PREDICTION OF CRACK GROWTH
IN AQUEOUS ENVIRONMENTS

Final Technical Report

July 1986

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SRI International Project No. PYU-4333

Reference: N00014-82-K-0343

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**Title:** Prediction of Crack Growth in Aqueous Environments

**Authors:** L. E. Eisenstein, M.C.H. McKubre, and R. D. Caligiuri

**Abstract:**

The report describes the results of a research program to simultaneously determine the mechanical and electrochemical process that occur within and near the tip of active stress corrosion and corrosion-fatigue cracks. Electrochemical/mechanical impedance analysis is one of the few techniques with this capability. Our approach was to make electrochemical/mechanical impedance measurements on HY80 steel in 3.5 wt% NaCl solutions under corrosion-fatigue conditions. The data were then analyzed by means of an AC transmission line model to determine the distribution of electrochemical and mechanical states within the crack and at the crack tip.

The bulk (uncracked) electrochemical parameters were measured for both HY80 and Ti-6Al-4V by AC impedance techniques. The electromechanical impedance of HY80 was measured and found to be sensitive to crack wall area at frequencies above 1 Hz and more sensitive to the crack tip at mechanical frequencies below 0.1 Hz. A DC transmission line model of the growing corrosion-fatigue cracks constructed from data on HY80 undergoing corrosion-

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**Abstract Security Classification:**

- **Unclassified**

**Security Classification of This Page:**

- **Unclassified**
19. ABSTRACT (concluded)

fatigue was used to predict crack growth rates and potential and chemistry distributions within the crack. The predicted crack growth rates were in reasonable agreement with the experimentally measured values. The model also predicted a reasonable \( \Delta K \) threshold for crack growth. At present the model treats the crack tip region rather simply, but several more realistic models exist that could be easily incorporated.

The results of this program have shown that a technique combining AC impedance, electrochemical/mechanical impedance, and transmission line modeling offers the potential to determine both the mechanical and electrochemical processes that occur within stress corrosion and corrosion-fatigue cracks. At present, it is one of the few techniques with this capability. The results did not conclusively show that the combination of AC impedance, electromechanical impedance, and transmission line modeling can be used to quantitatively predict crack growth rates because the transmission line model was not used to reproduce the electromechanical impedance. We recommend additional effort to use the transmission line model in conjunction with the electromechanical/electrochemical impedance to obtain the critical mechanical and chemical parameters at the crack tip. It is clear that, with more modeling and experimental work on a wider variety of materials, load cycles, and aqueous environments, the electrochemical/mechanical technique developed in this program can become an important research tool.
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ACKNOWLEDGMENTS

The authors would like to thank Dr. Larry Ablow for his contributions on modeling the diffusion within angular cracks, Mr. Andrew Werner and Mr. George Cartwright for their assistance with the design and operation of the experiments, and Ms. Mary Bartholomew, Mr. Lee Gerrans, Ms. Kitta Reeds, Ms. Caren Rickhoff, and Ms. Ruth Tanti for their efforts in preparing and editing this manuscript.
Section 1
INTRODUCTION

1.1 BACKGROUND

The load-bearing capacity of most alloys can be degraded by a corrosive environment. Two common forms of environment-sensitive mechanical property degradation are stress corrosion cracking (SCC) and corrosion fatigue (CF). Both forms greatly influence the safety, reliability, and economics of many components used in military and commercial power generation, transportation, and energy conversion systems. Therefore, substantial effort has been made to understand environment-assisted crack growth, to identify and develop materials that have better environment resistance, and to formulate predictive models.\textsuperscript{1-15}

These efforts have resulted in various quantitative models being proposed for predicting SCC, CF, or other types of environment-assisted crack growth. Wei and Landes,\textsuperscript{10} for example, considered the crack growth rate in a CF situation to consist of the sum of the crack growth rate in an inert environment and the rate in the environment of interest. The Wei and Landes theory has been shown to explain adequately many features of the CF behavior of Ti and Ti-6Al-4V in NaCl solutions.\textsuperscript{11} Furthermore, this work emphasized the need for a better understanding of the processes that occur at the crack tip, particularly at threshold load levels for crack growth and at low loading frequencies (< 1 Hz).

For SCC alone, Logan\textsuperscript{7} proposed a model for cracking in aqueous environments based on a slip-dissolution mechanism at the crack tip. This mechanism, now widely accepted,\textsuperscript{5-7} relates crack growth to the enhanced anodic dissolution current at the crack tip resulting from the intermittent mechanical rupture of an environmentally created film at the crack tip.
Logan's model has been modified to include a variety of rate-controlling processes that include repassivation rate, microcreep, solution renewal, and critical charge concepts. If the processes occurring within the crack were better understood, it would be possible to determine the appropriate slip-dissolution model for any given material, environment, and load application.

Quantitative modeling of the cracking process is difficult because it involves complex interactions between the cracking material, the environment, and the applied load. Because specimen microstructure, surface chemistry, electrochemistry, and loading conditions are expected to influence cracking behavior, they should be accounted for in attempts to model crack growth. Clearly, simultaneous characterization of the mechanical and electrochemical state at the crack tip is required for development of a reliable, predictive crack growth model.

The mechanical state at the crack tip is usually described in these models using classical fracture mechanics parameters such as the linear elastic stress intensity (K parameter) or, more recently, the elastic-plastic stress intensity (J parameter). Unfortunately, the electrochemical state of the crack tip is not so easily characterized because, until recently, no reliable experimental method existed that could either provide measurements directly within the crack or convert measurements made external to the crack into crack tip parameters. Some attempts have been made to measure the local chemistries that develop at crack tips by using microanalytical chemical techniques on specimens that are actually cracking or on artificial crevices that had been constructed to simulate stress corrosion cracks. However, most of the past crack growth models have used electrochemical data obtained on bulk specimens and have assumed that such data, for example, the free corrosion potential, are representative of values inside the crack, or these bulk values were extrapolated to crack tip values by means of some postulated model. However, crack growth rates predicted by such models can be several orders of magnitude different from those actually observed.
One possible method for evaluating the electrochemical state of material near a crack tip is the AC impedance technique. This technique, under development for the past several years, has only recently been applied to the problem of environmentally assisted cracking. This approach shows promise for determining crack tip electrochemical parameters by applying the transmission line model to deconvolve the measured AC impedance spectra of growing cracks.

1.2 PROGRAM OBJECTIVES

The above background discussion highlights the need to characterize simultaneously the electrochemical and mechanical states in a growing stress corrosion or corrosion fatigue crack. Thus, the objective of this research program was to generate electrochemical and mechanical data for actively growing corrosion fatigue cracks and then use these data to develop a preliminary predictive model for SCC and CF.

To accomplish these objectives we used standard fracture mechanics methods and analyses to characterize the mechanical state of the crack in Ti-6Al-4V and HY-80 steel in 3.5% NaCl solution and the AC impedance technique to characterize the electrochemical state. The electrochemical and mechanical data were used to calibrate a transmission line model, and this model was then used to predict quantitatively the electrochemical and mechanical state at the tip of an actively growing crack.

This report describes the results of our efforts to meet these objectives. Section 2 describes the development of the transmission line model. Section 3 reviews the electrochemical and mechanical experimental techniques employed in this program and the results obtained. In Section 4 the transmission line model is presented along with the experimental data used to develop a predictive model for crack growth. Section 5 outlines the conclusions and recommendations for additional work.
Section 2

DEVELOPMENT OF THE DISCRETE TRANSMISSION LINE MODEL

In the discrete transmission line model the stress corrosion or corrosion-fatigue crack is treated as a cracked electrode. The solid and electrolyte phases in the cracked electrode are represented by resistance elements parallel to the direction of the corrosion current flux, and the interfacial resistance is represented by an impedance distributed between the other two resistances. The electrode may be treated as "one-dimensional" if the potential (E), current flux (I), and reactant concentrations (c) vary only with the depth within the crack and not with the lateral position along the crack. In this case, the local values of E, I, and c may be replaced by their average values in a line perpendicular to the crack plane.

Ksenzheck and Stender\textsuperscript{27} discussed the conditions that are applicable to transforming a three-dimensional problem into a one-dimensional one. The mathematical model for the electrical representation shown in Figure 1 requires solutions to a set of differential equations of the following form:

\[
\frac{d^2 I_s}{dx^2} + \frac{1}{dx} \frac{d}{dx} \ln(Z) \frac{dI_s}{dx} - \frac{(r_g + r_e)I_s}{Z} = -\frac{r_e I}{Z},
\]

\[
\frac{d^2 I_e}{dx^2} + \frac{1}{dx} \frac{d}{dx} \ln(Z) \frac{dI_e}{dx} - \frac{(r_g + r_e)I_e}{Z} = -\frac{r_e I}{Z},
\]

\[
\frac{d^2 \Delta E}{dx^2} - \frac{(r_g + r_e)}{Z} \Delta E = 0
\]
FIGURE 1 TRANSMISSION LINE MODEL FOR A CRACK IN AN AQUEOUS ENVIRONMENT
where subscripts e and s refer to the electrolyte and solid phases, \( Z \) is the interfacial impedance, \( x \) is distance into the crack, \( r \) is the resistance, \( I = I_s + I_e \), and \( \Delta E = E_a - E_e \).

For the simplest set of boundary conditions shown in Figure 1, corresponding to an electrolyte-filled right cylindrical crack in which \( r_s \) and \( r_e \) are independent of \( x \) and the solid and electrolyte phase current contacts are diametrically opposed, the transmission line impedance \( Z_{tl} \) is given by

\[
Z_{tl} = \frac{4r_s r_e + (r_s^2 + r_e^2) (e^{\gamma l} + e^{-\gamma l})}{(r_s + r_e) (e^{\gamma l} - e^{-\gamma l})} + \frac{r_s r_e}{r_s + r_e} \tag{4}
\]

where \( l \) is the current crack length, and

\[
\gamma = \left[ \frac{(r_s + r_e)}{Z_t} \right]^{1/2} \tag{5}
\]

The interfacial impedance, \( Z_t \), in equation (5) is equivalent to that at a plane-parallel electrode. That is, it contains the information that would be available if it were possible to determine the electrochemical kinetic properties of each infinitesimal element, \( dx \), of the electrode thickness in the \( x \) direction.

The conventional\(^{22-24}\) equivalent circuit for \( Z_t \) is shown in Figure 2. The components of this circuit contain the electrochemical kinetic parameters that are important in evaluating the behavior of a cracked electrode. Brief descriptions of these parameters follow.

Double-Layer Capacitance, \( C \). The double-layer capacitance, \( C \), is directly proportional to the area of the electrolyte/solid phase interface. Thus, given a knowledge of the double-layer capacitance per unit area, \( C' \), under the prevailing conditions of reactant concentration, temperature, and potential, one can determine \( C \) by deconvolving the measured transmission line impedance. This value of \( C \) can then be used to estimate the total wetted area per unit electrode thickness,\(^{28}\)
FIGURE 2  INTERFACIAL IMPEDANCE ELEMENT; RANDLES' EQUIVALENT CIRCUIT
which we define as $A'$. Values of $C'$ may be available from the literature or can be measured directly for a plane-parallel electrode of known area.

**Warburg Coefficient, $\sigma$.** At moderate frequencies ($> 1 \text{ Hz}$), the Warburg impedance, $Z_w$, can be expressed as 22,24,29

$$Z_w = \sigma(1 - j)\omega^{1/2}$$  \hspace{1cm} (6)

where

$$\sigma = \frac{RT}{n^2 F c A''(2D)^{1/2}}$$ \hspace{1cm} (7)

in which $c$ is the reactant concentration and $A''$ expresses the electrode electrolyte area per unit length that is actively engaged in reaction. The other parameters in equation (7) have their usual meanings. The relationship between $A'$ and $A''$ can be used to define an area efficiency that accounts for the presence of passive zones, which do not contribute to the cell current during crack growth.

**Diffusion Layer Thickness, $\delta$.** At the limit of low frequency, an apparent resistive shunt to the Warburg impedance is observed.29-32 This resistance defines the steady-state DC operating behavior, and its value may be used in conjunction with $\sigma$ to calculate the effective diffusion layer thickness, $\delta$. In the derivation of equation (6), semi-infinite linear diffusion was assumed. However, in the wide regions near the crack mouth, natural convection will limit the thickness of the diffusion layer, whereas in the narrower regions near the crack tip, the dimension of the diffusion layer is proportional to the crack opening. Thus, we can account for the steady-state DC behavior22,30-35 in the model of the cracked electrode by introducing the Nernst diffusion layer thickness as a boundary condition.

**Interfacial Reaction Resistance, $R_r$.** The reaction resistance together with $A''$ and $\delta$ can be used to obtain information regarding the
electrode kinetics\textsuperscript{14,29,36} within the cracked electrode. The exchange
current density, $i_0$, can be determined from the relationship

$$R_t = \frac{RT}{nF Ai_0}$$

When used in conjunction with the Stern-Geary relationship,\textsuperscript{37} $R_t$
provides a measure of the instantaneous corrosion rate within the crack.

**Electrolyte Resistance**, $r_e$. The electrolyte resistance per unit
length in the cracked electrode, $r_e$, gives a measure of the amount,
composition, and distribution of electrolyte in the crack. The
electrolyte resistance is controlled primarily by the crack width and to
a smaller extent by the diffusion of reactant species from the bulk
electrolyte and the diffusion of reaction products from the crack tip.

**Solid Electrode Resistance**, $r_s$. The solid phase resistance per
unit length in the cracked electrode, $r_s$, provides a measure of the
resistive component in the cracked electrode. Reduction of the
impedance data to obtain the parameters of interest for cracked
electrodes involves applying nonlinear regression analysis to an
impedance model or equivalent circuit. Broers and coworkers\textsuperscript{38-40}
demonstrated the applicability of the transmission line model for
characterizing porous electrodes in molten carbonate fuel cells, and we
believe that these methods can be applied to a growing SC or CF crack.

An additional impedance element, $Z_{tip}$, has been included in Figure 1
to account for the special electrochemical characteristics of the crack
tip. For example, if the crack grows by a mechanism of film rupture and
anodic dissolution at the crack tip, then $Z_{tip}$ can be represented as a
special case of the equivalent circuit in Figure 2, with $R_t$ determined by
the exchange current density for metal dissolution (possibly involving
terms for precipitation of oxide and repassivation). Under the
conditions of a cyclic mechanical load, the area term $A'$ in equation (8)
must also be given as a periodic function about a mean value, $A'_0$. In
the simplest case, $A'$ would be a linear function of the mechanical load
or crack-opening displacement. Thus,
\[ A_{\text{tip}} = A_{\text{tip}}^0 \sin(\omega t + \phi) \]  

(9)

where \( \omega \) is the frequency of the load variation, and \( \phi \) is the phase delay between load variation and film rupture.

Equation (9) suggests a second method of evaluating the electrochemistry of the crack tip environment, using the transmission line model. Under a steady electrical bias (a small DC voltage more positive than the free corrosion potential), a DC current can be made to flow from the specimen to a suitable counterelectrode. This current originates with the anodic dissolution at the crack tip and is given by

\[ I(\omega t) = \frac{\eta}{R_r} \]  

(10)

where \( \eta = V_{\text{applied}} - V_{\text{free corrosion}} \).

Substituting equation (9) into equation (8) and then substituting the resulting expression for \( R_r \) into equation (10) yields

\[ I(\omega t) = \frac{\eta nF A_{\text{tip}}^0 \sin(\omega t + \phi)i}{RT} \]  

(10a)

This expression for \( I(\omega t) \) describes the crack tip current expected for cyclic load conditions.

This can be viewed as a sinusoidal current source originating at the crack tip. The current source is situated where the interfacial reaction resistance (\( R_r \) in Figure 2) is placed in \( Z_{\text{tip}} \) in Figure 1.

Alternatively, we can define an electrochemical/mechanical impedance,

\[ Z_{\text{em}} = Z/I \]  

(11)

which may be examined as a function of the frequency (and amplitude) of the mechanical load variation.
The advantage of an electrochemical/mechanical impedance study is that the perturbation is applied exactly at the point of interest (the crack tip). In the alternative method, a variable frequency electrical potential variation is applied to the mouth of a crack in a specimen cycled with a constant frequency mechanical load; however, this results in a perturbation that decreases in amplitude at the crack tip as the crack increases in length.
Section 3

EXPERIMENTAL METHODS AND RESULTS

3.1 TEST MATERIALS AND ENVIRONMENT

Two test materials were used in this program: a titanium alloy (Ti-6Al-4V) and a medium-strength low-alloy steel (HY 80). These materials were selected because of their possible application in submarine hull structures and for the range of electrochemical and corrosion-fatigue behavior these materials cover. The chemistry and mechanical properties of the Ti-6Al-4V and HY 80 are given in Tables 1 and 2, and the microstructures are shown in Figure 3. Note that the HY 80 has a bainitic microstructure typical of a quench and temper heat treatment, whereas the Ti-6Al-4V exhibits an alpha-beta structure typical of the mill-produced hot-rolled and annealed condition.

The test environment selected for this program was the standard 3.5% NaCl solution. This environment was created by dissolving the appropriate amount of reagent grade NaCl in deionized water. This solution was aerated and continuously refreshed into the test chamber at a rate of about 1 liter/hr.

3.2 ELECTROCHEMICAL/MECHANICAL EXPERIMENTS

To generate the electrochemical/mechanical data needed for the transmission line model, we performed three types of AC impedance-based experiments in this program: (1) planar (uncracked) electrode experiments to characterize the bulk electrochemical properties of the materials without any mechanical loading, (2) cracked electrode experiments to characterize the voltage/current response during active loading of a crack, and (3) cracked electrode electromechanical impedance experiments to characterize the voltage displacement response during active loading of a crack.
### Table 1

**PROPERTIES OF HY80 STEEL**

(5.08-cm-thick plate, M11-S-16216H, ASTM Grain Size 8)

<table>
<thead>
<tr>
<th>Element</th>
<th>wt%</th>
<th>Heat Treatment</th>
<th>Mechanical Properties$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.17</td>
<td>Austenitized at 1010°C for 120 minutes and water quenched; tempered at 682°C for 120 minutes and air cooled.</td>
<td>$\sigma_{ys}$ 87.8 ksi, $\sigma_{uts}$ 106 ksi, $%E$ 23.7%, $X_{RA}$ 66.7%, CVN 95 ft-lb at -120°F</td>
</tr>
<tr>
<td>Mn</td>
<td>0.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>0.010</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>0.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>0.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>1.56</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>2.88</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>0.24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>0.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>0.001</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Definitions:

$\sigma_{ys}$ = 0.2% offset yield strength.

$\sigma_{uts}$ = ultimate tensile strength.

$\%E$ = percent total tensile elongation to failure.

$X_{RA}$ = reduction in area of necked region at fracture.

