 0.1 < \( \xi \) < 0.4 decreases with increasing envelope area. A large notch is associated with a reduced area available for conduction of electrical current. Thus, Moulton's solution for a rectangular conductor with no notch area represents a lower limit to the primary resistance of the notched specimen. The influence of the notch is greatest for \( z_l/z_c \) equal to zero (\( \xi = 0.4 \)) and is a strong function of crack length in this region. The notch has a smaller influence on the resistance as the crack length increases and is associated with a uniform contribution to the primary resistance in the limit of \( \xi \rightarrow 0 \).

The primary resistance can therefore be represented by the sum of Moulton's solution and an additional resistance associated with the notch area. The additional resistance associated with notch area is presented in Fig. 5 as a function of crack length. This term is a function of notch area and electrode placement, but is relatively independent of block length. An interpolation formula for this term can be developed such that the primary resistance of the block is written

\[
WKR = WKR_m + \frac{m}{L} \left[ 0.5 \left( \frac{\mu}{1 - \mu} \right)^{1.5} - 0.10 \right] + \Delta_2 \quad [8]
\]

\[
\Delta_2 = 0.005 - 0.5(\xi - 0.44) \quad [9]
\]

\[
\Delta_3 = 0.10 - 0.25(\xi - 0.44) \quad [10]
\]

\[
\Delta_4 = 0.05 - 0.5(\xi - 0.44) \quad [11]
\]

**Fig. 3.** Moulton's solution for the primary resistance of a rectangular conductor with \( z_l/z_c = 0.4 \). The resistance of the specimen shown in Fig. 1 is obtained by multiplying the resistance given above by two.

**Fig. 4.** Primary resistance of a sectioned cell with dimensions \( z_l/z_c = 0.4, z_l/z_h = 0.16, z_c/z_h = 0.6, \) and \( \beta = 0.25 \). Moulton's solution for a rectangular conductor is given by dashed lines. The resistance of the specimen shown in Fig. 1 is obtained by multiplying the resistance shown above by two.
where $\text{WeR}_n$ is the solution obtained by Moulton, $\Gamma$ is a function of the notch area given by

$$\Gamma = \left\{ \frac{z_m}{0.02z_m} \left[ z_m - \frac{1}{2} z_m \tan [\pi(1/2 - \delta)] \right] \right\}^{1.221} \tag{9}$$

$\xi$ is $(z_n - z_m)/z_m$, $\mu$ is $z_m/z_n$, and $\Delta_\xi$ is a difference variable plotted in Fig. 6 as a function of $\xi$. Neglect of $\Delta_\xi$ results in an error of less than 5% for the primary resistance of a notched test specimen with dimension close to the ASTM standards.

These results suggest that Eq. (7) provides a suitable form for calibration curves for compact tension specimens with small notch areas. This work does not address the question of potential lead placement. Aronson and Ritchie (26) state that the top surface close to the notch is the preferred location for positioning leads for measurement of potential differences across the cracked region. This location minimizes errors associated with the uncertainty of probe location. The resistance obtained as a function of crack length with leads separated from the notch decreases the sensitivity of resistance to crack length in the region of primary importance to crack-length measurements; this advantage is offset by the disadvantage that the resistance in this region can no longer be represented by Eq. (7).

An expression is presented for the primary resistance of a notched test specimen. This expression is accurate to within 5%, and can be used to predict the resistance of such objects. This work should not be used, however, to calculate independent calibration curves for test blocks.

The calculations presented here involve the assumption of a uniform specimen conductivity. A nonuniform conductivity is frequently the result of localized stress such as expected near the crack tip. This work, however, predicts the shape of the calibration curve and facilitates the optimal design of the test block for sensitivity of crack measurement.

**Acknowledgment**

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**APPENDIX A**

**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

$$z = x + jy$$

The $z$ coordinate system is related to the $t$ coordinate system of Fig. 2b by

$$z = \int_0^t \frac{(e-t)^{\alpha} \mu}{1/(a-t)^{\alpha}(b-t)^{\beta}(c-t)^{\gamma}(d-t)^{\delta} } dt \tag{A-1}$$

where $\alpha, \beta, \gamma, \delta$, and $\epsilon$ are the values of $t$ corresponding to $z$ values of $A, B, C, D,$ and $E$, respectively. The outside angle at $D$ is represented by $\beta$ such that $\beta/\pi = 1/2$ for a right-angle corner. The electrodes $PQ$ and $CS$ correspond to $p$ and $c$, respectively, in the $t$ plane. Along the electrode $PQ$, Eq. (A-1) can be expressed by

$$\frac{dz}{dt} \bigg|_{pq} = jf(t) \tag{A-2}$$

where

$$f(t) = \frac{(e-t)^{\beta}}{1/(a-t)^{\alpha}(b-t)^{\beta}(c-t)^{\gamma}(d-t)^{\delta} } \tag{A-3}$$

