Corrosion cells and first estimates of crevice corrosion behavior
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**ABSTRACT**

Computational simulations using boundary element techniques are used to determine the spatial distribution of electrical current and potential in coplanar concentric corrosion cells. Conditions of unequal depths of electrolyte above the anode and cathode are considered as well as conditions of equal depths of electrolyte. The conditions of unequal electrolyte depths are a first approximation in determining the effects of the differing volumes of electrolyte above regions of localized corrosion, such as found in cracks and crevices. Localized corrosion such as crevice corrosion is a synergistic phenomenon involving electrolyte composition, material composition as well as geometric effects. This work addresses one aspect of geometric constraint on electrochemical response.

**INTRODUCTION**

Localized corrosion is distinguished from other forms of corrosion by the concentration of corrosion attack at a specific geometric location. This concentration of corrosion attack may be the result of anodic and cathodic regions being fixed in time, such as when pieces of two different materials are joined, or may be due to geometric intricacies which result in differences in ion...
concentrations in the surrounding electrolyte with time. Localized corrosion takes on many forms and includes such phenomenon as crevice corrosion, pitting, stress corrosion cracking and filiform corrosion beneath organic coatings. Localized corrosion is of great concern to the designer because it often goes unobserved until failure occurs.

Computational methods, both finite element and boundary element, have been applied with success to large scale corrosion systems [1]. Computational methods provide a means for determining the electrical current and potential at all points along the electrolyte-material interface. Electrical current can be directly related to material loss through Faraday’s Law [2]. Calculated values of electrical current or the associated electrical potential can be used to directly determine the spatial variation of corrosion attack. The higher the electrical current, the greater the corrosion damage at that location. The present work evaluates the use of boundary element methods to examine the mechanisms of localized corrosion.

Crevice corrosion can be divided for analysis purposes into three stages - initiation, steady growth of corrosion products, and repassivation in some materials which results in the inhabitation of corrosion. Initiation and repassivation have been modeled as primarily driven by either chemical changes occurring within the crevice or electrical potential change occurring within the crevice [3]. During a period in the growth stage of corrosion the process can be considered to occur in an environment which has reached steady state with respect to electrolyte composition. This is the stage of localized corrosion of interest in the current study.

In the present work, boundary element techniques are applied to a coplanar circular corrosion cell. Localized corrosion systems such as pitting and crevice corrosion under o-rings or washers have a coplanar circular cross section. The initial analysis compares the boundary element results with analytical and experimental results for a uniform depth of electrolyte covering both anode and cathode regions. The second phase of the analysis examines the variation in electrical current distribution caused by changes in the depth of electrolyte cover over the anode and...
cathode regions. The electrolyte depth over the anode is reduced to 1/10 and 1/30 of that over the cathode. The altered geometry results in a relatively large crevice for the first approximation of electrolyte coverage effects. While not a true crevice, which often have dimensions of the order of surface roughness, this geometry is representative of structural details. Effects of ion concentration variation or oxygen depletion which will effect the electrochemical response in actual crevices, are not included in this first approximation of crevice corrosion cell behavior. In this geometry, both electrolyte layers are between thin film and bulk electrolyte depth [4].

**McCafferty Corrosion Cell**

A mathematical model has been developed for the coplanar concentric corrosion cell shown in Figure 1 [5]. The concentric anode and cathode are submerged in a uniform depth of electrolyte. The analytical evaluation is based on the electrostatic potential defined by LaPlace's equation:

\[ \nabla^2 \Phi = 0 \]

which requires that the electrolyte to be electroneutral, to be without concentration gradients and to be without electron sources or sinks.

The anode and cathode material have unequal polarization response. The resulting polarization response for this relatively simple geometry is not a simple relationship. Addition of geometric complexities will lead to even more complex solution. The ability to utilize computational techniques will aid in the solution of the more geometrically complex problems.

The polarization responses used in the analytical derivation for the McCafferty cell are linear. While this limits the solution applicability there are corrosion systems for which linear polarization response is applicable. Linear polarization over an distinct extent of the current domain has been observed for specific combinations of materials and electrolytes [5]. Assumptions of linear polarization response is not inherently wrong but must be
carefully considered. The use of nonlinear polarization response, standard options in many computational methods, would remove this limitation.