CVN = charpy V-notch impact energy; CVN was determined under the following conditions: Type A, notch V, full size, longitudinal orientations.
### Table 2

**PROPERTIES OF Ti-6Al-4V**  
(AMS 4911, 40.6-cm-thick plate)

<table>
<thead>
<tr>
<th>Elemental Analysis</th>
<th>Mechanical Properties&lt;sup&gt;a&lt;/sup&gt;</th>
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<tbody>
<tr>
<td><strong>Element</strong></td>
<td><strong>wt%</strong></td>
</tr>
<tr>
<td>C</td>
<td>0.03</td>
</tr>
<tr>
<td>Al</td>
<td>6.25</td>
</tr>
<tr>
<td>Fe</td>
<td>0.07</td>
</tr>
<tr>
<td>V</td>
<td>3.95</td>
</tr>
<tr>
<td>O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.162</td>
</tr>
<tr>
<td>N&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.015</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.002</td>
</tr>
</tbody>
</table>

**Heat Treatment**: Hot rolled and annealed

---

<sup>a</sup>Definitions:

- $\sigma_{ys}$ = 0.2% offset yield strength.
- $\sigma_{uts}$ = ultimate tensile strength.
- $\%E$ = percent total tensile elongation to failure.
- $\%RA$ = present reduction in area of necked region at fracture.
- CVN = charpy V-notch impact energy.
(a) HY80 (Looking onto plane of crack path)

(b) Ti-6Al-4V (Looking onto plane of crack path)

FIGURE 3 MICROSTRUCTURE OF ALLOYS TESTED
The methods used and the results obtained for each of these three experiments are discussed in the following subsections. However, before discussing these experiments, it is important first to review some of the advantages and limitations encountered when applying these electrochemical techniques.

To calculate accurately the many electrochemical parameters that can be obtained from AC measurements, it is necessary to obtain high-precision impedance measurements over a wide range of frequencies, particularly at very low frequencies. The unavailability of adequate instrumentation has been the principal limitation to the characterization of cracked or porous systems by AC techniques and is largely responsible for the only modest success of Broers and coworkers. More recently, Mund et al. analyzed the performance of hydrogen electrodes in alkaline fuel cells systems from AC impedance measurements applied to a transmission line model.

The current work of Hills and coworkers provides good verification for the application of the transmission line model and the extension of equilibrium AC measurements for predicting the steady-state electrochemical parameters. In one set of experiments, the interfacial impedance components were calculated from the measured impedance of a packed bed of graphite spheres using the transmission line model, and the results were compared with the interfacial impedance measured directly for a single sphere.

Figure 4 shows the impedance data obtained for a packed-bed electrode superimposed on the least-squares best fit of data to equation (4). The tabulated values of the double-layer capacitance, Warburg coefficient, and exchange current density for the packed bed were calculated from this regression fit. These values were compared with the interfacial impedance parameters measured directly for a single graphite sphere isolated from the bed. The substantial agreement between the two sets of calculated impedance parameters is strong verification for the applicability of the transmission line model to characterizing porous or cracked electrodes.
Electrolyte = 5.0 x 10^{-4} M CuSO_4, 0.25 M H_2SO_4

FIGURE 4 MEASURED AND CALCULATED IMPEDANCE SPECTRA FOR A BED OF 600-µm GRAPHITE SPHERES
(From Reference 4)
This previous research clearly shows that many important operating parameters of porous and cracked electrodes are contained within the measured impedance dispersion. However, two factors are fundamental in the application of this method to the in situ determination of electrode characteristics. First, impedance measurements must be of sufficient precision (better than 0.1% for each impedance component), and second, the measurements must be made over a frequency range wide enough (10^{-3} to 10^{4} Hz) to adequately resolve the impedance spectrum and to allow subsequent deconvolution to obtain the electrochemical parameters.

The requirements for a high-speed, high-precision, impedance measurement system capable of operating at very low frequencies have been presented in detail by Macdonald and McKubre. In general, these requirements are in conflict. Maximum acquisition speed is available from noise or transform methods, but these methods are not very precise. High precision is best achieved with a frequency-by-frequency measurement technique such as phase-sensitive detection, but the measurements are time consuming. Fortunately, this is not a serious hindrance when such equipment is automated and the experiments are computer-controlled. We used such automated, computer-controlled equipment in the experiments described in the following subsections.

3.2.1 Planar Electrode Experiments

Experiments were performed on planar uncracked electrodes of HY80 and Ti-6Al-4V exposed to aerated 3.5 wt% NaCl to obtain the electrochemical parameters needed for developing the DC, crack propagation model and to aid in interpreting the results of electromechanical impedance testing. The experimental setup for these tests is shown in Figure 5. Specimens were mounted with one planar surface exposed to the electrolyte.

Figure 6 presents the Tafel plot obtained for Ti-6Al-4V at very low sweep rates; the sweep was initiated at the cathodic limit of -500 mV versus the saturated calomel electrode (SCE). The apparently well-behaved Tafel law behavior evidenced by the region of linear
FIGURE 5   EXPERIMENTAL CONFIGURATION FOR AC AND DC TEST ON PLANE PARALLEL ELECTRODES
FIGURE 6   TAFEL PLOT FOR A PLANE PARALLEL ELECTRODE
OF Ti-6Al-4V EXPOSED TO 3.5 wt% NaCl AND 25°C,
VOLTAGE SWEEP RATE = 0.01 mV s⁻¹
relationship between voltage and the logarithm of current suggests charge-transfer kinetic rate control in both the anodic and cathodic regions.

The AC impedance behavior of this electrode, however, strongly indicates that the reaction kinetics of the Ti-6Al-4V electrode surface is dominated by the presence of a semiconducting oxide film such as TiO$_2$. Evidence of the dominance of semiconductor-electrochemical effects can be seen in the Mott-Schottky plot presented as Figure 7. The reciprocal of the measured capacitance squared is plotted versus potential at 25 mV steps from -200 to -1200 mV versus SCE. Regions of linearity in such a plot indicate the presence of a space-charge layer$^{45,46}$ (band bending within the oxide film). The type of frequency dispersion shown in Figure 7 (that is, the lines at each frequency do not superimpose) is unusual and may be due to impedance effects within the electrolyte phase (the electrical double layer) or to heterogeneity within the oxide itself. The extrapolated intercept of this family of lines with the axis at $C = (1/C^2 + 0)$ indicates the position of minimum band bending (the "flat-band" potential), which is a characteristic of each semiconducting oxide.$^{45,46}$ This intercept of ~1100 mV SCE is within 100 mV of that expected for pure TiO$_2$. This 100 mV offset is a result of the defect structure and doping of the Ti-6Al-4V film that forms in the chloride environment.

The HY80 specimen showed a more conventional bulk electrochemical response than the Ti-6Al-4V. The HY80 specimen did not show Mott-Schottky behavior, which is not surprising because the corrosion film that develops is porous and without uniform composition through its thickness; that is, the donor density varies through the film thickness. Figure 8 shows the impedance locus or Nyquist$^{47}$ response of a plane parallel electrode of HY80 exposed to aerated 3.5 wt% NaCl, at the free corrosion potential. The depressed semicircular form is that expected for a metal electrode actively corroding under mixed kinetic/mass transport control. Figure 9 presents data collected at the same electrode, covering a range of potentials more cathodic than the
FIGURE 7  MOTT-SCHOTTKY PLOT FOR A PLANE PARALLEL ELECTRODE OF Ti-6Al-4V EXPOSED TO 3.5 wt% NaCl AT 25°C
FIGURE 8  IMPEDANCE LOCUS PLOT FOR A PLANE PARALLEL ELECTRODE OF HY80 EXPOSED TO 3.5 wt% NaCl AT 25°C
Figure 9: Reduced admittance versus $\omega^{1/2}$ for a planar parallel electrode of HY80 exposed to 3.5 wt% NaCl at 25°C, cathodic potential range.
free corrosion potential of HY80 (~ -600 mV versus SCE in aerated 3.5 wt% NaCl). These data are plotted as the reduced admittance, $B$, versus the square root of the angular frequency, $\omega^{1/2}$,

$$B = -X/[(R - R_s)^2 + X^2]$$  \hspace{1cm} (12)$$

where $\omega^{1/2} = (2\pi f)^{1/2}$, $X$ is the imaginary component of the impedance, $R$ is the real component of the impedance, $R_s$ is the uncompensated series electrolyte resistance, and $f$ is the frequency of the impedance measurement in Hz.

The family of straight lines in Figure 9 indicates that, at potentials more negative than (cathodic to) the free corrosion potential, the impedance of an HY80 surface is dominated by diffusional effects within the electrolyte. At potentials higher than -700 mV, however, deviation from a linear $B$ versus $\omega^{1/2}$ dependence occurs, as shown by the data at -550, -450, and -400 mV, plotted in Figure 10. These data are replotted in Figure 11 versus $\omega$. The straight lines shown are regression fits to the data points; this linearity indicates that the imaginary part of the admittance is dominated by a capacitance of approximately 20 $\mu$F cm$^{-2}$. The slope of $dB/d\omega$ is equal to the double-layer capacitance and can be seen in this potential range because of the absence of diffusional control effects.

At -300 mV versus SCE, the electrode admittance increases greatly and again displays linearity versus $\omega^{1/2}$, as shown in Figure 10. This is the transpassive region for HY80, and the electrode impedance becomes dominated by the mass transport of corrosion products from the electrode surface.

In summary, the results of planar electrode experiments on bulk Ti-6Al-4V and HY80 specimens showed that, over an extended potential range, the Ti-6Al-4V specimen behaved as if it were covered by a dense semiconducting oxide layer. It exhibited the characteristic linear $1/C^2$...
Figure 10: Reduced admittance versus $\omega^{1/2}$ for a plane parallel electrode of HY80 exposed to 3.5 wt% NaCl at 25°C. Anodic potential range.
FIGURE 11  REDUCED ADMITTANCE VERSUS $\omega$ FOR A PLANE PARALLEL ELECTRODE OF HY80 EXPOSED TO 3.5 wt% NaCl AT 25°C
versus voltage behavior. On the other hand, the dependence of the impedance response on voltage for HY80 was more complex although more typical of a corroding electrode. At potentials less than and equal to the free corrosion potential, the electrode impedance response was dominated by diffusion, presumably of reactant (dissolved O₂) to the electrode. At potentials up to 200 mV more positive than the free corrosion potential, in the potential range where a pseudo-passive film is expected to form, the impedance appears to be dominated by an essentially voltage-independent capacitance, almost certainly due to the electrical double layer in the electrolyte. At still more positive potentials, in the transpassive range, the electrode impedance appears to be dominated by the diffusion of reaction products from the electrode surface.

3.2.2 Mechanically loaded Cracked Electrode Experiments

We developed an experimental facility designed to obtain data on crack electrochemistry during CF and SCC of various materials in aqueous solutions at room temperature and pressure. Figure 12 diagrams the experiment arranged for impedance measurement of specimens under mechanical load conditions. Photographs of the setup are shown in Figure 13 (electronics), Figure 14 (test chamber), and Figure 15 (test specimen).

As detailed in Figure 12, impedance measurements were obtained using a Solartron Model 1250 frequency response analyzer (FRA) operated under microcomputer control. The Model 1250 is an automated, digitally demodulated, stepped frequency, impedance meter capable of 0.01% precision for each impedance component in the frequency range 10^-4 to 6 x 10^4 Hz. This instrument and the preceding series of frequency response analyzers (Solartron Model 1172 and 1174) have been used extensively in recent years to measure impedances in electrochemical systems.48-52

The FRA was operated under the control of an Apple II-Plus microcomputer equipped with 64 kbyte of internal random access memory (RAM),
FIGURE 12  SCHEMATIC OF IMPEDANCE MEASUREMENT SYSTEM FOR STRESS CORROSION CRACK AND CORROSION FATIGUE TESTS
FIGURE 13  FACILITY FOR MEASURING IMPEDANCE SPECTRA OF STRESS CORROSION CRACKING OR CORROSION FATIGUE TEST SPECIMENS
FIGURE 15 DETAIL OF TEST SPECIMEN
320 kbyte of external RAM (Axlon "Ramdisk 320"), and a 20-mbyte rigid
disk (Corvus Model 20 MB/M). The control program was written at SRI in
Basic and 6502 Machine languages and is included as Appendix A.

Some experiments were performed under potentiostatic control, using
a Princeton Applied Research Model 173/276 potentiostat; however, most
of the experiments were performed under pseudo-galvanostatic control.
In the latter mode, a resistance several orders of magnitude larger than
the cell impedance is placed in series with the counter electrode, and a
large AC voltage is applied. To a good approximation, the current is
determined by the AC voltage divided by the series resistance,
independent of cell impedance.

For experiments in which the load is cycled, the periods of the
mechanical and electrical cycles must be synchronized by integrating
the impedance data over one complete cycle of the mechanical load.
Thus, the results represent an average over a full cycle of crack-
opening displacement. If these cycles are not synchronized, the data
may contain a large amount of systematic error and will inevitably show
considerable scatter. For example, if the impedance measurements are
integrated over a time that is shorter than the mechanical load cycle,
multiple determinations (at different electrical perturbation
frequencies) may be made during a single mechanical cycle. These
determinations will cover the range from maximum to minimum crack
opening and will appear as scatter in the data set.

Because it is necessary to integrate over at least one cycle at the
electrical perturbation, some error will be introduced at low frequen-
cies when the impedance data are integrated over more than one (but not
an integer number of) mechanical cycle. This error is inevitable and
results in some scatter in our data at very low frequencies (< 0.01 Hz).

An environmental chamber was constructed that attaches to a servo-
hydraulic mechanical testing machine. This chamber and the associated
attachments allow us to circulate aerated or deaerated 3.5% NaCl
solution (or other electrolytes) at controlled temperatures past our
fatigue precracked compact tension specimens. The crack growth can be
measured by optical methods or by the compliance method, by means of a water-immersible LVDT mounted on the specimen. A special composite reference/counter electrode incorporates a silver/silver chloride electrode in a 0.25-inch-diameter Lugin probe, positioned about 0.1 inch from the start of the fatigue precrack. The fatigue precrack is at the bottom of a 2.00-inch-deep notch (1.50 inches wide by 0.010 inch thick), and the tip of the 0.25-inch-diameter Lugin probe is centered at the bottom of this notch to minimize "edge effects" on the electrochemical measurements. The counter electrode is located in a chamber to which the Lugin probe is attached. This arrangement allows us to polarize only the area at the Lugin probe tip and thus measure the response of this area.

The cracked electrochemical AC impedance measurements were obtained on Ti-6Al-4V in aerated 3.5% NaCl solutions. These tests were performed under load control with $\Delta K$ varying from $10^{-3}$ to $10^{-4}$ ksi $\sqrt{\text{in.}}$ with $R$ values of 0 to 0.2. No experiments of this type were performed on HY-80.

Figures 16 and 17 show impedance data for the growth of a crack in Ti-6Al-4V. The data designated as "no crack" in Figure 16 show the impedance response in the range $10^{-3} < f < 10^4$ Hz for a specimen subjected to a 5-Hz cyclic load, but showing no superficial indication of having cracked. In the Nyquist domain this data set appears as a semicircle whose center is located above the real axis. The low-frequency intercept on the real axis is very close to 2000 $\Omega$. The high-frequency region is shown in an amplified form in Figure 16(b). A second semicircular region is observed with a high-frequency intercept on the real axis at 52.8 $\Omega$. The high-frequency intercept corresponds to the series resistance due to the electrolyte path between the tip of the reference electrode and the base of the notch in the specimen.

In the Bode plot (Figure 16(c)), these data exhibit a single minimum in the phase occurring at approximately 0.15 Hz. The magnitude information shows two limiting plateaus (corresponding to the intercepts with the real axis in the Nyquist plot) separated by linear regions of slope $-1/2$, $-1$, and $-1/4$ with increasing frequency.
FIGURE 16: IMPEDEANCE RESPONSE OF THE Ti-6Al-4V SPECIMEN BEFORE AND AFTER THE APPEARANCE OF A MACROSCOPIC CRACK IN AERATED 3.5% NaCl SOLUTION.

\[ \Delta K = 22 \text{ ksi} \sqrt{\text{in.}} \]
\[ R = 0.10 \frac{K_{\text{min}}}{K_{\text{max}}} \]
Load Cycle = 5 Hz
\[ Z = R + jX \]
Z = R + jX

Crack
a = 41.3 mm

No Crack
a = 35.2 mm

ΔK = 22 ksi√in.
R = 0.10 = K_{min}/K_{max}
Load Cycle = 5 Hz
Z = R + jX

Increasing Frequency

**FIGURE 16** IMPEDANCE RESPONSE OF THE Ti-6Al-4V SPECIMEN BEFORE AND AFTER THE APPEARANCE OF A MACROSCOPIC CRACK IN AERATED 3.5% NaCl SOLUTION (Continued)
FIGURE 16 IMPEDANCE RESPONSE OF THE Ti-6Al-4V SPECIMEN BEFORE AND AFTER THE APPEARANCE OF A MACROSCOPIC CRACK IN AERATED 3.5% NaCl SOLUTION (Concluded)
Figure 17: The effect of load on the impedance response of a mature crack in Ti-6Al-4V in aerated 3.5% NaCl solution.

a = 55.1 mm
Load Cycle = 0.02 Hz
Z = R + jX

Increasing Frequency

ΔK = 30
R = 0.2

ΔK = 20
R = 0.1

ΔK = 10
R = 0
Examining these linear regions in order of decreasing frequency, we see that the region at slope $-1/4$ corresponds to the high-frequency semicircle in the Nyquist plot, shown in Figure 16(b). This region is present for unstressed specimens before cyclic loading and appears to be completely unchanged during the entire growth of the crack. We speculate that this region is associated with diffusion in the plane of the machined notch and perpendicular to the axis of the reference electrode. Although the region of slope $-1/4$ has significant extent in the Bode plot, the impedances involved are very small and have little significance in a linear (e.g., Nyquist) plot of the data. We will not consider this zone further in this report.

At intermediate frequencies, all data sets obtained show a region with a slope of $-1$. This region corresponds to a $f^{-1}$ dependence and is the form expected for the equivalent circuit in Figure 2, at intermediate and high frequencies, when diffusion of metal ions from the electrode surface are not rate limiting. A region of slope $-1$ in a Bode plot corresponds to a semicircle with its center located on the real axis in the Nyquist representation. The beginnings of a semicircle of great magnitude (on the scale shown) can be seen in Figure 16(b); the parameters of this semicircle are determined by the interfacial reaction resistance, $R_r$, and the double-layer capacitance, $C$ (see Section 2).

Impedance data obtained from unstressed specimens before the application of a cyclic load display a $f^{-1}$ dependence (Bode slope $=-1$) down to limitingly low frequencies. Only under cyclic loading conditions does a region of slope $-1/2$ appear, and this region becomes increasingly significant as a crack grows. Thus, we associate the region of slope $-1/2$ in a Bode plot with the presence of a crack.