These equations will be used to calculate the derivative of the potential at the electrode; $z$ is the direction normal to the electrode in the $z$ plane, and $z$ is the direction normal to the electrode in the $t$ plane. Along the $c$ electrode, the relationship can be expressed as

$$\frac{dz}{dt} \bigg|_{cz} = -j\frac{dz}{dt} \tag{A-4}$$

where $f(t)$ is given by Eq. (A-3).
The variable \( \chi \) [see Fig. 2c] is related to the \( t \) variables by the Schwarz-Christoffel transformation

\[
\chi = \int_0^t \frac{1}{(t - p)^{a}(q - t)^{b}(c - t)^{c}(s - t)^{d}} \, dt \quad [A-5]
\]

Along the electrode \( pq \), this equation can be expressed as

\[
\frac{dz}{dt}|_{pq} = jg(t)
\]

and along electrodes \( cs \) by

\[
\frac{dz}{dt}|_{cs} = -jg(t)\quad [A-7]
\]

where

\[
g(t) = \frac{1}{(t - p)^{a}(q - t)^{b}(c - t)^{c}(s - t)^{d}}\quad [A-8]
\]

The variable \( \chi_i \) is normal to the electrode in \( \chi \) space, and \( t_i \) is normal to the electrode in \( t \) space.

The current density is related to the potential derivative at the electrodes. In the \( \chi \) system, this derivative is given by

\[
\frac{\partial \phi}{\partial \chi_i}|_{pq} = \frac{V}{\chi_{i,\text{max}}}
\]

The potential derivative at the electrode \( pq \) in the \( t \) system is

\[
\frac{\partial \phi}{\partial t_i}|_{pq} = \frac{\partial \phi}{\partial \chi_i}|_{pq} \frac{\partial \chi_i}{\partial t_i}|_{pq}
\]

and the potential derivative in the \( z \) system is given by

\[
\frac{\partial \phi}{\partial z_i}|_{pq} = \frac{\partial \phi}{\partial t_i}|_{pq} \frac{\partial t_i}{\partial z_i}|_{pq}
\]

From these relationships, the potential derivatives along the electrodes in the original \( z \) coordinate system are obtained as functions of \( t \),

\[
\frac{\partial \phi}{\partial z_i}|_{pq} = g(t) \frac{V}{\chi_{i,\text{max}}}
\]

and

\[
\frac{\partial \phi}{\partial z_i}|_{pq} = g(t) \frac{V}{\chi_{i,\text{max}}}
\]

respectively.

The current distribution along the electrode \( PQ \) is therefore given by

\[
\frac{i}{t_{\text{sys}}} = \int_0^t g(t) \, dt
\]

A similar expression results for the electrode \( CS \). The primary cell resistance is given by

\[
W_{z}R = \frac{\chi_{i,\text{max}}}{\int_0^t g(t) \, dt}
\]

The primary current distribution and the dimensionless cell resistance \( W_{z}R \) are functions only of geometric ratios.

### APPENDIX B

**Numerical Method**

The Schwarz-Christoffel transformation is coupled here with numerical integration of the transformation equations. The solution of these equations involves two steps: determination of \( t \) variable parameters, and integration of Eq. \([A-15]\) and \([A-16]\) to get the primary current distribution and cell resistance.

Determination of the \( t \) variable parameters \((a, b, c, d, e, p, q, \text{ and } s)\) associated with the locations of the corners and electrode edges in the \( z \) coordinate system involves the solution of eight coupled equations of the form

\[
G(x) = \text{Re}(A) - \int_a^b \frac{(e - t)^{\nu}}{t^{a}(a - t)^{b}(b - t)^{c}(c - t)^{d}(s - t)^{e}} \, dt
\]

where \( G(x) = 0, \) and \( x \) is a vector denoting the unknown values \( a \) through \( s. \) Through use of a Taylor series expansion about a trial solution denoted by the superscript \( o, \) the series of equations can be written in the form

\[
G^o = B^o \Delta x
\]

where \( B^o \) is related to the Jacobian of the function \( G^o, \) i.e.

\[
B^o_{ij} = \frac{\partial G^o}{\partial x_i}
\]

and \( \Delta x = x^o - x. \) The Jacobian is a strong function of \( x \) and is evaluated numerically. The inverse of the Jacobian is evaluated, and a converged solution is obtained through Newton-Raphson iteration. The amount of time associated with this computation is strongly dependent upon the value of \( x^o. \) In order to reduce computation times, the inverse of the Jacobian was used to calculate a parameter sensitivity coefficient [see, e.g., Ref. (28)]

\[
d_k = B^{-1} \delta_k
\]

where \( s_k \) is the vector \((\delta G/\delta p)_k, \) and \( p \) represents a given parameter, e.g., dimensionless crack length. Thus, from the converged solution for parameters \( p^o \) a first approximation for \( x(p + dp) \) is obtained as

\[
x(p + dp) = x^o + \sum_{i=1}^{n} d_i dp_i + O(dp^2)
\]

The predicted value for \( x \) is further refined by Newton-Raphson iteration.