**BOUNDARY ELEMENT ANALYSES**

A commercial boundary element code [6] is used to model a McCafferty cell of platinum and iron with dimensions as shown in Figure 2. Material polarization response is for quiescent conditions as defined in Reference 5. Two dimensional quadratic elements were used. Models consisted of 795 elements comprised of 1595 mesh points. The electrolyte is 0.05M NaCl open to the air with a conductivity of $5.5 \times 10^3$ Ohm$^{-1}$ cm$^{-1}$. All potential values are given in terms of Ag/AgCl electrode.

Analytical, experimental and computational results are shown in Table 1. Very good agreement is shown between analytical and computational as well as computational and experimental results.

**TABLE 1**

Summary of data for Pt/Fe couple, electrolyte depth = 3.0 cm.

<table>
<thead>
<tr>
<th></th>
<th>Center of Anode</th>
<th>Center of Cathode</th>
<th>Current</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analytical*</td>
<td>-0.565</td>
<td>-0.550</td>
<td>0.29mAmps</td>
</tr>
<tr>
<td>Experimental*</td>
<td>-0.584</td>
<td>-0.577</td>
<td>0.33mAmps</td>
</tr>
<tr>
<td>Computational</td>
<td>-0.584</td>
<td>-0.572</td>
<td>0.28mAmps</td>
</tr>
</tbody>
</table>

*McCafferty [5]

For electrolyte depths equal to or greater than the sum of anode and cathode widths, the electrolyte generally behaves as if it is infinitely deep [4]. As the depth of electrolyte decreases the concentration of corrosion attack at the anode-cathode interface increases. As the depth decreases approaching very thin film conditions the potential profile along the anode-cathode length
approaches an ideal step function [4]. The McCafferty cell model was analyzed with uniform electrolyte depths of 30.0 cm (bulk response), 3.0 cm, 0.3 cm and 0.1 cm. The potentials and total current values are given in Table 2. Potential profiles are shown in Figure 3.

### TABLE 2
Summary of data for Pt/Fe couple

<table>
<thead>
<tr>
<th>Electrolyte Depth</th>
<th>Potential:</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Anode Center</td>
<td>Cathode Center</td>
</tr>
<tr>
<td>0.1cm</td>
<td>-0.600</td>
<td>-0.532</td>
</tr>
<tr>
<td>0.3cm</td>
<td>-0.588</td>
<td>-0.562</td>
</tr>
<tr>
<td>3.0cm</td>
<td>-0.584</td>
<td>-0.572</td>
</tr>
<tr>
<td>30.0cm</td>
<td>-0.574</td>
<td>-0.560</td>
</tr>
</tbody>
</table>

In an initial modeling attempt at crevice corrosion the electrolyte depth was reduced over the anode. The depths of electrolyte considered were 3.0 cm over the cathode combined with either 0.3 or 0.1 cm over the anode. Results are shown in Table 3. The potential profile for a crevice of 0.1 and 3.0 cm depths is compared with uniform thickness results in Figure 4.

### TABLE 3
Summary of data for Pt/Fe couple

<table>
<thead>
<tr>
<th>Electrolyte Depth</th>
<th>Potential:</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Anode Center</td>
<td>Cathode Center</td>
</tr>
<tr>
<td>Anode 0.3cm</td>
<td>-0.588</td>
<td>-0.562</td>
</tr>
<tr>
<td>Cathode 3.0cm</td>
<td>-0.601</td>
<td>-0.541</td>
</tr>
</tbody>
</table>
SUMMARY

The work has validated the use of boundary element by comparison of analytical and experimental results for a McCafferty cell of platinum and iron. The effects of uniform changes in electrolyte depth over anode and cathode were consistent with previous work. Changes in electrolyte depth while maintaining a constant composition were found to have an effect on the electrochemical response of the coplanar corrosion cell studied. The effect, as represented by the potential profile, is not a linear combination of the responses of coplanar corrosion cells of equivalent equal depths. The variation in electrolyte depths examined (1/10 and 1/30 depth over anode to depth over cathode) while not representative of crack dimensions are representative of structural features. The current work does not include the complications of electrolyte ion concentration variations which can occur as true crevices and cracks become occluded regions over time. Future work would both reduce the depth of electrolyte coverage over the anode and incorporate effects of concentration gradients.

REFERENCES


**FIGURE 1** - Coplanar corrosion cell per McCafferty [5]

**FIGURE 2** - Platinum-Iron coplanar corrosion cell.
FIGURE 3 - Potential profiles, Platinum-Iron coplanar corrosion cell. Equal depths of electrolyte covering anode and cathode.

FIGURE 4 - Potential profiles, Platinum-Iron coplanar corrosion cell. Unequal depths of electrolyte covering anode and cathode.