Figures 16(a), (b), and (c) each show two curves: one labeled "crack" and the other labeled "no crack" on the basis of visual inspection of the aides of the compact tension specimen. Because both show a region of $f^{-1/2}$ dependence, the curve designated as "no crack" in Figure 16(c) must have at least a vestigial rupture, associated with cyclic loading of the oxide film at the crack tip. The curve labeled
"crack" was obtained when a crack of about 3 mm was observed at the side of the specimen.

A region of apparent $f^{-1/2}$ dependence (slope -1/2) for the impedance within the crack is predicted by equations (4) and (5). The transmission line impedance, $Z_{t1}$, contains terms in $e^{\gamma 1}$, which can be expanded as a Taylor series:

$$e^{\gamma 1} = 1 + \gamma 1 + (\gamma 1)^2/2! + (\gamma 1)^3/3! + \ldots$$  

For $\gamma 1 < < 1$, the third and subsequent terms in this series can be neglected. Substituting equation (13) into equation (4), we obtain an expression of the form

$$Z_{t1} = a + b/\gamma + \text{additional terms}$$  

where $a$ and $b$ are undetermined constants and the higher order terms have decreasing significance.

Because $\gamma$ is a function of $Z_1^{-1/2}$ [see equation (5)], the impedance of $Z_1$ placed in a transmission line will have a major component that has the square root of the frequency power dependence of the interfacial impedance itself. Thus, for $Z_1$ containing parallel resistance ($R_p$) and capacitive ($C_p$) elements only,

$$1/Z_1 = 1/R_p + j2\pi fC_p$$  

and $\gamma$ will be a function of $f^{1/2}$; from equation (14), $Z_{t1}$ will be a function of $f^{-1/2}$, which is the form observed.

The preceding discussion is important because an $f^{-1/2}$ dependence is often attributed to diffusional processes at a plane-parallel electrode.22-24 By mathematically fitting the measured impedance data to the form predicted by equation (4), we can clearly see that the observed responses is due to a capacitive element contained within a
transmission line, rather than to diffusion; the coefficients obtained
do not correspond to any known diffusional process.

The capacitance under consideration is simply that of the
electrical double layer on the sides of the growing crack. A resistance
appears in parallel with this capacitance and is associated with
faradaic processes on the crack wall. At present, we are unable to
determine whether this faradaic process is anodic (metal dissolution) or
cathodic (reprecipitation of metal or hydrogen evolution). To resolve
this and other important issues, we constructed a discrete (finite
element) transmission line model for the growing crack based on the
electromechanical parameters calculated from impedance measurements, as
discussed in Section 4.

The two data sets presented in Figure 16 are not greatly different
in form; the major changes observed are in the characteristic frequency
and the intercept with the real axis at limiting low frequencies. The
characteristic frequency ($f_0$ = frequency of minimum phase) moves from
0.14 to 0.32 Hz between the first and second data sets, and the limiting
low-frequency intercept decreases from 3915 to 1995 Ω. This decrease is
believed to be an effect of crack opening. For the data set labeled "no
crack," the vestigial crack, although short, is very tight and the
impedance is large. Under the same load conditions, the crack-opening
displacement increases as the crack grows, and the impedance becomes
less. In fact, a plot of limiting resistance versus crack length shows
a minimum at about 1-cm crack length, the resistance then increasing as
the crack lengthens, indicating that effects of crack length become more
important than the average crack-opening displacement.

The effects of crack-opening displacement were examined by varying
the cyclic load conditions. Specimens were cycled at a mean load, plus
and minus the cyclic load perturbation. Figure 17 shows the effects of
varying both the mean and the perturbation stress levels for a mature
-crack (~ 2 cm long) cycled at 0.02 Hz. For these data (and for all
impedance data presented in this report), each impedance determination
represents an average taken over one complete period of the cyclic load
and thus reflects some weighted average of crack opening displacements. Figure 17 clearly shows the effect of crack opening (proportional to load) on the limiting low-frequency resistance. From a superficial examination, it appears that the effects of the load perturbation level are more significant than those of mean load. However, we have not attempted to separate the effects of mean and perturbation stress levels quantitatively.

In summary, the results of electrochemical experiments on a cracked Ti-6Al-4V specimen under cyclic load conditions in 3.5% NaCl suggest that the AC impedance appears to be due to faradaic processes at the crack tip and a transmission line impedance associated with the crack walls. We also observed that, at least qualitatively, crack length and crack opening displacement appear to affect the measured impedance.

3.2.3 Electrochemical/Mechanical Impedance Experiments

It is also possible to define an impedance in terms of the electrochemical response of a fractured specimen to a mechanical input that causes crack propagation. One case in which this analysis can be applied usefully is for the electrochemically assisted (stress corrosion) cracking of metals submerged in an electrolyte and subjected to a cyclic mechanical load or stress. With some simplification, crack growth due to cyclical film rupture at the growing crack tip, followed by metal dissolution, can be considered as described below.

Figure 18 shows schematically the case of a crack growing in to a metal, under constant current control and cyclic load conditions. The loading conditions can be controlled to achieve a sinusoidal variation in the specimen load:

\[ p = \bar{p} + \tilde{p} \sin(\omega t) \]  

(16)
C = Counter Electrode
R = Reference Electrode
COD = Crack Opening Displacement
CTOD = Crack Tip Opening Displacement
a = Crack Length
w = Specimen Width
B = Specimen Thickness
p = Load

FIGURE 18  CT SPECIMEN GEOMETRY FOR DETERMINING THF ELECTROCHEMICAL MECHANICAL IMPEDANCE FOR THE PROPAGATION OF A CRACK
where $p$ is the mean specimen load and $\bar{p}$ the amplitude of the superimposed sinusoidal perturbation. To a first approximation, the area exposed at the crack tip can be considered to be proportional to the crack tip opening displacement.

\[
A = \gamma B(\text{CTOD}) \tag{17}
\]

\[
\text{CTOD} = \frac{K^2}{2E\sigma_y} \tag{18}
\]

\[
A = \frac{\gamma B K^2}{2E\sigma_y} \tag{19}
\]

where

$\gamma$ = a proportionally constant determined by the mechanical properties of the oxide film and metal at the crack tip

$B$ = specimen thickness

CTOD = crack tip opening displacement

$E$ = Elastic modulus of the specimen

$\sigma_y$ = yield strength of the specimen

$K$ = stress intensity factor = $p/B f(a/w)^{53}$

where

\[
f(a/w) = w^{-1/2}(1-a/w)^{-3/2} \left(2 + a/w\right) \left[0.886 + 4.64 \frac{(a/w)}{2} - 13.32 (a/w)^{2} + 14.72 (a/w)^{3} - 5.6 (a/w)^{4}\right] \tag{20}
\]

where

$p$ = applied load

$a$ = crack length

$w$ = specimen width

and $(a/w)$ is determined from$^{54}$

45
\[(a/w) = 1.0012 - 49.6U + 23.057U^2 - 323.91U^3 + 1789.3U^4 - 3513.2U^5 \] (21)

where

\[U = \left(\frac{(BE[COD]/p)^{1/2} + 1}{1} \right)^{-1} \]

COD = crack opening displacement measured at a distance 0.345 \(w\) from the load line towards the front face of the specimen.

The value for COD is determined from

\[COD = p \ g(a/w) \] (22)

where

\[g(a/w) = \frac{1}{EB}(1 + \frac{0.345}{a/w}) \left( \frac{1 + a/w}{1 - a/w} \right) \left[ 1.6396 + 11.02(a/w) - 6.449(a/w)^2 \right. \]

\[-31.14(a/w)^3 + 47.251(a/w)^4 - 18.343(a/w)^5 \] (23)

Combining equations (22) and (16), we obtain

\[COD = [p + p \sin(\omega t)] \ g(a/w) \] (24)

Figure 19 shows the approximate * equivalent circuit for the inside of the crack, with the impedance of the oxide-passivated walls appearing in parallel with the impedance element due to dissolution of exposed metal at the crack tip. The variation in applied load described by equation (16) results in a sinusoidal perturbation of the exposed crack tip area such that

---

*Because of the potential distribution along the crack, this equivalent circuit should more properly be represented as a nonuniform, finite transmission line for the oxide wall impedance, with the crack tip as a terminating impedance. Such a case is shown in Figure 1.
\( R_{\text{ep}} \)  = Electrolyte Resistance to Crack Walls
\( R_p \)  = Charge Transfer Resistance at Passive Walls
\( C_p \)  = Double Layer Capacitance at Passive Oxide
\( Z_w \)  = Diffusional Impedance at Passive Walls
\( Z_p \)  = Interfacial Impedance at Passive Walls
\( R_{\text{ea}} \)  = Electrolyte Resistance to Crack Tip
\( R_{\text{tip}} \)  = Charge Transfer Resistance at Exposed Metal
\( C_{\text{tip}} \)  = Double Layer Capacitance of Exposed Metal
\( Z_{\text{tip}} \)  = Interfacial Impedance at Crack Tip

**FIGURE 19** SIMPLIFIED EQUIVALENT CIRCUIT FOR A STRESS CORROSION CRACK
Without going through the algebra, for the equivalent circuit shown in Figure 19, we can obtain an expression for the electrochemical/mechanical impedance \( Z_{em} \) for this system, defined as the ratio of the AC voltage that appears at the reference electrode, to the COD due to the sinusoidal load variation under DC galvanostatic conditions:

\[
Z_{em} = \tilde{V}_{Ref} \frac{\tilde{V}_{tip}}{d} = \tilde{V}_{tip} \left( R_{ep} + Z_p \right) \left( \frac{1}{R_{tip}^o} + j\omega C_{tip}^o \right) \frac{Y}{a} \tag{27}
\]

Under optimal conditions, \( Z_{em} \), measured over a range of frequencies, can be used to deconvolve the equivalent circuit parameters in a manner analogous to that of electrochemical impedance analysis. The advantage of this method, in the example given, is that measurements can be made under dynamic load conditions and that the perturbation is imposed at the point of principal interest, near the crack tip.

In this experiment we galvanostatically imposed a 0.5 mA current between the counter electrode and the crack tip. The potential was measured with the Ag/AgCl reference electrode located at the crack tip. The mechanical frequency \( \omega \) in equation (24) was varied from 20 mHz to 10 Hz.

Figure 20 presents the real versus imaginary components of the electrochemical/mechanical impedance response measured for an HY80 steel specimen of geometry shown in Figures 15 and 18, immersed in 3.5 wt% NaCl. Because of the form of equation (24), these plots are somewhat more complex than a conventional Nyquist plot. Nevertheless, these data are amenable to standard methods of electrical analysis. We observe that the processes at the growing crack tip dominate at low frequencies,
FIGURE 20  COMPLEX PLANE PLOT OF THE ELECTROCHEMICAL/MECHANICAL IMPEDANCE FOR THE PROPAGATION OF A CRACK THROUGH HY80 STEEL IN 3.5% NaCl SOLUTION AT 25°C UNDER SINUSOIDAL LOADING CONDITIONS

\[ \Delta K = 22 \text{ ksi} \sqrt{\text{in.}} \]
\[ R = 0.1 = K_{\text{min}} / K_{\text{max}} \]
\[ a = 38 \text{ mm} \]

Increasing \( \omega \)
and the properties of greatest interest, $R_{\text{tip}}$ and $C_{\text{tip}}$, can be deconvolved at limitingly low frequencies.

Figure 21 shows the logarithm of the electrochemical/mechanical admittance ($Y_{\text{em}} = 1/Z_{\text{em}}$) plotted versus log frequency, for a typical data set, as a function of the number of mechanical load cycles experienced by the specimen during crack growth. These data show some evolution in the crack tip parameters (the low-frequency, descending portion of the curves), but considerably more changes appear in the crack wall impedance, reflecting the effect of increased crack wall area with increasing crack length. Also, note that the crack grew about 5.7 mm during this portion of the test.

To summarize the experimental results of the electrochemical/mechanical impedance data, we found that this technique was sensitive to crack wall area at frequencies above about 1 Hz and more sensitive to the crack tip at mechanical frequencies below 0.1 Hz. To understand the details of these data and the electrochemical impedance, a more detailed electrochemical/mechanical model needs to be constructed. This model together with the impedance data can then be used to measure the relevant electrochemical and mechanical parameters that occur in a growing SCC or CF crack. As described in the next section, this approach was implemented by modeling the cracking process as a discrete transmission line.
### Figure 21

**LOG (1/Z
t) VERSUS LOG (FREQUENCY) FOR AN HY80 SPECIMEN EXPOSED TO 3.5 wt% NaCl AT 25°C**

<table>
<thead>
<tr>
<th>Cycles</th>
<th>a (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>38.1</td>
</tr>
<tr>
<td>B</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>43.8</td>
</tr>
<tr>
<td>D</td>
<td></td>
</tr>
</tbody>
</table>

ΔK ≈ 20 ksi√in.
R = 0.1 = \(K_{\text{min}}/K_{\text{max}}\)

Crack Tip Dominated
Crack Wall Area Dominated
Crack Mouth Dominated

**LOG (f) (rad/s)**

- \(10^{-3}\) to \(10^{-1}\)
- \(10^{-2}\) to \(10^{-1}\)
- \(10^{-1}\) to \(10\)
- 1 to 10
Section 4

APPLICATIONS OF THE DISCRETE TRANSMISSION LINE MODEL
TO CRACK GROWTH PREDICTION

4.1 OVERVIEW

In developing a quantitative model intended to predict the combined effects of electrochemical corrosion and mechanical stress on crack growth, the first concern is to calculate the chemical, electrochemical, and mechanical parameters at the crack tip, from the prevailing conditions external to the specimen. The problem of computing the mechanical stress and strains in the elastic/plastic zone surrounding the crack tip, from the externally measured load and crack opening displacement, has been addressed by numerous authors$^{18,19,55-59}$ and is not the subject of this report.

Instead, we are concerned with the manner in which the DC potential, the anodic and cathodic currents, the solution pH and conductivity, and the concentrations of metal oxide and metal ions vary with distance and time within the interpenetrating electrolyte volume of a crack growing in a metal, submerged in a bulk volume of electrolyte.

In general, two distinct types of models can be used to obtain the required distributions. A system of first- and second-order nonlinear differential equations can be used to describe the processes of diffusion and interfacial reaction and the static potential distribution. Inevitably, this system of equations cannot be solved analytically, and numerical methods and mathematical approximations must be used to obtain a solution.

An alternative approach has been developed by McKubre for studying porous stripping electrodes$^{28,31,42-44}$ in which the transmission line equivalent circuit, described in Section 2, is considered to consist of a large, but finite number of discrete elements. This type of model
also requires a numerical solution, but offers the advantage of modeling most of the important physical and chemical processes by taken into account the full degree of nonlinearity of electrochemical systems. Of particular significance is that many of the electrochemical parameters necessary to solve the discrete transmission line can be obtained by making low-frequency AC measurements close to the potential of zero current and solving analytically for the continuous transmission line impedance.

The basic features of the discrete transmission line model, applied to a stressed crack, can be seen in Figure 1. Briefly, we consider the resistivities of the solid (metal) and electrolyte phases to be inter-connected by the impedance of the metal/electrolyte interface where charge carriers change from electrons to ions. In the discrete model the electrical equivalent circuit is assumed to consist of N discrete zones, each of length a/N, associated with the crack walls, plus an additional zone representing the tip. In general, the interfacial impedance of an arbitrary section of crack wall will depend on the local potential difference between the metal and electrolyte phases, the nature and concentration of dissolved species (principally metal and hydrogen ions and oxygen), and the presence and character of an interfacial oxide film.

The selection of the tip impedance determines the nature of the electrochemically assisted cracking. We are concerned here only with mechanisms of crack growth by anodic dissolution following film rupture. With appropriate modification, the model may nevertheless be used to test mechanisms of crack growth involving de-alloying or hydrogen embrittlement.

Because of the geometry and possible concentration gradients within the crack, the electrolyte resistance at each element of the transmission line is not constant with time or distance. Generally, the metal phase resistance is much less than that of the electrolyte and can be considered to be constant.
The current that flows into the crack (or the potential at the crack surface near the crack tip) was imposed, in our experiments, by a potentiostat with respect to an external counter electrode. Under open circuit conditions this current (or potential) is imposed by the reaction of redox species on the exposed surface of the specimen.

4.2 ASSUMPTIONS

We consider electrochemical and chemical reactions occurring at the crack tip (t) on the crack walls (w), and in the crack electrolyte volume (v). The important reactions are taken to be as follows:

<table>
<thead>
<tr>
<th>Site(s)</th>
<th>Reaction</th>
<th>No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>t , w</td>
<td>$M + M^{a+} + ae^-$</td>
<td>(5.1)</td>
</tr>
<tr>
<td>v</td>
<td>$M^{a+} + a/2 H_2O \leftrightarrow MO_{a/2} + aH^+$</td>
<td>(5.2)</td>
</tr>
<tr>
<td>w , t</td>
<td>$a/2 H_2 + aH^+ + ae^-$</td>
<td>(5.3)</td>
</tr>
<tr>
<td>w , t</td>
<td>$M + a/2 H_2O + MO_{a/2} + aH^+ + ae^-$</td>
<td>(5.4)</td>
</tr>
</tbody>
</table>

All reactions are considered to be reversible. Reaction (5.1) accounts for metal dissolution, which in conjunction with the chemical reaction (5.2) accounts for oxide formation by dissolution/precipitation. Reaction (5.3) is simple electrolysis, and reaction (5.4) accounts for the direct electrochemical reaction between metal and surface metal oxide film.

The following concepts and assumptions have been applied to simplify the model:

- Only metal dissolution (reaction 5.1) and the crack tip is influenced by the crack opening displacement.
- There is no oxygen within the crack volume and thus reaction (5.3) is the only source of net cathodic current.
The crack is considered to be a wedge and the area of metal exposed at the crack tip is determined by the tangent of the crack opening angle, $\theta$.

\[ \tan(\theta) = \frac{\text{COD}}{a} \]  \hspace{1cm} (28)

where COD = crack opening displacement, $a =$ crack length.

- In the electrochemical reactions all symmetry factors ($\alpha$) are considered to be equal to 1/2.
- The chemical reaction (5.2) rapidly achieves equilibrium.
- At the steady state the activities of $H_2O$ and $H_2$ are invariant.
- The activity of the metal oxide phase is equal to the monolayer surface coverage, $\theta$, with a maximum of 1.
- At all points the crack is so thin that there exists no limitation due to diffusion perpendicular to the walls.
- The presence of an (NaCl) ensures that the electrolyte phase resistivity does not change significantly with metal or hydrogen ion concentrations.