Once the values of \( a, b, c, d, e, p, q, \text{ and } s \) are obtained, the current distribution can be obtained through numerical integration of Eq. \([A-15]\). \( \chi_{i,\text{max}} \) can be obtained through integration of Eq. \([A-5]\) from \( p \) to \( q, \) and the primary resistance can be obtained from evaluation of Eq. \([A-16]\).

### LIST OF SYMBOLS

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<th>Greek Characters</th>
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<tr>
<td>( \alpha )</td>
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**List of Symbols**

- \( i \) current density (mA/cm²)
- \( j \) \( V \)
- \( R \) half-cell resistance (Ω)
- \( V \) half-cell potential (V)
- \( W \) cell thickness (cm) (see Fig. 1)
- \( z_c \) crack length (cm) (see Fig. 2a)
- \( z_h \) cell height (cm) (see Fig. 2a)
- \( z_q \) height of electrode for resistance measurement (cm) (see Fig. 2a)
- \( z_r \) length of half-cell (cm) (see Fig. 2a)
- \( z_{m,\text{avg}} \) half-width of starter-crack notch (cm) (see Fig. 2a)
- \( z_{n,\text{avg}} \) width of electrode for resistance measurement (cm) (see Fig. 2a)
- \( \alpha \) angle at corner of electrode and insulating wall
- \( \beta \) angle of notch (see point D in Fig. 2a)
- \( \gamma \) conductivity (mho/cm)
- \( \phi \) electrical potential (V)
An Ellipsometric Study of Electrodeposition and Electrochemical Conversion of Lead Dioxide Films

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ABSTRACT

An automated ellipsometer is used to study the galvanostatic electrodeposition of lead dioxide films onto a platinum substrate from an electrolyte containing lead acetate. The films exhibit regular optical properties over the thickness range from 0 to 600 nm. At a wavelength of 632.8 nm, the refractive index and extinction coefficient are 2.03 and 0.045, respectively. If the deposition process is assumed to require the transfer of two electrons per molecule deposited, the density of the deposited film is calculated to be 7.13 g/cm³. When the lead dioxide films are subjected to alternate anodic and cathodic galvanostatic cycles in neutral borate electrolyte, the optical data exhibit a complex but reproducible structure with inflections at points where the potential-time curve is featureless. A limited quantitative analysis of the optical cycling data can be carried out by requiring consistency between results at widely different film thicknesses. It is possible that the complex optical cycling behavior is due to the presence of two different types of sites for hydrogen within the film.

The experiments whose results are reported in this paper form part of our continuing study of electrochemical conversion in thin film systems. We have found ellipsometry to be a very effective technique for studying such processes both in electrochromic systems, where optical properties are of direct interest, and in battery systems, where they are only of indirect interest. Systems which dictate whether conversion is a homogeneous or heterogeneous process both in electrochromic systems, where optical properties are of direct interest, and in battery systems, where they are only of indirect interest. Systems which dictate whether conversion is a homogeneous or heterogeneous process.

Although there is an extensive literature on the electrochemical conversion of lead dioxide films, ellipsometric studies are usually referenced (7, 8) as unpublished work or work to be published. One exception is the paper by Naegle and Pliech (9), who used an automated ellipsometer to study the galvanostatic deposition of PbO₂ on platinum. They present 1000 data points recorded at 0.25s intervals, but use an analysis technique which they state is not valid for thicknesses beyond 65 nm, and analyze only their first 70 points. Their analysis indicates that the refractive index varies by 20% and the extinction coefficient by a factor of 5 over the range of thickness spanned by their 70 data points, and they conclude only that the optical properties show irregular behavior below 50 nm.

The work we report in this paper has two specific objectives: (i) to study the optical properties of the deposited film to see whether they are as irregular as has been reported, and (ii) to study the optical changes associated with electrochemical conversion of the film to see what ellipsometry can add to our understanding of the processes involved. Our objectives here are similar to those in our recent study of MnO₂ films (10). A priori, we expect electrochemical conversion to be a more complicated process in PbO₂ than in MnO₂, but the ease with which we can observe it...