4.3 EQUATIONS

Anodic dissolution at the crack tip is considered to proceed via the Butler-Volmer equation, with the area exposed, $A_t$, being proportional to $D$.

\[ A_t = \gamma \frac{\text{COD}}{a} \]  \hspace{1cm} (29)

where $\gamma$ is a constant, and

\[ \text{COD} = \bar{D} + |d| \sin(\omega t) \]  \hspace{1cm} (30)
These equations (29 and 30) were used as a simplified version of Equations (19) and (24) to reduce the model run time. Equations (19) and (24) will be incorporated in the future. Equation (30) considers the effect of sinusoidal COD loading of the compact tension on the dynamics of crack growth, and a model is being developed to calculate the electromechanical impedance under dynamic conditions that also includes modeling of the $\gamma$ factor in equation (29). In this section we consider only steady-state conditions, and we define an effective opening displacement, $\bar{D}$, which is a function of COD, $d$ and the sinusoidal loading rate.

The current associated with metal dissolution at the crack tip, due to an applied overvoltage, under steady-state conditions can be expressed as

$$I_{M/M^+} = I_0^{N/M} a^+ (\gamma D/a) \left\{ \exp \left[ \frac{aF}{RT} (\Delta V_N - \nu^o_{N/M} a^+ - \nu_{cp}) \right] - \exp \left[ \frac{-aF}{RT} (\Delta V_N - \nu^o_{N/M} a^+ - \nu_{cp}) \right] \right\}$$

(31)

where $\Delta V_N$ is the interfacial overvoltage in element $N$, $F$ is Faraday's constant, $T$ is temperature in Kelvin, $\nu^o$ is the equilibrium potential, $I_0$ is the exchange current density, subscript $M/M^+$ refers to the metal dissolution reaction (5.1), and $\nu_{cp}$ is the local concentration overvoltage determined by

$$\nu_{cp}(N) = -(nF/RT) \ln \|H^+\|$$

(32)

The standard state for $I_0$ and $\nu_{cp}$ is taken to be 1 molar.

Crack growth is determined at discrete, equal time steps. Within each time interval reactions (5.1), (5.3), and (5.4) are evaluated on the crack walls in each segment of the transmission line, according to the local conditions of concentration and potential.

At the end of each time interval, reaction (5.2) in each segment is considered to be at an equilibrium determined by
where the activity of water, \([H_2O]\), is considered to be unity, and the activity of the oxide film, \([MO_{a/2}]\), is taken to be equal to the fractional area coverage with a maximum of 1.0 (at one monolayer coverage).

The extent of crack growth in each time interval, \(t\), is calculated from the volume of metal dissolved at the crack tip in a rectangular parallelepiped whose width is the width \(B\) of the crack opening angle and \(\gamma\) and whose depth is the increased crack length, \(\Delta a\). Thus,

\[
\Delta L = \frac{\left(\frac{\text{tip}a^+}{M/M^+}\right)(t)}{nF \overline{\omega} \overline{\rho} \gamma \theta B} \tag{34}
\]

where \(\overline{\omega}\) and \(\overline{\rho}\) are the average molecular weight and density of the dissolved metal, respectively, and the other symbols have been previously defined.

The concentrations within each segment of the transmission line are modified by the combined effects of (1) chemical and electrochemical reactions, (2) the diluting effect as the volume is increased with crack growth (in flow of bulk electrolyte from outside the crack), and (3) diffusion. The effects of diffusion along the crack length are accounted for at the same discrete time intervals as crack growth. A comprehensive model for transverse diffusion is presented in Appendix B. Briefly, we consider the propagation of concentration profiles between nearest neighbors that initially have uniform, but different concentrations. Adjacent zones have different cross-sectional areas and different volumes in the wedge-shaped crack profile. Different approximations are used for long and short times.

The final consideration is of the thickness of the "passivating" metal oxide film. This film has an important role in localizing the
metal dissolution process at the crack tip. We consider the metal oxide to conduct both electrons and ions. The electronic conductive properties are accounted for by the solid-state reaction between metal and metal oxide [reaction (5.4)]. The primary role we envisage for the metal oxide, however, is as a diffusion barrier. At greater than monolayer coverages, we consider that the direct metal dissolution reaction on the crack walls is impeded by the diffusion of metal ions across the metal oxide membrane. The passive current density, $i_p$, is therefore given by

$$i_p = nFD \frac{C_S - C_N}{y_N}$$

(35)

where $D$ is the diffusion coefficient, $C_S$ is the saturation solubility of metal ions in the metal oxide phase, $C_N$ is the concentration of metal ions at the crack electrolyte/metal oxide interface, and $y_N$ is the oxide film thickness. We simplified the calculation by assuming that metal salt will precipitate when the activity of metal ions reaches unity within the oxide phase. We can therefore define the maximum passive current density (for $C_S = 1$ and $C_N = 0$) as

$$i_p^0 = -nFD/y_N$$

(36)

and the passive dissolution current in each segment is given by

$$I_N = i_p^0 \frac{1 - C_N}{y_N}$$

(37)

*Note that we have not specified whether or not the film is porous. In the event that it is, the values of $C_S$ and $D$ would change, but the principle of a diffusion barrier remains the same.
4.4 IMPLEMENTATION

The model described in this section has been implemented as a computer program written in BASIC for the Apple II microcomputer. A listing is provided as Appendix C, and a schematic flow chart is given in Figure 22. Briefly, the program allows for the initialization of the physical and electrochemical parameters used to define crack-growth conditions. These parameters are stored in the array ZM(26) and have the meanings shown in Table 3.

The transmission line is considered to consist of \( N \) segments, where \( N < 200 \). Data are saved in the array \( ZN(9,200) \) for the metal and electrolyte phase voltages and resistances, the interfacial currents for the electrochemical reactions \( M + \text{H}^+ + \frac{1}{2} \text{H}_2 \), \( M + \text{H}_2 \), and \( M + \text{MO}_x/2 \), and for the hydrogen and metal ion concentrations in the crack electrolyte, and the oxide monolayer thickness, in each segment. The allocation of these variables is shown in Table 4.

Before the application of stress or potential, a vestigial crack is considered to exist, filled with electrolyte at the bulk pH, with the walls covered in a monolayer of oxide, and the metal ion concentration in chemical equilibrium. The data array is initialized with these concentrations at the outset of computation. The program then guesses an initial value of the applied potential that will result in the net DC current. The resistances, potentials, and currents are then calculated in each mesh of the transmission line, progressively, from the reference electrode to the crack tip. If the sum of the calculated interfacial currents is not equal to the net DC current that enters the crack (within the specified tolerance), then the initial value of applied potential is adjusted and the computation loop reiterated.

Following a successful solution of the current and potential profiles, the changes in concentration resulting from chemical and electrochemical reactions, the crack advancement, and effects of diffusion are evaluated, and the resultant profiles are output to printer and/or disk.
FIGURE 22 CRACK GROWTH FLOW CHART
### Table 3

**PARAMETER ARRAY**

<table>
<thead>
<tr>
<th>Array Element</th>
<th>Parameter</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$ZM(x)$</td>
<td>DC current</td>
<td>A</td>
</tr>
<tr>
<td>$x = 1$</td>
<td>Specimen width</td>
<td>cm</td>
</tr>
<tr>
<td>2</td>
<td>Specimen height</td>
<td>cm</td>
</tr>
<tr>
<td>3</td>
<td>Specimen length</td>
<td>cm</td>
</tr>
<tr>
<td>4</td>
<td>Crack opening angle</td>
<td>radians</td>
</tr>
<tr>
<td>5</td>
<td>Bulk electrolyte pH</td>
<td>---</td>
</tr>
<tr>
<td>6</td>
<td>Electrolyte resistivity</td>
<td>$\Omega \ cm$</td>
</tr>
<tr>
<td>7</td>
<td>Metal resistivity</td>
<td>$\Omega \ cm$</td>
</tr>
<tr>
<td>8</td>
<td>Mechanical stress factor, $\gamma$</td>
<td>cm</td>
</tr>
<tr>
<td>9</td>
<td>Number of electrons/ion</td>
<td>--</td>
</tr>
<tr>
<td>10</td>
<td>Computation interval</td>
<td>s</td>
</tr>
<tr>
<td>11</td>
<td>Number of elements</td>
<td>--</td>
</tr>
<tr>
<td>12</td>
<td>Computation tolerance</td>
<td>mV</td>
</tr>
<tr>
<td>13</td>
<td>Maximum number of iterations</td>
<td>--</td>
</tr>
<tr>
<td>14</td>
<td>Exchange current density, $M/Na^+$</td>
<td>A cm$^{-2}$</td>
</tr>
<tr>
<td>15</td>
<td>Equilibrium potential, $M/Na^+$</td>
<td>V</td>
</tr>
<tr>
<td>16</td>
<td>Exchange current density, $M/NO_a/2$</td>
<td>A cm$^{-2}$</td>
</tr>
<tr>
<td>17</td>
<td>Equilibrium potential, $M/NO_a/2$</td>
<td>V</td>
</tr>
<tr>
<td>18</td>
<td>Exchange current density, $H/H^+$</td>
<td>A cm$^{-2}$</td>
</tr>
<tr>
<td>19</td>
<td>Equilibrium potential, $H/H^+$</td>
<td>V</td>
</tr>
<tr>
<td>20</td>
<td>Chemical equilibrium constant</td>
<td>--</td>
</tr>
<tr>
<td>21</td>
<td>Charge per monolayer of oxide</td>
<td>C cm$^{-2}$</td>
</tr>
<tr>
<td>22</td>
<td>Charge per volume of oxide</td>
<td>C cm$^{-3}$</td>
</tr>
<tr>
<td>23</td>
<td>Metal ion diffusion coefficient</td>
<td>cm$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>24</td>
<td>Passive current density</td>
<td>A cm$^{-2}$</td>
</tr>
<tr>
<td>25</td>
<td>Mechanical loading frequency</td>
<td>Hz</td>
</tr>
<tr>
<td>26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Array Element ZM(x)</td>
<td>Parameter</td>
<td>Units</td>
</tr>
<tr>
<td>---------------------</td>
<td>--------------------------------------------------</td>
<td>----------------</td>
</tr>
<tr>
<td>M = 0</td>
<td>Solid phase voltage, $V_{s,N}$</td>
<td>V</td>
</tr>
<tr>
<td></td>
<td>Electrolyte phase voltage, $V_{e,N}$</td>
<td>V</td>
</tr>
<tr>
<td>1</td>
<td>Solid phase resistance, $R_{s,N}$</td>
<td>$\Omega \text{ cm}^{-1}$</td>
</tr>
<tr>
<td>2</td>
<td>Electrolyte phase resistance, $R_{e,N}$</td>
<td>$\Omega \text{ cm}^{-1}$</td>
</tr>
<tr>
<td>3</td>
<td>Interfacial current, M/H$^{a+}$</td>
<td>A</td>
</tr>
<tr>
<td>4</td>
<td>Interfacial current, H/H$^{+}$</td>
<td>A</td>
</tr>
<tr>
<td>5</td>
<td>Interfacial current, M/MO$^{a/2}$</td>
<td>A</td>
</tr>
<tr>
<td>6</td>
<td>Hydrogen ion concentration, $[H^{+}]$</td>
<td>mole dm$^{-3}$</td>
</tr>
<tr>
<td>7</td>
<td>Metal ion concentration, $[M^{a+}]$</td>
<td>mole dm$^{-3}$</td>
</tr>
<tr>
<td>8</td>
<td>Metal oxide thickness, $X_N$</td>
<td>monolayers</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
This procedure is repeated at the interval specified until the crack achieves its desired length.

4.5 RESULTS

A series of computations was performed in a preliminary attempt to verify the model predictions, using estimated physical and electrochemical parameters for HY80 steel in 3.5 wt% NaCl. The parameters used are summarized in Table 5. Figures 23 through 26 show the results of computations that conform closely to the initial crack velocities measured experimentally for the compact tension specimens. We measured the crack velocity to be about $2.3 \times 10^{-7}$ m s$^{-1}$ and the model predicts an initial velocity of $6 \times 10^{-7}$ m s$^{-1}$ (see Figure 21).

For the first computation (parameters C1 in Table 5), a crack was grown from $a = a^0 + 0.05$ cm to $a = a^0 + 0.76$ cm where $a^0 = 3.6$ cm at a constant crack current of +1 mA. This computation used a COD cycling at 1 Hz, which corresponds to a $\Delta K$ of $\sim 20$ ksi $\sqrt{\text{in}}$; this $\Delta K$ value did not change appreciably as the crack grew over this small distance. Figure 23 shows the time dependence of the crack velocity, crack length, and potential at the orifice. The crack propagates initially at an essentially constant rate of $0.6 \mu$m s$^{-1}$, but after about 10 days, the crack decelerates rapidly; at 30 days the crack velocity is essentially zero. Under constant current conditions the potential at the orifice increases monotonically with time, as the active zone at the crack tip becomes further removed. Because the crack velocity decreases rapidly after the crack has grown approximately 0.5 cm, one is inclined to attribute this decrease to a decreasing $\Delta K$ or correspondingly a significantly lower crack tip ruptured area that decreases as the crack length increases. This is not the case because the stress intensity and area exposed at the tip have changed very gradually and only by a small amount over the total range of crack lengths calculated. It nevertheless appears that the model is predicting a $\Delta K$ threshold value near 20 ksi $\sqrt{\text{in}}$. This decrease in crack growth rate seems to be due to precipitation of oxide along the crack length.
Table 5

PHYSICAL AND ELECTROCHEMICAL PARAMETERS
USED FOR MODEL COMPUTATIONS

<table>
<thead>
<tr>
<th>Parameter Number</th>
<th>Description</th>
<th>Computation Number</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Applied DC current</td>
<td>10^-3</td>
<td>A</td>
</tr>
<tr>
<td>5</td>
<td>Crack opening angle</td>
<td>0.003</td>
<td>rad</td>
</tr>
<tr>
<td>6</td>
<td>Bulk electrolyte pH</td>
<td>6.0</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>Electrolyte resistivity</td>
<td>20.0</td>
<td>Ω cm</td>
</tr>
<tr>
<td>8</td>
<td>Metal resistivity</td>
<td>10^-5</td>
<td>Ω cm</td>
</tr>
<tr>
<td>9</td>
<td>Mechanical stress factor</td>
<td>7 x 10^-4</td>
<td>cm</td>
</tr>
<tr>
<td>15</td>
<td>Exchange current, M/H^2+</td>
<td>10^-2</td>
<td>A cm^-2</td>
</tr>
<tr>
<td>16</td>
<td>Equilibrium potential, M/H^2+</td>
<td>-200</td>
<td>mV</td>
</tr>
<tr>
<td>17</td>
<td>Exchange current, M/HO_a/2</td>
<td>10^-4</td>
<td>A cm^-2</td>
</tr>
<tr>
<td>18</td>
<td>Equilibrium potential, M/HO_a/2</td>
<td>-100</td>
<td>mV</td>
</tr>
<tr>
<td>19</td>
<td>Exchange current, M/H^+</td>
<td>10^-4</td>
<td>A cm^-2</td>
</tr>
<tr>
<td>20</td>
<td>Equilibrium potential, M/H^+</td>
<td>0</td>
<td>mV</td>
</tr>
<tr>
<td>21</td>
<td>Chemical equilibrium constant</td>
<td>10^-6, 10^-3</td>
<td>-</td>
</tr>
<tr>
<td>24</td>
<td>Diffusion coefficient, M^+</td>
<td>2 x 10^-5</td>
<td>cm^2 s^-1</td>
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<tr>
<td>25</td>
<td>Passive current density</td>
<td>10^-6</td>
<td>A cm^-2</td>
</tr>
<tr>
<td>26</td>
<td>Mechanical loading frequency</td>
<td>1</td>
<td>Hz</td>
</tr>
</tbody>
</table>
FIGURE 23 DC TRANSMISSION LINE MODEL CALCULATION OF THE POTENTIAL, CRACK LENGTH, AND CRACK VELOCITY AS A FUNCTION OF TIME FOR A CRACK GROWN AT CONSTANT CURRENT IN HY80 STEEL.

Initial conditions C1 in Table 5.
FIGURE 24  DC TRANSMISSION LINE MODEL CALCULATION OF THE POTENTIAL VERSUS DISTANCE INTO THE CRACK AS A FUNCTION OF TIME FOR HY80 IN 3.5% NaCl

Initial conditions C1 in Table 5.
FIGURE 25  DC TRANSMISSION LINE MODEL CALCULATIONS OF INTERFACIAL CURRENT, METAL-ion CONCENTRATION, AND CRACK ELECTROLYTE pH AS A FUNCTION OF DISTANCE INTO CRACK

(a) Interfacial Current, \( I \rightarrow M^{++} \)

(1, 0.1) = Time (days), Length (cm)
FIGURE 25 DC TRANSMISSION LINE MODEL CALCULATIONS OF INTERFACE CURRENT, METAL ION CONCENTRATION, AND CRACK ELECTROLYTE pH AS A FUNCTION OF DISTANCE INTO CRACK (Continued)
FIGURE 25 DC TRANSMISSION LINE MODEL CALCULATIONS OF INTERFACIAL CURRENT, METAL ION CONCENTRATION, AND CRACK ELECTROLYTE pH AS A FUNCTION OF DISTANCE INTO CRACK (Concluded)
FIGURE 26 DC TRANSMISSION LINE MODEL CALCULATIONS OF VELOCITY VERSUS APPLIED POTENTIAL, VELOCITY VERSUS POTENTIAL (EXPANDED), AND LOG (VELOCITY) VERSUS APPLIED CURRENT
(b) Velocity Versus Potential (Expanded Scale)

FIGURE 26 DC TRANSMISSION LINE MODEL CALCULATIONS OF VELOCITY VERSUS APPLIED POTENTIAL, VELOCITY VERSUS POTENTIAL (EXPANDED), AND LOG (VELOCITY) VERSUS APPLIED CURRENT (Continued)
Critical Current for Crack Growth

FIGURE 26  DC TRANSMISSION LINE MODEL CALCULATIONS OF VELOCITY VERSUS APPLIED POTENTIAL, VELOCITY VERSUS POTENTIAL (EXPANDED), AND LOG (VELOCITY) VERSUS APPLIED CURRENT (Concluded)
Figure 24 presents profiles of the potential difference between the solid and electrolyte phases (the potential driving force for electrochemical reaction) as a function of distance and time. For this example the equilibrium potential for metal dissolution is taken to be -200 mV versus the standard hydrogen electrode (SHE); thus, the baseline of this plot represents the approximate potential of zero dissolution current. As expected, the potential decreases between the crack orifice and the crack tip due to the finite conductivity of the electrolyte, the existence of electrochemical reactions at the crack walls, and the presence of reaction products in the crack electrolyte volume. Somewhat unexpectedly, for the conditions chosen, this potential drop is not a large fraction of the total overvoltage driving metal dissolution, and the potential drop decreases (as a percentage) with increasing crack length.

This observation is surprising in view of the results of previous calculations. Nevertheless, it is necessary that a significant fraction of the externally imposed potential be reflected at the growing crack tip to account for the observation of a critical potential for crack growth.

The origins of the deceleration in crack growth rate observed after 10 days for computation Cl can be seen clearly in Figures 25(a) through (c). These figures show a normalized crack length, with the time of growth and actual length given in parentheses. Figure 25(a) presents the component of the total interfacial current due to metal dissolution via reaction (5.1), as a function of time and length. The ordinate is plotted logarithmically to accommodate the large range of interfacial currents. Independent of time and length, the majority of the dissolution current flows from the region of film rupture at the crack tip. Despite the presence of a passivating oxide film, some metal dissolution also occurs on the walls of the crack. To a first approximation, however, the crack can be considered as active at the tip, partially active at the orifice, and passive (with respect to metal dissolution) in the central segments.
Figure 25(b) shows the concentration of metal ions (plotted as $-\log[\text{metal ion}]$) within the crack volume. For the example calculated the concentration is constant before the imposition of an external current, at a value determined by the chemical equilibrium between metal ions, hydrogen ions, and the surface metal oxide. As the crack grows, metal ions become depleted in the central segments due to the formation of metal oxide. Metal ions are produced by dissolution at the crack tip, but the effect of this concentration does not propagate deeply along the crack length.

Because reaction (5.2) is assumed to be at equilibrium, the depletion of metal ions in the central segments requires that the hydrogen ion concentration also be low. Thus, Figure 25(c) shows a trend toward alkalinity in the crack volume, with local acidification at the crack tip.

A second series of calculations was performed to determine the effect of crack current (or external potential) on the initial crack velocity. The parameters used are listed as "C2" in Table 5, and the results are summarized in Figures 26(a) through (c). Figure 26(a) shows the steady state crack velocity for a vestigial crack 0.1 cm long, plotted versus the potential of the electrolyte at the crack orifice for $K = 10^{-6}$. This plot exhibits a discontinuity at about 275 mV versus SHE. Below this potential the crack grows very slowly, whereas at higher potentials crack velocity increases roughly linearly with potential. One can interpret this discontinuity as a crack initiation potential although a closer inspection of the velocity versus potential profile near 200 mV [see Figure 26(b)] reveals two abrupt steps in velocity, one at 180 mV and the other at 275 mV. Figure 26(c) shows the same data plotted as the logarithm of crack velocity versus the current that flows into the crack, which allows us to determine the critical current for crack growth of $\sim 18$ mA for the conditions selected.

The results obtained for a chemical rate constant of $10^{-3}$ are not plotted but show that, with larger values of the chemical rate constant, the discontinuities in velocity, shown in Figure 26, disappear, and the
crack growth rate becomes a simple monotonic function of potential (or current). A second major effect of the chemical rate constant is that large values of the chemical rate constant result in general acidification of the crack electrolyte.
CONCLUSIONS

From the results of this program, we draw the following conclusions regarding the use of AC impedance techniques and transmission line modeling to obtain electrochemical/mechanical properties states distributed within actively growing environmentally assisted cracks:

- The AC impedance response of the uncracked Ti-6Al-4V was found to behave as if the titanium alloy were covered with a dense TiO$_2$ semiconducting oxide layer. The HY80 exhibited more complex behavior although more typical of a corroding electrode. At transpassive and cathodic potentials the electrode impedance behavior was dominated by diffusional behavior, whereas in the potential range where a pseudo-passive film is expected to form, the impedance response was dominated by the double-layer capacitance in the electrolyte.

- The AC impedance response measured on cracked Ti-6Al-4V specimens under corrosion-fatigue conditions was found to depend on environmentally induced crack growth, total crack length, and change in stress intensity ($\Delta K$). The electromechanical impedance of HY80 steel undergoing corrosion fatigue was modeled as a simplified equivalent circuit. The electromechanical impedance HY80 was also measured. This electromechanical impedance technique was sensitive to crack wall area at frequencies above 1 Hz and more sensitive to the crack tip at mechanical frequencies below 0.1 Hz.

- A DC transmission line model of growing corrosion-fatigue cracks constructed from HY80 undergoing corrosion fatigue was used to predict crack growth rates and potential and chemistry distributions within the crack. The predicted crack growth rates were in reasonable agreement with the experimentally measured values. The model also predicted a reasonable $\Delta K$ threshold for crack growth. At present, the model treats the crack tip region rather simply, but several models exist that could be incorporated rather easily in the future.

The results of this program have shown that a technique combining AC impedance, electrochemical/mechanical impedance, and transmission line
modeling offers the potential to determine both the mechanical and electrochemical processes that occur within stress corrosion and corrosion-fatigue cracks. At present, it is one of the few techniques with this capability. The results did not conclusively show that the combination of AC impedance, electromechanical impedance, and transmission line modeling can be used quantitatively to predict crack growth rates because the transmission line model was not used to reproduce the electromechanical impedance. We recommend additional effort to use the transmission line model in conjunction with the electromechanical/electrochemical impedance to obtain the critical mechanical and chemical parameters at the crack tip. It is clear that, with more modeling and experimental work on a wider variety of materials, load cycles, and aqueous environments, the electrochemical/mechanical technique developed in this program can become an important research tool.
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Appendix A

IMPEEDANCE DATA MANAGEMENT AND CONTROL PROGRAM

1 REM *DMSS.BAIN 15/JUN/1983
3 REM BY HEH. HCHN 15/JUN/1983
10 DIM ZM(128),ZM(55),ZM(9),ZM(32),ZM(18)
110 PRINT CHR$(4);"LOAD " B.FRAS"
140 ZH(1) = 1;ZH(2) = 1;ZH(11) = 100;ZH(12) = 1;ZH(21) = 1;ZH(22) = 1;ZH(23) = 1;ZH(24) = 1
150 ZH(51) = 1;ZH(53) = 1;ZH(55) = 1;ZH(56) = ZNX;ZH(57) = 1;ZH(58) = 2;ZH(59) = 2;ZH(60) = 2;ZH(61) = 2;ZH(62) = 1
160 X = FRF <0>:SBX = 6:DB1 = 1:VBX = 23
170 IF SX < 4 OR SI > 6 THEN SI = 5:DX = IIVX = 0
200 60SUB 20000
300 DATA "FR","AM","B1","MF","MD","IS","LE","SR","SL","AC","AS","AV","AE","AP","QA","OB","OM","SQ","S
6","R6"
320 DATA "IS","IC","NS","NC","HA","AU","RA","OE","OC","IP","SA","SI","RE","HA","NI","GO","GO","GS","GR
","WH","HS","SS","HS","SC","SO","CD"
340 DATA "VE","AA","PO","II","XH","XL","XO","YI","YH","YL","YO","SP","PL","SM","ST","PG","VA","UP","O
N","FD","FO","FC","LL"
360 DATA "BK","NL","IE","IC","IF","IB","IO","II","IQ","IP","EP","CP","TN","TT","OP","FN"
380 DATA "AF","BF","RF","IF","UA","UB","UA","UT","US","LA","LB","LR","LT","LS","SV","PP","PS","OS","OT
","RR","RH"
400 DATA "NR","NA","PD","ER","AI","AR","TS"
1000 TEXT : POKE 34,0: HOME : PRINT
1100 PRINT : PRINT "PROGRAM OPTIONS ARE:" 2
1120 PRINT : PRINT 1. SET UP SOLARTROH"
1140 PRINT : PRINT 2. HELP"
1160 PRINT : PRINT 3. TAKe MEASUREMENTS"
1180 PRINT : PRINT 4. CHAIN BOOE PLOT"
1200 PRINT : PRINT 5. CHAIN NYQUIST PLOT"
1220 PRINT : PRINT 6. SAVE DATA ON DISK"
1240 PRINT : PRINT 7. RETRIEVE DATA FROM DISK"
1260 PRINT : PRINT 8. SET TIME"
1280 PRINT : PRINT 9. CHAIN ANALYSIS PROGRAM"
1300 PRINT : PRINT 0. EXIT PROGRAM"
1260 ZI(5) = 0: VTAB (23):ZI(4) = 0:ZI(5) = N: GOSUB 10100
1280 IF IEZ(4) = 1 THEN 1000
1300 ON ZI(5) GOSUB 1000,2500,3000,4000,5000,6000,7000,8000,9700
1320 HOME : VTAB 9: PRINT "EXIT PROGRAM": PRINT PRINT "TYPE GOTO 1000 TO RESUME": END
1500 GOSUB 15000: GOTO 1000
1520 ZM(128) = 1:MS = "TIFO": GOSUB 29000:ZI(4) = ZI(5):MS = "TIFO": GOSUB 29000: PRINT PRINT "RS = "

A-1
;ZZ(4); PRINT : INPUT "USE THIS VALUE (Y/M) ? " ; NM; IF NM < > "Y" THEN 15000
1920 ZM(51) = ZZ(4); GOTO 1500; REM RP
2000 NAME : PRINT "INITIALISE";
2020 60SUB 20000:N$ = "*;"; 60SUB 21000
2040 60SUB 29000; REM KEITHLEY
2060 GOTO 15000
2500 NAME : VTAB 5; PRINT "HELP"; PRINT ""; VTAB 10; PRINT "THERE IS NO HELP AVAILABLE HERE."; PRINT "LIFE IS LIKE THAT. IT CAN SOMETIMES BE HARD AND CRUEL."; PRINT "IF YOU DON'T KNOW WHAT YOU ARE DOING"
2510 PRINT "IT IS POSSIBLE THAT YOU SHOULD NOT DO IT."; PRINT "PLEASE DO NOT HESITATE TO CALL HE,"
2520 VTAB 23: GOTO 1000
3000 NAME : VTAB 3; PRINT "NAME AND LOCATION OF SAVE DATA FILE"
3010 GOSUB 11500; PRINT : PRINT "FILE NAME WILL BE PRECEDED BY DMSS(D)-": PRINT : INPUT "ENTER FILE NAME = DHSS(D)-" ; ZD$(0)
3015 X = FRE(0); ZF# = ZD$(0); ZZ(8) = 76: ZDII(0) = "DHSS(D)-" ; ZF#; GOSUB 11400: ZF# = "DHSS(D)-" ; ZF#; T: ZZ(8) = 78
3020 PRINT : PRINT "STARTING FILE NAME": ZZ(3) = X; ZZ(4) = 0; ZZ(5) = 100; ZZ(6) = 1 = GOSUB 10100; IF ZE
3030 ZF# = ZZ(3); ZH(3) = ZZ(118)
3040 X = FRE(0); POKE 34,0: VTAB 1: PRINT "MEASUREMENT MODE preamble": ZH(127): VTAB 2: PRINT ZF#; VTAB 3; PRINT "SCALE FACTOR": ZH(53)
3050 ZM(47) = 0: NAME : VTAB 5; PRINT "TOTAL # OF POINTS": ZH(19): PRINT "DM": IF ZM(125) = 0 THEN VTAB 19: PRINT "OFF"
3060 VTAB 12: PRINT "DC VOLTAGE SWEEP":; VTAB 19: PRINT "ON": IF ZM(120) = 0 THEN VTAB 12: VTAB 19: PRINT "OFF"
3070 VTAB 14: PRINT "AC VOLTAGE SWEEP":; VTAB 19: PRINT "ON": IF ZM(124) = ZM(125) THEN VTAB 14: VTAB 19 : PRINT "OFF"
3080 VTAB 16: PRINT "HARMONIC SWEEP";: VTAB 19: PRINT "ON": IF ZM(122) = ZM(123) THEN VTAB 16: VTAB 19: PRINT "OFF"
3090 VTAB 18: PRINT "INPUT FRONT/REAR":; VTAB 19: PRINT "FRONT": IF ZM(54) = 1 THEN VTAB 18: VTAB 19: PRINT "REAR": IF ZM(56) = 1 THEN VTAB 18: VTAB 19: PRINT "BOTH"
3100 VTAB 2: VTAB 19: PRINT "START": IF ZM(124) = 1 THEN VTAB 29: PRINT "STOP": IF ZM(125) = 1 THEN VTAB 19: PRINT "OFF"
3110 IF ZM(126) > 0 THEN 60SUB 18200: IF ZZ(5) = ZZ(4) / 60 < ZM(124) THEN FOR II = 1 TO 4444: NEXT
3120 FPC = 1: IF ZM(50) = 2 THEN FR = 2
3130 ZM(56) = INT (ZM/ FPC ; ZM(55) = ZM(51))
3140 ZM(59) = (ZM(34) / ZM(35)) / (1 / ZM(56))
3145 ZM(0,0) = ZM: 60SUB 18200:ZM(1,0) = ZZ(5) + ZZ(4) / 60 < ZM(124) THEN FOR II = 1 TO 4444: NEXT
3150 VTAB 23: PRINT ZM(39),ZM(57),ZM(56)
3160 VTAB 5: CALL = 958: PRINT
3170 J = 0: IF ZM(121) = 1 THEN ZM(3) = ZM(118): REM INITIAL DC
3175 60SUB 19000; REM SET DISPLAY
3180 11 = 1: 60SUB 17000
3190 FOR J2M = 1 TO 441: II = (M(117): REM J2M
3200 ZM(11) = ZM(35): REM F MIN.
3210 11 = 1: 60SUB 17000
3220 ZM(29) = 0: IF ZM(111) > ZM(49) THEN ZM(29) = 1: REM COUPLING
3230 11 = 29: 60SUB 17000
3240 ZM(25) = ZM(122): REM INITIAL HARMONIC
3250 II = 25: GOSUB 17000
3260 FRX = 0: ZM(150) = 0: IF ZM(150) = 1 THEN ZM(30) = 1: FRX = 1: REM REAR
3270 II = 30: GOSUB 17100: ZM(45) = 0100: IF ZM(127) = 2 THEN ZM(45) = 0200
3280 IF ZM(127) = 0 THEN ZM(45) = 0201
3290 J = J • 1: IF J = ZN(128) AND ZH(127) = 1 THEN 3620
3295 IF J > ZN(128) THEN 3580: REM FULL
3300 II = 45: GOSUB 17000: GOSUB 18000: II = 32: GOSUB 16900: REM MEASURE
3310 M4 = ":"0P2,1": II = 4: GOSUB 24000: IF ZH(40) > 0 THEN 3300
3320 FOR ZS = 1 TO 3: ZN(ZS - 1, J) = ZZ(ZS): NEXT ZS
3330 IF ZH(127) > 3 THEN II = 45: ZH(45) = 0200: GOSUB 17000: GOSUB 18000: M4 = ":"0P2,1": II = 4: GOSUB 24000: REM CH2
3340 IF ZM(127) < 3 THEN ZM(1, J) = 1: ZM(4, J) = 0
3350 IF ZM(127) = 3 THEN ZM(3, J) = ZM(1, J) • ZM(4, J) = ZM(1, J): ZM(4, J) = ZM(1, J) • ZM(2, J)
3360 IF ZM(127) = 4 THEN ZM(3, J) = ZM(2, J) • ZM(4, J) = ZM(3, J) • ZM(2, J)
3370 IF ZM(127) = 5 THEN ZM(3, J) = ZM(3, J) • ZM(1, J): ZM(4, J) = ZM(2, J) • ZM(2, J)
3380 IF ZM(127) = 6 THEN GOSUB 3800: GOTO 3420
3390 GOSUB 9500: ZM(3, J) = 1 / (ZM(1, J) • ZM(2, J) • ZM(3, J)) • ZM(2, J)
3400 GOSUB 9500: ZM(3, J) = ZM(3, J) • ZM(1, J) • ZM(2, J) • ZM(3, J) • ZM(1, J)
3410 INVERSE: VTAB 20: HTAB 12: PRINT ZM(II)
3420 IF ZM(128) = 1 THEN ZM(30) = 1: PRINT "FRONT": IF ZM(30) = 1 THEN ZM(0) = "REAR"
3430 PRINT ZM(0);: HTAB 2B: ZM(0); = "OC": IF ZM(29) = 1 THEN ZM(0) = "AC"
3440 PRINT ZM(0);: HTAB 36: ZM(0); = "OFF": IF ZM(14) = 1 THEN ZM(0) = "ON"
3450 PRINT ZM(0);: NORMAL
3460 VTAB 4: CALL - B9B: IF ZM(47) = 999 THEN PRINT "TERMINATE"
3470 IF ZM(50) = 2 AND FRX = 0 THEN ZM(30) = 1: FRX = 1: GOTO 3270: REM REAR
3500 IF ZM(125) < ZM(123): ZM(125) = ZM(123)
3510 IF ZM(1) = ZM(34) THEN 3540
3520 ZM(1) = ZM(1) • ZM(34): IF ZM(1) > ZM(34) THEN ZM(1) = ZM(34)
3530 GOTO 3210
3540 IF ZM(120) • ZM(119) - ZM(3) • ZM(2) THEN ZM(3) = ZM(120) • ZM(119) - ZM(3) • ZM(2)
3550 REM DC LIMIT REACHED
3560 IF ZM(121) = 1 THEN 3180
3570 GOTO 3210
3580 REM FULL
3590 GOSUB 18000
3600 ZM(124) = ZM(124) • ZM(126): REM INC.TIME
3610 IF FRX(0): ZM(47) = 2: ZM(100) = ZM(47) • STR$(ZM(12)) = 7B: GOSUB 11400: REM SAVE DATA
3612 IF ZM(125) • ZM(125) / 100: ZM(125) OR ZM(47) = 999 THEN 1000: REM TERMINATE
3616 IF ZM(121) = 2 THEN ZM(3) = ZM(3) • ZM(120): IF ZM(121) = ZM(121) • ZM(121) THEN 1000: REM DC LIMIT
3618 GOTO 3040: REM CLOSE LOOP
3620 ZM(II) = 60:11:1 = 1: GOSUB 17000: ZM(1, 1) = 60: FOR A = 1 TO 441: NEXT A: M4 = "T1F1": GOSUB 29200: ZM(1, 1) = ZM(1, 1)
A-3
3630 \( Z_{1}(18) = 0; II = 18 \); GOSUB 17000: FOR II = 1 TO 441: NEXT II: \( M = \text{ "TIF1" } \); GOSUB 297200: \( Z_{2}(4,2M) = Z \) \( Z(3): M = \text{ "TIF0" } \); GOSUB 29200: \( Z(5,2M) = Z \)

3640 II = 20; GOSUB 16900; GOTO 3420

3800 REM CH1 = CM2 = V
3820 \( Z(3, J) = Z(25); Z(4, J) = Z(2); \) \( Z(5, J) = Z(3) \)
3840 \( Z(2) = 1; Z(15): Z(13) = 6.282354 \times 10^{2} \times Z(4) = Z(1, J) \times Z(2) - Z(2, J) \times Z(3); \) \( Z(2, J) = Z(1, J) \times Z(3) + Z(2, J) \times Z(2, J) = Z(4); \) REM 1 = E / R
3860 \( Z(1, J) = Z(1, J) \times Z(5, J) = Z(2, J) \times Z(3); \) \( Z(4, J) = Z(4, J) \times Z(5, J) = Z(5, J) \times Z(53): \) REM SCALE MULTIPLIER

3880 RETURN

3900 REM DISPLAY

3920 REM

3930 VTAB 6: CALL - 958; HTAB 6: PRINT "H DCV FREQUENCY:" PRINT "INIT."; PRINT "FINAL."; PRINT "STEP:" PRINT "CURR."; FOR II = 0 TO 5: VTAB (13 + II): PRINT "#"; II: NEXT II

3940 VTAB 21: PRINT "INPUT FREH:" COPLG: COHP "

3960 VTAB 21: PRINT "LAST ERROR:" RETURN

3990 VTAB ZN(3): HTAB 7: CALL - 868: PRINT ZN(4); TAB( U); ZN(5); TAB( 18); ZN(6): RETURN

4000 ZD*(0) = "BODE": GOSUB 19900

4020 NPX = 1: CALL 520DHS.S.BODE'

5000 ZD*(0) = "NYQUIST": GOSUB 19900

5020 NPX = 1: CALL 520DHS.S.NYQUIST'

6000 REM SAVE DATA TO DISK

6010 GOSUB 11500: PRINT "FILE NAME WILL BE PRECEDED BY DHSS(D)-": PRINT "ENTER DATE NAME = DHSS(D)-": ZD*(0): ZD*(0) = "DHSS(D)-" • ZD*(0): IF ZDKO) < > "DHSSID)-" THEN ZD*(0) = "DHSS(D)-"

6500 ZDKO) = ZD*(0) • STRI (INT (ZZI3) • 0.5)): RETURN

7000 REM RETRIEVE DATA FROM DISK

7040 X = FRE (0): GOSUB 11500: PRINT "CURRENT FILE NAME = "JZFX: PRINT "NEW FILE NAME = "JZFX: PRINT "NEW FILE NAME = DHSS(D)-": ZD*(0): ZD*(0) = "DHSS(D)-" + ZD*(0): IF ZDKO) < > "DHSS(D)-" THEN ZF$ = Z

7080 Z(8) = 78: GOSUB 11420: GOTO 1000

8000 HOME: REM SET TIME

8020 GOSUB 18200: VTAB B: PRINT "NEW " TIME": HTAB 9: PRINT "HOURS":; JZN: IF JZN > 99 OR JZN < 0 THEN B 020

8040 VTAB 11: HTAB 7: INPUT "MINUTES":; ZM(83): IF ZM(83) > 59 OR ZM(83) < 0 THEN B 040

8060 II = 83: GOSUB 17200: GOTO 1000

9000 REM DISPLAY COUNTER ROUTINE

9010 HTAB 30: PRINT ";: ;JZN; ""; RETUR N

9240 PR$ 5: PRINT "A:" ; PRINT "": PRINT "": ZD*(0): ZD*(0) = ZF$ + "" + STR$ (ZFX)

9500 REM COMPLEX DIVISION

9520 Z(5) = Z(13, J) \times Z(3, J) + Z(4, J) \times Z(4, J)

9540 Z(6) = (Z(11, J) \times Z(3, J) + Z(2, J) \times Z(4, J)) / Z(5)

9560 Z(7) = (Z(12, J) \times Z(3, J) - Z(11, J) \times Z(4, J)) / Z(5)

9580 Z(8) = Z(6) \times Z(2, J) = Z(4): RETURN

9700 ZD*(0) = "ANALYSIS": GOSUB 19900

9720 CALL 520DHS.ANALYSIS'

9770 REM MAG. & PHASE

9880 ZN(3, J) = SQR (Z(1, J) \times Z(1, J) + Z(2, J) \times Z(2, J))

9900 ZN(4, J) = ATN (Z(12, J) / Z(11, J)) \times 180 / 3.14159265

9990 ZN(5, J) = LOG (Z(13, J)) / LOG (10): RETURN

9999 PRINT CHRI (13): CHRI (4): "SAVEDHSS MAIN": END
10000 REM Y/N SUBR
10010 ZEZ(0) = 0: PRINT "YES ":* GET ZD$(0): ZR(3) = PEEK (36) - 4: IF ZD$(0) = "y" OR ITD$(0) = CHR$(
13) THEN ZZ(5) = 2: PRINT "": RETURN
10020 IF ZD$(0) = "n" THEN POKE 36, ZZ(3); PRINT "NO ": ZZ(3) = 1: RETURN
10030 ZEZ(0) = 1: GOSUB 10050: RETURN
10050 REM ERROR SUBR
10060 PRINT CHR$(7); ZEZ(0) = 1: RETURN
10100 REM I/P SUBR
10110 CALL 68B
10120 ZEZ(0) = 0: PRINT ZZ(3): INPUT "": ZD$(0): IF ZD$(0) = "" THEN ZZ(7) = ZZ(3): GOTO 10170
10130 FOR I = 1 TO LEN (ZD$(0)); ZZ = MID$(ZD$(0), 1, 1)
10140 IF ZZ = "*" OR ZZ = "" OR ZZ = "" OR ZZ = "." OR ZZ = "#" THEN 10160
10150 IF ZZ < "0" OR ZZ > "9" THEN 10050
10160 NEXT I: ZZ(7) = VAL (ZD$(0))
10170 IF ZZ(7) < ZZ(4) OR ZZ(7) > ZZ(5) THEN 10050
10180 ZZ(5) = ZZ(7): IF ZZ(6) = 1 THEN ZZ(3) = INT (ZZ(7))
10190 FOR I = 0 TO 200: NEXT I: RETURN
11300 REN : LOAD ARRAY
11320 POKE 98, 90: POKE 99, ZZ(8): CALL 38152
11330 PRINT CHR$(4); "LOAD" ; ZZ(0); "A": PEEK (38394) + PEEK (38395) I 256
11340 RETURN
11400 REM : SAVE ARRAY
11420 POKE 98, 90: POKE 99, ZZ(8): CALL 38104
11430 PRINT CHR$(4); "SAVE" ; ZZ(0); "A": PEEK (38394) + PEEK (38395) I 256*L:* PEEK (38396) + PEEK (38397) # 256
11440 RETURN
11500 REM ASK SLOT, DRIVE AND VOLUME
11510 VTAB 6: CALL 958: PRINT "POINTERs CURRENTLY SET AT "*: VTAB 8: PRINT "SLOT ": VTAB 2: PRINT "DRIVE ": VTAB 3: PRINT ",": VTAB 4: PRINT "VOLUME ": VTAB 5: PRINT ""
11520 VTAB 12: PRINT "CHANGE POINTERS (Y/N) ? "*: GET ZD$(0): IF ZD$(0) = "n" THEN 11550
11530 PRINT : PRINT : PRINT ZZ(3) = S: ZZ(4) = 4: ZZ(5) = 6: ZZ(6) = 1: PRINT "": SLOT "*: GOSUB 10120: IF ZEZ(0) = 1 THEN 11530
11532 S = INT (ZZ(3) + 0.5)
11535 PRINT : PRINT ZZ(3) = D: ZZ(4) = 1: ZZ(5) = 2: ZZ(6) = 0: PRINT "": DRIVE "*: GOSUB 10120: IF ZEZ(0) = 1 THEN 11535
11537 D = INT (ZZ(3) + 0.5): IF S < 6 THEN V = 0: GOTO 11550: REM FLOPPY
11540 PRINT : PRINT ZZ(3) = V: ZZ(4) = 1: ZZ(5) = 6: ZZ(6) = 0: PRINT "": VOLUME "*: GOSUB 10120: IF ZEZ(0) = 1 THEN 11540
11542 V = INT (ZZ(3) + 0.5)
11550 PRINT : PRINT "PRESS ANY KEY TO CATALOG "*: GET ZD$(0): PRINT : PRINT CHR(4); "CATALOG.S"S: S: D: "D":, "V": V
11560 PRINT : PRINT "ANOTHER CATALOG Y/N ? "*: GOSUB 10000: IF ZEZ(0) = 1 THEN 11560
11570 IF ZZ(3) = 2 THEN 11500
11580 RETURN
15000 TEXT : POKE 34, 0: HOME : VTAB 5; PRINT "SET-UP OPTIONS ARE:" 15020 PRINT : PRINT "1...RETURN TO MAIN MENU"
15040 PRINT : PRINT "2...CREATE/MODIFY SET-UP FILE"
15060 PRINT : PRINT "3...RETRIEVE SET-UP FILE FROM DISK"
15080 PRINT : PRINT "4...SAVE SET-UP FILE TO DISK"
15100 PRINT : PRINT "5...EXECUTE SET-UP FILE"
15120 PRINT : PRINT "6...RESET (INITIALIZE) SOLARTRON"
15140 PRINT : PRINT "7...RESET (INITIALIZE) KEITHLEY"
15200 ZZ(3) = 1: VTAB (23):ZZ(4) = 1: ZZ(5) = 7: GOSUB 10100: IF ZEZ(0) = 1 THEN 15000
15220 ON ZZ(3) GOTO 1000,15300,16600,16640,16700,2000,1900
15300 HOME : VTAB 5: PRINT "SET-UP WHICH SUBSYSTEM:"
15320 PRINT : PRINT " 1.GENERATOR"
15340 PRINT : PRINT " 2.ANALYSER"
15360 PRINT : PRINT " 3.SNIP(S)"
15380 PRINT : PRINT " 4.IMPEDANCE STANDARD"
15400 PRINT : PRINT " 5.MEASUREMENT CONFIGURATION"
15420 PRINT : PRINT " 0.RETURN TO SET-UP OPTIONS"
15440 ZZ(3) = 0: VTAB (23):ZZ(4) = 0: ZZ(5) = 5: GOSUB 10100: IF ZEZ(0) = 1 THEN 15300
15500 ON ZZ(3) GOTO 15000,15600,15800,16000,16300,16500
15520 HOME : VTAB 3: PRINT 'GENERATOR'
15540 VTAB 6: PRINT 'FREQUENCY *': ZZ(3) = ZH(1):ZZ(4) = 1E - 5: ZZ(5) = 1023:ZZ(6) = 0: GOSUB 10100: IF ZEZ(0) = 1 THEN 15560
15560 ZZ(3) = ZZ(3)
15580 IF ZM(2) +ABS(ZM(3)) > 14 THEN VTAB 8: PRINT "COMBINED VOLTAGE TOO LARGE": GOTO 15630
15600 VTAB 15: PRINT 'WAVEFORM (SIN=0,SQR=1) ': ZZ(3) = ZM(4):ZZ(4) = 0: ZZ(5) = 1: ZZ(6) = 1: GOSUB 10100: IF ZEZ(0) = 1 THEN 15650
15620 IF ZZ(3) = ZZ(3)
15640 IF ZM(2) + ABS(ZM(3)) > 14 THEN VTAB 8: PRINT 'COMBINED VOLTAGE TOO LARGE': GOTO 15630
15650 VTAB 12: PRINT 'D.C. BIAS *': ZZ(3) = ZM(3):ZZ(4) = - 10.23:ZZ(5) = 10.23:ZZ(6) = 0: GOSUB 10100: IF ZEZ(0) = 1 THEN 15650
15660 IF ZZ(3) = ZZ(3)
15670 IF ZM(2) + ABS(ZM(3)) > 14 THEN VTAB 8: PRINT 'COMBINED VOLTAGE TOO LARGE': GOTO 15630
15680 IF ZZ(3) = ZZ(3)
15690 IF ZM(2) + ABS(ZM(3)) > 14 THEN VTAB 8: PRINT 'COMBINED VOLTAGE TOO LARGE': GOTO 15630
15700 IF ZM(14) = 0 THEN 15300
15710 IF ZM(14) = 0 THEN 15300
15720 HOME : VTAB 3: PRINT 'AMPLITUDE COMPRESSION ON'
15730 VTAB 8: PRINT 'SOURCE CHANNEL *': ZZ(3) = ZM(11):ZZ(4) = 1: ZZ(5) = 2: ZZ(6) = 1: GOSUB 10100: IF ZEZ(0) = 1 THEN 15730
15740 IF ZZ(3) = INT(100 * ZZ(3) + 0.5)
15750 VTAB 12: PRINT 'VOLTAGE LEVEL *': ZZ(3) = ZM(12):ZZ(4) = 1E - 4: ZZ(5) = 300: ZZ(6) = 0: GOSUB 10100: IF ZEZ(0) = 1 THEN 15750
15760 IF ZZ(3) = ZZ(3)
15770 IF ZZ(3) = ZZ(3)
15780 IF ZZ(3) = ZZ(3)
15790 GOTO 15300
15800 HOME : VTAB 3: PRINT 'ANALYSER'
15810 VTAB 6: PRINT 'INTEGRATION TIME (SECONDS) ': ZZ(3) = ZM(2):ZZ(4) = 0: ZZ(5) = 1E+22:ZZ(6) = 0: GOSUB 10100: IF ZEZ(0) = 1 THEN 15810
15820 IF ZZ(3) = ZZ(3)
15830 VTAB 9: PRINT 'MEASUREMENT DELAY ': GOSUB 15950:ZZ(3) = ZM(11):ZZ(4) = 0: ZZ(5) = 1E5: ZZ(6) = 0: GOSUB 10100: IF ZEZ(0) = 1 THEN 15830
15840 IF ZZ(3) = ZZ(3)
15850 VTAB 14: PRINT 'INITIAL HARMONIC *': ZZ(3) = ZM(25):ZZ(4) = 1: ZZ(5) = 16: ZZ(6) = 1: GOSUB 10100: IF ZEZ(0) = 1 THEN 15850
15860 IF ZZ(3) = ZZ(3)
15870 VTA8 1B: PRINT "AUTO INTEGRATE OFF=0"; PRINT "CH1(L)=1, CH2(L)=2, CH1(S)=3, CH2(S)=4: ZZ(3) = ZM(2) 6); ZZ(4) = 0; ZZ(5) = 4; ZZ(6) = 1: GOSUB 10100: IF ZE2(0) = 1 THEN 15870
15890 ZM(26) = ZZ(3)
15900 VTA8 6: CALL -958; VTA8 B: PRINT "INPUT VOLTAGE RANGE AUTO=0": PRINT "300V=1, 3000V=2, 3V=3, 30V=4, 300V=5": ZZ(3) = ZM(27); ZZ(4) = 0; ZZ(5) = 5; ZZ(6) = 1: GOSUB 10100: IF ZE2(0) = 1 THEN 15900
15910 ZM(27) = ZZ(3)
15920 VTA8 13: PRINT "INPUT COUPLING": PRINT "DC=0, AC=1, FREQUENCY TO CHANGE=XXX": ZZ(3) = ZM(27); ZZ(4) = 0; ZZ(5) = 9999; ZZ(6) = 1: GOSUB 10100: IF ZE2(0) = 1 THEN 15920
15930 ZM(49) = ZZ(3)
15940 VTA8 10: PRINT "INPUT (FRONT=0, REAR=1, BOTH=2):": ZZ(3) = ZM(30); ZZ(4) = 0; ZZ(5) = 2; ZZ(6) = 1: GOSUB 10100: IF ZE2(0) = 1 THEN 15940
15950 ZM(30) = ZZ(3)
15960 VTA8 10: PRINT "SNEEP (S)... I OF MEASUREMENTS = "; ZZ(3) = ZM(31); ZZ(4) = 0; ZZ(5) = 2; ZZ(6) = 1: GOSUB 10100: IF ZE2(0) = 1 THEN 15960
15970 VTA8 20: PRINT "DC VOLTAGE SWEET (Y/N)": ZZ(3) = ZM(32); ZZ(4) = 0; ZZ(5) = 2; ZZ(6) = 1: GOSUB 10100: IF ZE2(0) = 1 THEN 15970
15980 ZM(32) = ZZ(3)
15990 VTA8 20: PRINT "FINAL DC VOLTAGE": ZZ(3) = ZM(33); ZZ(4) = 0; ZZ(5) = 2; ZZ(6) = 1: GOSUB 10100: IF ZE2(0) = 1 THEN 15990
16000 VTA8 20: PRINT "DC VOLTAGE STEP": ZZ(3) = ZM(34); ZZ(4) = 0; ZZ(5) = 2; ZZ(6) = 1: GOSUB 10100: IF ZE2(0) = 1 THEN 16000
16010 VTA8 20: PRINT "ARE YOU GOING TO CIRCLE INFINITY?": ZZ(3) = ZM(35); ZZ(4) = 0; ZZ(5) = 2; ZZ(6) = 1: GOSUB 10100: IF ZE2(0) = 1 THEN 16010
16020 IF ZZ(3) = 1 THEN ZM(11B) = ZM(3); ZM(119) = ZM(3); ZM(120) = 0: GOTO 16100
16030 VTA8 9: PRINT "INITIAL DC VOLTAGE": ZZ(3) = ZM(33); ZZ(4) = 0; ZZ(5) = 2; ZZ(6) = 1: GOSUB 10100: IF ZE2(0) = 1 THEN 16030
16040 ZM(118) = ZZ(3)
16050 VTA8 12: PRINT "FINAL DC VOLTAGE": ZZ(3) = ZM(119); ZZ(4) = 0; ZZ(5) = 2; ZZ(6) = 1: GOSUB 10100: IF ZE2(0) = 1 THEN 16050
16060 ZM(119) = ZZ(3)
16070 VTA8 15: PRINT "DC VOLTAGE STEP": ZZ(3) = ZM(120); ZZ(4) = 0; ZZ(5) = 2; ZZ(6) = 1: GOSUB 10100: IF ZE2(0) = 1 THEN 16070
16080 ZM(120) = ZZ(3)
16090 IF SGN(ZM(119) - ZM(11B)) < 0 THEN VTA8 B: PRINT "ARE YOU GOING TO CIRCLE 1 INF INFINITY?": GOTO 16030
16098 IF ZM(120) = 0 THEN ZM(121) = 2; ZM(57) = 1; ZM(117) = 0: GOTO 16100
16099 VTA8 1B: PRINT "FILL ARRAY BETWEEN DC STEPS (Y/N)": GOSUB 10000; ZM(121) = ZZ(3); IF ZM(121) = 2 THEN 16100
16100 ZM(57) = INT(1.5 * (ZM(119) - ZM(11B)) / ZM(120))
16109 VTA8 20: PRINT "DELAY BETWEEN DCV (S)": ZZ(3) = ZM(121); ZZ(4) = 0; ZZ(5) = 1000; ZZ(6) = 0: GOSUB 10100: IF ZE2(0) = 1 THEN 16109
16110 ZM(117) = ZZ(3)
16110 VTA8 6: CALL -958; PRINT "FREQUENCY SWEET (Y/N)": ZZ(3) = ZM(126); ZZ(4) = 0; ZZ(5) = 1: GOSUB 10000: ZM(56) = 1: IF ZE2(0) = 1 THEN 16110
16115 IF ZZ(3) = 1 THEN ZM(14) = 1; ZM(11) = 1; GOSUB 25000; ZM(11) = 1; GOSUB 15200: GOTO 16120
16119 VTA8 9: PRINT "FREQUENCY MAXIMUM": ZZ(3) = ZM(3) + ZM(5); ZZ(4) = 1 - S2; ZZ(5) = 65353; ZZ(6) = 0: GOSUB 10100: IF ZE2(0) = 1 THEN 16119
16120 ZM(35) = ZZ(3); ZZ(1) = 35; GOSUB 17000
16122 VTA8 12: PRINT "FREQUENCY MAXIMUM": ZZ(3) = ZM(34); ZZ(4) = 1 - S2; ZZ(5) = 65353; ZZ(6) = 0: GOSUB 10100: IF ZE2(0) = 1 THEN 16122
16124 ZM(34) = ZZ(3); ZZ(1) = 34; GOSUB 17000
16126 ZM(35) = 1: IF ZM(34) > 32767 THEN ZM(257) = 1: GOTO 16200: REM NO HARMONIC POSSIBLE
16128 VTA8 4: CALL -958; PRINT "HARMONIC SWEET (Y/N)": ZZ(3) = ZM(126); ZZ(4) = 0: GOSUB 10000: IF ZE2(0) = 1 THEN 16128
16130 IF ZZ(3) = 1 THEN ZM(122) = ZM(257); ZM(12) = ZM(257): GOTO 16200
16135 VTAB 10: PRINT "SECONDS": II = 24: PRINT "CYCLES": II = 23
16140 RETURN
16170 VTAB 9: PRINT "INITIAL HARMONIC #: ZZ(3) = ZM(122): ZZ(4) = 1: ZZ(5) = INT (65535 / ZM(34)): ZZ(6) = 1: GOSUB 10100: IF ZE(0) = 1 THEN 16170
16180 ZM(122) = ZZ(3)
16190 VTAB 12: PRINT "FINAL HARMONIC #: ZZ(3) = ZN(122): ZZ(4) = ZN(123): ZZ(5) = INT (65535 / ZN(34)): ZZ(6) = 1: BOSUB 10100: IF ZEX(0) = 1 THEN 16190
16195 ZH(122) = ZZ(3)
16200 VTAB 6: CALL 958: PRINT "TIMED SHEEP (Y/N) ?": 60SUB 10100: IF ZEX(0) = 1 THEN 16200
16210 IF Z2C3 = 1 THEN ZH(124) = 0: ZH(125) = ZH(124): ZH(126) = ZH(125): 60T0 16290
16220 60SUB 18000: VTAB 9: PRINT "SCALE FACTORS:" ZH(51) = ZZ(3): ZZ(4) = 1E9: ZZ(6) = 0: 60SUB 10100: IF ZEZ(0) = 1 THEN 16220
16230 ZM(126) = ZZ(3)
16240 ZM(124) = ZZ(3)
16250 VTAB 15: PRINT "STOP MEASUREMENTS #: ZZ(3) = ZM(126): ZZ(4) = ZM(125): ZZ(5) = 99.59: ZZ(6) = 0: GOSUB 10100: IF ZE(0) = 1 THEN 16250
16260 ZM(125) = ZZ(3)
16270 VTAB 13: PRINT "STOP MEASUREMENT INTERVAL #: ZZ(3) = ZM(126): ZZ(4) = 0: ZZ(5) = 24: ZZ(6) = 0: GOSUB 10100: IF ZE(0) = 1 THEN 16270
16280 ZM(124) = ZZ(3)
16290 ZM(56) = INT (ZM / (ZM(55) * ZM(57))): GOTO 15300
16300 HOME: VTAB 3: PRINT "MEASUREMENT MODE:" H: VTAB 14: PRINT "INPUT(S): 0=2/1": H: VTAB 14: PRINT "1=1": H: VTAB 14: PRINT "2=2": H: VTAB 14: PRINT "3=3/2": H: VTAB 14: PRINT "4=4/2": H: VTAB 14: PRINT "5=5/2": H: 16520 VTAB 11: ZZ(3) = ZM(127): ZZ(4) = 0: ZZ(5) = 5: ZZ(6) = 1: GOSUB 10100: IF ZE(0) = 1 THEN 16520
16525 ZM(127) = ZZ(3)
16545 ZM(116) = ZZ(3)
16550 VTAB 20: PRINT "COORDINATES 0=A/B": H: VTAB 14: PRINT "1=R/THETA": H: VTAB 14: PRINT "2=LOG.R/THETA": H: VTAB 14: PRINT "3=1/R/THETA": H: VTAB 14: PRINT "4=1/R/THETA": 16560 VTAB 23: ZZ(4) = ZM(16): ZZ(4) = 4: ZZ(5) = 2: ZZ(6) = 0: GOSUB 10100: IF ZE(0) = 1 THEN 16560
16570 GOTO 15300
16580 HOME: VTAB 3: PRINT "RETRIEVE SET-UP FILE" 16590 GOSUB 16680: ZZ(8) = 77: GOSUB 11300: GOTO 15000
16600 HOME: VTAB 3: PRINT "SAVE SET-UP FILE TO DISK" 16610 GOSUB 16680: ZZ(16) = 77: GOSUB 11400: GOTO 15000
16620 HOME: VTAB 3: PRINT "EXECUTE SET-UP FILE" 16630 FOR ii = 1 TO 6: GOSUB 17000: NEXT II
16720  II = 14: GOSUB 17000: IF ZH(14) = 1 THEN FOR II = 11 TO 13: GOSUB 17000: NEXT II
16730  II = 20: GOSUB 16900
16740  II = 21: GOSUB 17000: II = 24: IF ZH(23) > 0 THEN II = 23
16750  FOR II = 27 TO 30: FOR JZN = 1 TO 2: GOSUB 17000: NEXT JZN: NEXT II
16760  ZN(45) = 0201: IF ZN(127) > 0 THEN ZN(45) = 0100: IF ZN(127) > 1 THEN ZN(45) = 0200: IF ZN(127) > 2 THEN ZN(45) = 0000
16770  II = 45: GOSUB 17000: II = 68: GOSUB 17000
16771  RESTORE: FOR II = 1 TO II: READ HI: NEXT II: HI = V • HI • "": GOSUB 21000: RETURN
16780  RESTORE: FOR II = 1 TO II: READ HI: NEXT II: HI = V • HI • STRI (ZH(II)) • "": GOSUB 21000: RETURN
16790  FOR JZN = 1 TO 2: RESTORE: FOR II = 1 TO II: READ HI: NEXT II: HI = V • HI • STRI (ZII(II)) • "": GOSUB 21000: RETURN
16800  FOR JZN = 1 TO 2: RESTORE: FOR II = 1 TO II: READ HI: NEXT II: HI = V • HI • STRI (ZII(II)) • "": GOSUB 21000: RETURN
16810  RESTORE: FOR II = 1 TO II: READ HI: NEXT II: HI = V • HI • STRI (JZN) • V • STRI (ZH(II)) • "": GOSUB 21000: RETURN
16820  GOTO 1000
16900  RESTORE: FOR I = 1 TO II: READ M: NEXT I: M = "": GOSUB 21000: RETURN
17000  RESTORE: FOR I = 1 TO II: READ M: NEXT I: M = "": M = STRI (ZH(II)) • "": GOSUB 21000: RETURN
17100  FOR JZN = 1 TO 2: RESTORE: FOR I = 1 TO II: READ M: NEXT I: M = "": M = STRI (JZN) • "": GOSUB 21000: RETURN
17200  RESTORE: FOR I = 1 TO II: READ M: NEXT I: M = "": M = STRI (JZN) • "": M = STRI (ZH(II)) • "": GOSUB 21000: RETURN
18000  IF ZH(3) = 1 THEN GOTO 1000: IF ZH(3) = 19 THEN GOTO 1000: IF ZH(3) = 20 THEN ZH(47) = 999: IF ZH(3) = 21 THEN GOTO 1000: RETURN
18100  IF JZN = 1 THEN RETURN
18200  IF JZN = 2 THEN RETURN: IF JZN = 3 THEN RETURN: IF JZN = 4 THEN RETURN: IF JZN = 5 THEN RETURN
18300  RESTORE: FOR I = 1 TO II: READ HI: NEXT II: HI = V • HI • STRI (ZH(I)) • V: RETURN
18400  RESTORE: FOR I = 1 TO II: READ HI: NEXT II: HI = V • HI • STRI (JZN) • V • STRI (ZH(I)) • "": RETURN
18500  RESTORE: FOR I = 1 TO II: READ HI: NEXT II: HI = V • HI • STRI (ZII(II)) • "": RETURN
18610  RESTORE: FOR I = 1 TO II: READ HI: NEXT II: HI = V • HI • STRI (JZN) • V • STRI (ZH(I)) • "": GOSUB 21000: RETURN
18700  RESTORE: FOR I = 1 TO II: READ HI: NEXT II: HI = V • HI • STRI (JZN) • V • STRI (ZH(I)) • "": GOSUB 21000: RETURN
18800  RESTORE: FOR I = 1 TO II: READ HI: NEXT II: HI = V • HI • STRI (JZN) • V • STRI (ZH(I)) • "": GOSUB 21000: RETURN
18900  RESTORE: FOR I = 1 TO II: READ HI: NEXT II: HI = V • HI • STRI (JZN) • V • STRI (ZH(I)) • "": GOSUB 21000: RETURN
19000  RESTORE: FOR I = 1 TO II: READ HI: NEXT II: HI = V • HI • STRI (JZN) • V • STRI (ZH(I)) • "": GOSUB 21000: RETURN
19100  RESTORE: FOR I = 1 TO II: READ HI: NEXT II: HI = V • HI • STRI (JZN) • V • STRI (ZH(I)) • "": GOSUB 21000: RETURN
19200  RESTORE: FOR I = 1 TO II: READ HI: NEXT II: HI = V • HI • STRI (JZN) • V • STRI (ZH(I)) • "": GOSUB 21000: RETURN
19300  RESTORE: FOR I = 1 TO II: READ HI: NEXT II: HI = V • HI • STRI (JZN) • V • STRI (ZH(I)) • "": GOSUB 21000: RETURN
19400  RESTORE: FOR I = 1 TO II: READ HI: NEXT II: HI = V • HI • STRI (JZN) • V • STRI (ZH(I)) • "": GOSUB 21000: RETURN
19500  RESTORE: FOR I = 1 TO II: READ HI: NEXT II: HI = V • HI • STRI (JZN) • V • STRI (ZH(I)) • "": GOSUB 21000: RETURN
19600  RESTORE: FOR I = 1 TO II: READ HI: NEXT II: HI = V • HI • STRI (JZN) • V • STRI (ZH(I)) • "": GOSUB 21000: RETURN
19700  RESTORE: FOR I = 1 TO II: READ HI: NEXT II: HI = V • HI • STRI (JZN) • V • STRI (ZH(I)) • "": GOSUB 21000: RETURN
19800  RESTORE: FOR I = 1 TO II: READ HI: NEXT II: HI = V • HI • STRI (JZN) • V • STRI (ZH(I)) • "": GOSUB 21000: RETURN
19900  RESTORE: FOR I = 1 TO II: READ HI: NEXT II: HI = V • HI • STRI (JZN) • V • STRI (ZH(I)) • "": GOSUB 21000: RETURN
20000  RESTORE: FOR I = 1 TO II: READ HI: NEXT II: HI = V • HI • STRI (JZN) • V • STRI (ZH(I)) • "": GOSUB 21000: RETURN
20100  RESTORE: FOR I = 1 TO II: READ HI: NEXT II: HI = V • HI • STRI (JZN) • V • STRI (ZH(I)) • "": GOSUB 21000: RETURN
20200  RESTORE: FOR I = 1 TO II: READ HI: NEXT II: HI = V • HI • STRI (JZN) • V • STRI (ZH(I)) • "": GOSUB 21000: RETURN
20300  RESTORE: FOR I = 1 TO II: READ HI: NEXT II: HI = V • HI • STRI (JZN) • V • STRI (ZH(I)) • "": GOSUB 21000: RETURN
20400  RESTORE: FOR I = 1 TO II: READ HI: NEXT II: HI = V • HI • STRI (JZN) • V • STRI (ZH(I)) • "": GOSUB 21000: RETURN
20500  RESTORE: FOR I = 1 TO II: READ HI: NEXT II: HI = V • HI • STRI (JZN) • V • STRI (ZH(I)) • "": GOSUB 21000: RETURN
20600  RESTORE: FOR I = 1 TO II: READ HI: NEXT II: HI = V • HI • STRI (JZN) • V • STRI (ZH(I)) • "": GOSUB 21000: RETURN
A-9
21470 PRINT ZD$(7)
21500 RETURN
24000 REM DATA RETRIEVE
24030 PRINT ZD$(8); PRINT ZD$(5)
28500 PRINT CHR$(13);ZD$(4);"**": PRINT ZD$(7): VTAB 23
28501 GOTO 1 86TO 28504, 28506, 28508
28502 INPUT ZZ(1): PRINT ZD$(6): RETURN
28504 INPUT ZZ(1), ZZ(2): PRINT ZD$(8): RETURN
28506 INPUT ZZ(1), ZZ(2), ZZ(3): PRINT ZD$(9): RETURN
28508 INPUT ZZ(1), ZZ(2), ZZ(3), ZZ(4): PRINT ZD$(8): RETURN
29000 REM KEITHLEY MODEL 192 SET-UP
29200 ZD$(0) = M$ + "ROKOGOSHSZONI"
29220 VTAB 23
29240 PRINT ZD$(9): PRINT A$: ZD$(9); 86$: PRINT ZD$(7): INPUT ZD$(9): PRINT ZD$(6): VTAB 23: PRINT "0"
29260 ZZ(5) = VAL ( MID$(ZD$(5), 5)): RETURN
Appendix B

DIFFUSION IN AN ANGULAR CRACK
This appendix gives the solution concentration as a function of time and position in an angular crack. The mathematical representation of the crack is shown in Figure B.1. A crack tip rupture and dissolution provides the concentration \( C = 1 \) up to the \( r = a \) cell element of the angular crack. In this case, \( r_m \) is the distance from the crack origin to the \( m^{th} \) cell segment and \( \Delta \) is the distance between cell segments. Thus,

\[
r_m = m\Delta
\]

(B-1)

We need to solve for \( c_m(t) \) where \( c_m(t) \) = average concentration in \( r_{m-1} < r < r_m \) at time \( t \) and

\( m = 1, 2, 3, \ldots \)

Let \( c = c(a, r, t) \) be the solution of the standard diffusion equation

\[
\frac{\partial c}{\partial t} = D \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial c}{\partial r} \right)
\]

(B-2)

where \( D \) = diffusion coefficient with

\[
c = \begin{cases} 
1 & \text{for } r < a \\
0 & \text{for } a < r 
\end{cases} \text{ at } t = 0
\]

Assuming only nearest neighbors interact over short time \( t \) givea

\[
c_1(t) = c_2(0) + [c_1(0) - c_2(0)] J_1(1)
\]

(B-3)

and for \( m = 2, 3, 4, \ldots \); the solution for the concentration as a function of time and position along the crack is given by
FIGURE B.1  MATHEMATICAL REPRESENTATION OF DIFFUSION IN AN ANGULAR CRACK
\[ c_m(t) = c_{m+1}(0) + [c_m(0) - c_{m+1}(0)] J_-(m) + [c_{m-1}(0) - c_m(0)] J_+ (m-1) \]  

(B-4)

where \( J_-(m) \), a function of \( t \) as well as \( m \), is the average concentration in cell \( m \) just to the left of a unit jump in concentration at \( r = r_m \) and \( J_+(m) \) is the average concentration in cell \( (m+1) \) just to the right of the unit jump at \( r = r_m \). That is,

\[
J_-(m) = \frac{\int_{m-1}^{m} c(m\Delta, r, t) \, dr}{\int_{m-1}^{m} \Delta} 
\]

(B-5)

\[
J_+(m) = \frac{\int_{m}^{m+1} c(m\Delta, r, t) \, dr}{\int_{m}^{m+1} \Delta} 
\]

(B-6)

Approximate values valid for \( \sqrt{Dt/\Delta} \ll 1 \) are

\[
J_-(m) = 1 - \frac{\sqrt{Dt/\Delta}}{2m} \frac{2m}{(2m - 1)\sqrt{\pi}} 
\]

(B-7)

\[
J_+(m) = \frac{\sqrt{Dt/\Delta}}{2m} \frac{2m}{(2m + 1)\sqrt{\pi}} 
\]

(B-8)

The derivation of solution (B-4) is given as follows.

Let \( \bar{c} = \text{Laplace transform of } c \); therefore,

\[
\bar{c} = \int_0^\infty e^{-pt} c \, dt 
\]

(B-9)
Then the transform of the basic problem is

$$\mathcal{D} \left( \frac{d^2 c}{dr^2} + \frac{1}{r} \frac{dc}{dr} - \frac{p}{r} c = -c_{oo} \right) \quad (B-10)$$

where $c_{oo}$, a function of $r$, is the initial value of $c$:

$$c_{oo} = \begin{cases} 1 & r < s \\ 0 & a < r \end{cases}$$

Solving for $r < a$ yields

$$c = AI_0(qr) + BK_0(qr) + 1/p \quad (B-11)$$

where $I_0$ and $K_0$ are the modified Bessel functions; $q = \sqrt{p/D}$; and $A$ and $B$ are constants of integration. Now $B = 0$ because $K_0 \to \infty$ as $r \to 0$.

Solving for $a < r$ gives

$$c = HI_0(qr) + GK_0(qr) \quad (B-12)$$

where $H$ and $G$ are constants of integration and $H = 0$ because $I_0 \to 0$ as $r \to \infty$.

Both $c$ and $dc/dr$ are continuous at $r = a$. Therefore,

$$AI_0(qa) + 1/p = GK_0(qa) \quad (B-13)$$

$$AI_0'(qa) = GK_0'(qa) \quad (B-14)$$

Then
\[ A = \frac{q a K_0(qa)}{p} \]  
\[ B = \frac{q a I_0(qa)}{p} \]  

by use of \( K_0(x)I_0(x) - I_0(x)K_0(x) = \frac{1}{x} \). Therefore,

\[ -c = \begin{cases} 
\frac{1}{p} - \frac{q a K_1(qa) I_0(qr)}{p} & r < a \\
\frac{q a I_1(qa) K_0(qa)}{p} & a < r 
\end{cases} \]  

(B-17)

Early time approximation is as follows:

\[ \frac{\sqrt{D t}}{\Delta} \ll 1 \sim \frac{1}{qa} \ll 1 \sim \frac{1}{qa} \ll 1 \]

Then

\[ K_0(qa) \approx K_1(qa) = \sqrt{\frac{\pi}{2qa}} e^{-qa} \]  

(B-19)

\[ I_0(qa) \approx I_1(qa) = \frac{e^{qa}}{\sqrt{2\pi qa}} \]  

(B-20)

\[ -c = \begin{cases} 
\frac{1}{p} - \frac{1}{2p} \frac{\sqrt{a}}{r} e^{-q(a-r)} & r < a \\
\frac{1}{2p} \frac{\sqrt{a}}{r} e^{-q(r-a)} & a < r 
\end{cases} \]  

(B-21)

(B-22)
Inversion of the transforms gives

\[
\begin{cases}
1 - \frac{1}{2} \sqrt{\frac{a}{r}} \ erfc \frac{a - r}{2\sqrt{Dt}} & r < a \\
\frac{1}{2} \sqrt{\frac{a}{r}} \ erfc \frac{r - 1}{2\sqrt{Dt}} & a < r
\end{cases}
\]  

(B-23)

(B-24)

With \( J_+(m) \) and \( J_-(m) \) defined after equation (B-4) and with \( I_+(m) \) and \( I_-(m) \) being the integrals of the concentration in those definitions, one finds

\[
J_+(m) = \frac{I_+(m)}{\int (m+1) \Delta \ r \ dr} = \frac{2}{(2m+1) \Delta^2} I_+(m)
\]

\[
I_+(m) = \int (m+1) \Delta \ \frac{1}{2} \sqrt{\frac{a}{r}} \ erfc \frac{r - a}{2\sqrt{Dt}} \ r \ dr
\]  

(B-25)

where \( a = m \Delta \). The order of accuracy is \( 1/Q \). Approximations correct to this order can be found as follows:

\[
J_-(m) = 1 - \frac{2}{(2m - 1) \Delta^2} I_-(m)
\]

\[
I_-(m) = \int (m-1) \Delta \ \frac{1}{2} \sqrt{\frac{a}{r}} \ erfc \frac{a - r}{2\sqrt{Dt}} \ r \ dr
\]  

(B-26)

Let \( Q = \Delta/2\sqrt{Dt} \). Then \( Q > > 1 \) by assumption. Integrations are needed to order of accuracy \( 1/Q \).

Function \( \text{erfc}(x) \) is defined by
\[ \text{ierfc}(x) = \int_{x}^{\infty} \text{erfc}(x) \, dx = \frac{1}{\sqrt{\pi}} e^{-x^2} - x \text{erfc}(x) \quad \text{(B-27)} \]

\[ I_+^\Delta = \int_{a}^{a+\Delta} \frac{1}{2} \sqrt{\pi \tau} \text{erfc} \left( \frac{r-a}{2\sqrt{\Delta t}} \right) \, dr \quad a = mA \quad \text{(B-28)} \]

Let \( x = \frac{r-a}{2\sqrt{\Delta t}} \). Then \( r = a (1 + x/mQ) \) and

\[
I_+^m = \int_{0}^{Q} \frac{1}{2} a \sqrt{1 + x/mQ} \text{erfc}(x) \frac{a}{mQ} \, dx \\
= \frac{a^2}{2mQ} \int_{0}^{Q} \sqrt{1 + x/mQ} \text{erfc}(x) \, dx \\
= \frac{mA^2}{2Q} [H_+(m) + K_+(m)]
\]

where

\[
H_+ = \int_{0}^{1} \sqrt{1 + x/mQ} \text{erfc}(x) \, dx \\
K_+ = \int_{0}^{Q} \sqrt{1 + x/mQ} \text{erfc}(x) \, dx
\]

\( H_+ \) can be approximated by

\[
H_+ = \int_{0}^{1} \left[ 1 + \frac{1}{2} \frac{y}{mQ} + \ldots \right] \text{erfc}(x) \, dx \\
\approx \int_{0}^{1} \text{erfc}(x) \, dx
\]
and to lowest \( (Q^0) \) order

\[
H_+ = -\text{ierfc}(x) \bigg|_0^1
= \frac{1}{\sqrt{\pi}} - \text{ierfc}(1)
\]

(B-30)

For \( H_- \) we get

\[
H_- = \int_1^Q \sqrt{1 + x/mQ} \text{erfc}(x) \, dx
= \sqrt{1 + x/mQ} (-\text{ierfc}(x)) \int_1^Q - \int_1^Q (-\text{ierfc}(x)) \frac{1}{2mQ} (1 + \frac{x}{mQ})^{-1/2} \, dx
\]

Then

\[
H_- = \text{ierfc}(1)
\]

(B-31)

to lowest order. Therefore,

\[
I_+ (m) = \frac{m \Delta^2}{2 \sqrt{\pi} Q^2}
\]

\[
J_+ (m) = \frac{m}{(2m+1) \sqrt{\pi}}
\]

For \( I_- (m) \) we get

\[
I_- (m) = \int_{a-\Delta}^a \frac{1}{\sqrt{2\pi r}} \text{erfc} \frac{a - r}{2\sqrt{Dr}} \, dr
\]
where

\[ a = m\Delta \]
\[ Q = \Delta / 2\sqrt{Dr} \]

Then, with \( z = (a - r)/2\sqrt{Dr} \), \( r = a(l - x/mQ) \). Thus,

\[ I_-(m) = \frac{a^2}{2mQ} \int_0^Q \sqrt{1 - x/mQ} \text{erfc}(x) \, dx \]

\[ I_+(m) = \frac{a^2}{2mQ} \frac{1}{\sqrt{\pi}} \]

(B-32)

to lowest order, as before.

\[ J_-(m) = \frac{m}{(2m - 1)Q\sqrt{\pi}} \]

(B-33)
Appendix C

DC TRANSMISSION LINE MODEL
REM "SCC TL DC 16/April/1985
REM "Transmission Line Model for Stress Corrosion Cracking
REM "BY M.C.H. McKubre
PRINT CHR$(13);CHR$(4);"SAVE SCC TL DC#60"
DIM Zn(9,200),Zm(26)
F = 96478
DATA 14.,IDC,AMPS,0,WIDTH,CM,10.,HEIGHT,CM,5.,LENGTH,CM,1.,
.ANGLE,RAD.,02.,BULK,pH,-,6.,RHO-E,OHM-CM,20.,RHO-S,OHM-CM,1E-5,
.GAMMA,CM,1E-4,#.E-/.ATOM,2,INTERVAL,SEC.,3600,NUMBER,SEGMENTS,20,
TOLERANCE,MV,1.,MAX.ITER.,LOOPS,99
DATA 26,IO.M/M,AM+,A.CM-2,1E-3,V..M/M*A+,VOLT,0,IO.M/MO,A
.CM-2,1E-5,V..M/M,VOLT,1,IO.H/H2,A.CM-2,1E-5,V..H/H2,VOLT,2,
K,--,1E-6,MONOLAYER,COUL/CM2,1E-4,N=F*MW*RH0,COUL/CM
A3,8.4E7,D,
CM2,S-1,2E-5,PASSIVE,I,A.CM-2,1E-6,?,?,0
RESTORE : READ II: FOR I = 1 TO II: READ ZQ$,ZT$,Zm(I): NEXT I:
N% = Zm(12)
TEXT : HOME: VTAB 3: PRINT "PROGRAM OPTIONS ARE:: PRINT
PRINT : PRINT " 1 ....SET UP NEW CONSTANTS"
PRINT : PRINT "2....CALCULATE STEADY STATE"
PRINT : PRINT "3....INITIALGUESS OF V"
PRINT : PRINT "4 ...SAVE ARRAY TO DISK"
PRINT : PRINT : PRINT "5....SEND ARAY TO PIPELINE"
PRINT : PRINT : PRINT "WELL ?";: GET ZQ$: IF ZQ$ = "0" THEN HOME :
VTAB 15: PRINT "PROGRAM EXITED - GOTO 1000 TO RESUME": END
IF VAL.(ZQ$) > 5 THEN 1000
HOME : VTAB 2: PRINT "SET-UP CONSTANTS - PAGE#1"
RESTORE : READ II: FOR I = 1 TO II: READ ZQ$,ZT$,J: VTAB (3 + I): HTAB 4:
PRINT I; "ZQ$": HTAB 20: PRINT Zm(I): HTAB 32: PRINT ZT$: NEXT I:
VTAB 23: INPUT "HIT # TO MODIFY "ZQ$:
IF VAL(ZQ$) < 1 OR VAL(ZQ$) > II THEN 1600
READ N: FOR I = 1 TO II: READ ZQ$,ZT$,N: NEXT I: NORMAL : PRINT
"CHANGE ";ZQ$;: INPUT " TO ";ZQ$: IF ZQ$ < > "" THEN Zm(I) = VAL(ZQ$)
VTAB 22: HATS 32: PRINT ZTS: GOTO 1500
HOME : VTAB 2: PRINT "SET-UP CONSTANTS -- PAGE#2"
RESTORE : READ II: FOR I = 1 TO II: READ ZQ$,ZT$,J: NEXT I: READ II:
FOR I = II + 1 TO II: READ ZQ$,ZT$,N: VTAB (3 + I - II): HTAB 4: PRINT I:"
"ZQ$": HTAB 20: PRINT Zm(I): HTAB 32: PRINT ZT$: NEXT I:
VTAB 23: INPUT "HIT # TO MODIFY "ZQ$: IF VAL(ZQ$) = 0 THEN RETURN
IF VAL(ZQ$) < II OR VAL(ZQ$) > II THEN 1600
II = VAL(ZQ$): VTAB 22: RESTORE : READ N: FOR I = 1 TO II: READ ZQ$,ZT$,N: NEXT I:
READ N: FOR I = II + 1 TO II: READ ZQ$,ZT$,N: NEXT I: NORMAL : PRINT "CHANGE"
"ZQ$": INPUT " TO ";ZQ$: IF ZQ$ < > "" THEN Zm(I) = VAL(ZQ$)
VTAB 22: HATS 32: PRINT ZTS: GOTO 1600
HOME : VTAB 2: PRINT "CALCULATING STEADY STATE CONDITIONS"
PRINT CHR$(13);CHR$(4);"PR#1": PRINT CHR$(15):
PRINT CHR$(9);"132N": PRINT CHR$(12)
RESTORE : READ II: FOR I = 1 TO II: READ ZQ$,ZT$,J: PRINT I;"
"ZQ$": "Zm(I);": ZTS: NEXT I: READ II: FOR I = II + 1 TO II: READ ZQ$,ZT$,J: PRINT I;"
"ZQ$": "Zm(I);": ZTS: NEXT I: PRINT "VERSION": " LIST 10
ZQ$ = " ; PRINT "LOOP";ZQ$;"NQ";ZQ$;"G";ZQ$;"SI";ZQ$;"I";ZQ$;"V";ZQ$ = "
APPENDIX ?? DC Transmission Line Model
C-2
APPENDIX ?? DC Transmission Line Model 0-3
5000 \texttt{REM "OUTPUT DATA TO PIPELINE}
5010 \texttt{GOSUB 5020: GOTO 1000}
5020 \texttt{PRINT CHR$(13); CHR$(4);"PR#1": PRINT CHR$(9);"132N: PRINT CHR$(15)
5040 \texttt{FOR N = 0 TO N%: FOR M = 0 TO 6: PRINT Zn(M,N): "": NEXT M: PRINT N: NEXT N}
5080 \texttt{PRINT CHR$(13); CHR$(4);"PR#0": PRINT CHR$(13); CHR$(4);"PR#0": RETURN}
9000 \texttt{REM "READ KEYBOARD}
9010 \texttt{ZZ(3) = PEEK (-16384) - 128: POKE -16386,0: IF ZZ(3) < 1 THEN RETURN}
9020 \texttt{PRINT CHR$(13); CHR$(4);"PR#0"
9030 \texttt{REM "CHANGE PARAMETERS}
9040 \texttt{IF ZZ(3) = 20 THEN POP: GOTO 1000}
9090 \texttt{PRINT CHR$(13); CHR$(4);"SAVE SCC TL DC#6A": END}
10000 \texttt{REM "INTERFACEAL ELECTRICS}
10100 \texttt{REM "METAL DISSOLUTION AT CRACK TIP DUE TO STRESS}
10110 \texttt{Zn(4,N) = 0: IF N < N\% THEN 10200}
10120 \texttt{ZZ(0) = Zm(15) * Zm(9) * Zm(2) * TAN (Zm(5)): ZZ(1) = Zm(10): ZZ(2) = Zm(16): ZZ(3) = Zn(8,N): GOSUB 10800: REM "B-V 0-10,1-N,2-V0.3-C}
10140 \texttt{Zn(4,N) = ZZ(5): DL = Zn(4,N) * Zm(11) / (Zm(23) * Zm(9) * Zm(5) * Zm(2)): IF DL < 0 THEN DL = 0: REM "DELTA-L}
10200 \texttt{REM "CHEMICAL PASSIVATION}
10300 \texttt{REM "HYDROGEN ION REDUCTION}
10320 \texttt{ZZ(0) = Zm(19) * 2 * Zm(2) * (Zm(4) / N\%): ZZ(1) = 1: ZZ(2) = Zm(20): ZZ(3) = Zn(7,N): GOSUB 10800: REM "B-V 0-10,1-N,2-V0.3-C}
10340 \texttt{Zn(5,N) = ZZ(5)}
10400 \texttt{REM "METAL OXIDE REDUCTION}
10410 \texttt{ZZ(0) = Zm(9,N): IF ZZ(0) > 1 THEN ZZ(0) = 1}
10420 \texttt{ZZ(0) = ZZ(0) * Zm(17) * 2 * Zm(2) * (Zm(4) / N\%): ZZ(1) = Zm(10): ZZ(2) = Zm(18): ZZ(3) = Zn(7,N): GOSUB 10800: REM "B-V 0-10,1-N,2-V0.3-C}
10440 \texttt{Zn(6,N) = ZZ(5)}
10500 \texttt{REM "METAL DISSOLUTION ON CRACK WALLS}
10510 \texttt{ZZ(9) = (1 - Zn(9,N)): IF ZZ(9) < 0 THEN ZZ(9) = 0: REM "ACTIVE/PASSIVE}
10520 \texttt{ZZ(0) = Zm(15) * 2 * Zm(2) * (Zm(4) / N\%): ZZ(1) = Zm(10): ZZ(2) = Zm(16): ZZ(3) = Zn(8,N): GOSUB 10800: REM "B-V 0-10,1-N,2-V0.3-C}
10540 \texttt{IF ZZ(0) > 0 THEN ZZ(6) = ZZ(5) * ZZ(0): GOTO 10590: REM "ACTIVE KINETICS}
10580 \texttt{ZZ(6) = SGN (ZZ(5)) * ABS (Zm(25) * 2 * Zm(2) * (Zm(4) / N\%) * Zm(8,N)) / (Zm(23) * Zm(9) * Zm(5)): IF ABS (ZZ(5)) < ZZ(6) THEN ZZ(6) = ZZ(5): REM "PASSIVE DIFFUSION}
10590 \texttt{Zn(4,N) = Zn(4,N) + ZZ(6)}
10600 \texttt{RETURN}
10800 \texttt{REM "COMPUTE BUTLER-VOLMER I}
10805 \texttt{ZZ(2) = Zm(1,N - 1) - Zm(N,N - 1) - ZZ(2) + (2 / (Zm(10) * C)) * LOG (ZZ(3)): REM "ZETA INCLUDING CONC.
10810 \texttt{ZZ(4) = ZZ(1) * C * (ZZ(2)): IF ABS (ZZ(4)) > 30 THEN ZZ(4) = SGN (ZZ(4)) * 30}
10820 \texttt{ZZ(5) = ZZ(0) * (EXP (ZZ(4)) - EXP (- ZZ(4)))}
10830 \texttt{ZZ(6) = Zm(2) * Zm(5) * (Zm(4) / N\%) ^ 2 * (2 * N\% - 2 * N + 1): REM "VOLUME}
10839 \texttt{IF N = N\% AND ZZ(5) > 0 THEN 10849: REM "NO LIMIT TO M->MO AT TIP}
10840 \texttt{IF ABS (ZZ(5)) > ABS (99 * ZZ(1) * F * ZZ(3) * ZZ(6) / Zm(11)) THEN ZZ(5) = SGN (ZZ(5)) * 99 * ZZ(1) * 96478 * ZZ(3) * ZZ(6) / Zm(11): REM "MAX DELTA-C

APPENDIX ?? DC Transmission Line Model
REM "ZQS = " : FOR NN = 0 TO 6: PRINT ZZ(NN);ZQS$;: NEXT NN: PRINT N
10850 RETURN

11000 REM "INTERFACIAL CHEMISTRY"
11020 ZZ(0) = Zm(2) * Zm(5) * (Zm(4) / N%) ^ 2 * (2 * N% - 2 * N + 1): REM "V
11040 ZZ(1) = Zm(4,N) * Zm(11) / (Zm(10) * F * ZZ(0)): IF ZZ(1) > Zm(8,N) / 2 THEN ZZ(1) =
11060 ZZ(2) = (Zm(5,N) + Zm(6,N)) * Zm(11) / (F * ZZ(0)): IF ZZ(2) > Zn(7,N) / 2 THEN ZZ(2) =
11080 ZZ(3) = Zn(6,N) * Zm(11) / (Zm(10) * Zm(22) * Zm(10) * ZZ(0)): IF ZZ(3) > Zm(9,N) / 2
11100 ZZ(4) = Zm(7,N) * ZZ(2):Zn(8,N) = Zm(8,N) - ZZ(1):Zn(9,N) = Zm(9,N) - ZZ(3): REM:
11120 ZZ(5) = Zm(7,N) * ZZ(2):Zn(8,N) = Zm(8,N) - ZZ(1):Zn(9,N) = Zm(9,N) - ZZ(3): REM:
11140 ZZ(6) = Zn(9,N): IF ZZ(5) > 1 THEN ZZ(5) = 1: REM "MO ACTIVITY
11160 ZZ(7) = (Zn(8,N) * Zm(21) / ZZ(5)) ** (1 / Zm(10)):Zm(8,N) = ZZ(5) * (Zm(7,N) ^ Zm(10)) /
11180 ZZ(8) = ZZ(5): Zn(9,N) = Zm(9,N) - ZZ(9): REM "CHEMISTRY
11200 RETURN

12000 REM "V N-1/N
12020 ZZ(3) = 2 * (N% - N):ZZ(1) = (ZZ(3) + 3) / (ZZ(3) + 1): REM "V N-1/N
12040 ZZ(2) = (ZZ(3) - 1) / (ZZ(3) + 1): IF ZZ(2) < 0 THEN ZZ(2) = 0: REM "V N-1/N
12080 IF ZZ(0) > .5 THEN 12200
12100 REM "SHORT TIME
12120 FOR M = 7 TO 8:Zm(M,N) = Zn(M,N) * (1 - ZZ(0)) + ZZ(1) * ZZ(0) * (3 * Zn(M,N) + Zn(M,N -
1)) / 4 + ZZ(2) * ZZ(0) * (3 * Zm(M,N) + Zn(M,N + 1)) / 8: NEXT M
12160 RETURN

12200 REM "LONG TIME
12220 FOR M = 7 TO 8:Zn(M,N) = ZZ(1) * (3 * Zn(M,N) + Zn(M,N - 1)) / 8 + ZZ(2) * (3 * Zn(M,N)
12260 RETURN

APPENDIX ?? DC Transmission Line Model