

Interactions among Localized Corrosion Sites Investigated with Electrode Arrays

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Interactions among local pit sites were investigated using an array of 25 electrodes. The 5 x 5 array consisted of closely spaced, flush-mounted 316 stainless steel wires polarized in 0.05 M NaCl solution. Two types of interactions occurred when either single or rows of actively corroding pits existed while the remaining electrodes were initially passive. Inhibition of pitting on nearby electrodes occurred due to ohmic potential drop near active pre-existing pits. Enhancement of pitting was observed due to alterations in the local solution composition near just deactivated pits. The former effect was stronger than the latter, but the concentration effect could persist after pit deactivation.

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It has often been assumed that pitting events occur randomly and that there is no effect of one event upon another. However, when a pit begins to form and current flows, the local environment is altered.¹ Harb and Alkire demonstrated that the concentration gradients in solution are altered up to three pit diameters away from the pit.² Potential gradients in solution and the nearby oxide film are also altered,³⁻⁵ which can affect the likelihood of formation of new pits at nearby sites. Presumably, the time periods vary over which these three effects continue to persist after the first pit dies. Ohmic drop would change instantaneously whereas concentration fields and oxide film damage would persist for longer times. Thus, the occurrence of one event can have, at least for a finite length of time, some influence on the probability of occurrence of future events.

Recent experimental and modeling studies have shown a dependence of current spikes associated with metastable pitting events on prior events.⁶ Metastable pitting data at low (10^{-3} M) Cl^- solution concentrations approached a Poissonian, or random, distribution of interevent times while at higher concentrations (1 M) of Cl^- the metastable pitting events no longer occurred at random times; the events tended to couple together as bursts of events. Autocorrelation analyses of the current-time data supported this finding by demonstrating a stronger self-correlation of the current-time data record at higher concentrations. In the present study, we expand upon that temporal investigation by exploring interactions between pit sites through the use of electrode arrays that enable examination of the spatial component of interactions.

Experimental

Experiments were performed on arrays containing 25 electrodes arranged in a 5 x 5 configuration of 0.25 mm diam 316 stainless steel wires (nominally 16.5-20% Cr, <2% Mn, 8-14% Ni, 0.12% C, 2.0-3.5% Mo, and balance Fe). The wires were arranged lengthwise in a notch of a plexiglass rod that was filled with insulating epoxy, as shown in Fig. 1. Specially coated wires were used which had a thin (0.009 mm) polyester coating to help prevent crevice corrosion between wire sides and epoxy. The wires were placed approximately 0.09 mm apart.

The electrode array was prepared by grinding the cross sections to a 1200 grit finish followed by 1 μm alumina polish. The array was then rinsed with deionized water and placed in a 3000 ppm (0.05 M) sodium chloride solution (pH 6) along with a saturated calomel reference electrode and a platinum wire mesh counter electrode. Experiments were carried out at 47°C. The reaction was controlled using a potentiostat (EG&G Princeton Applied Research model 273 or Pine bipotentiostat model AFRDE 4). Each electrode in the array

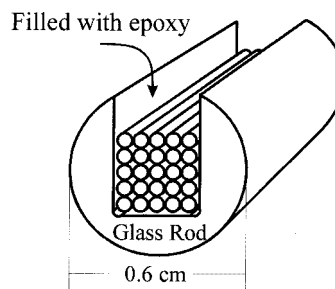


Figure 1. Schematic of the 5 x 5 electrode array configuration. Each of the electrode wires was positioned as close together as possible (0.09 mm spacing) within a notch of a glass rod, then covered with epoxy.

was linked to a zero resistance ammeter (ZRA). Data were collected at 20 Hz with a low pass filter (cutoff frequency of 10 Hz). For potentiodynamic experiments the current for each channel was recorded with the data acquisition system configured to a current range of 44 μA and a resolution of 21 nA. For the potentiostatic experiments, the range was 2.8 μA and the resolution was 1.35 nA in order to achieve a high resolution for the metastable pitting events.

Results

The potentiodynamic data were analyzed by examining the remotely sensed pitting potential (E_{pit}) values found when the anodic current exceeded 30 μA . Visual inspection confirmed pit formation at these current densities. Five types of potential sweep experiments were conducted on the 25 electrode array. Replicate scans indicate the cumulative probabilities of achieving various remotely sensed E_{pit} values for each of the five types of experiments as given in Fig. 2.

In the first experiments, all 25 electrodes were potentiodynamically scanned from 0 to 1.0 V vs. a saturated calomel electrode (SCE) simultaneously at a rate of 1 mV/s to establish baseline pitting potentials. Electrodes dissolved passively then exhibited an abrupt increase in current above 30 μA at some applied potential. The cumulative probability of measured [at the remote reference electrode (RE)] pitting potential from these experiments, as seen in Fig. 2, falls in the middle of the five curves as expected.

The next two types of experiments were designed to examine the solution concentration effect, in which no ohmic potential drop to the controlling RE was present. A potential of 1.0 V SCE was applied to the center electrode for 10 min and then turned off. When turned off, the pit bottom potential dropped to an open-circuit potential below the pitting repassivation potential which deactivates the pit. The other 24 electrodes were immediately scanned from 200 mV to 1.0 V SCE, before the concentrated solution could become diluted. A premise in these concentration-isolation experiments was that the potential change in the fluid was instantaneous when the voltage

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was no longer applied to the center electrode because the pit external current was instantly zero. However, the altered concentration field required a longer time period to become diluted in the unstirred cell. The result was a shift in the cumulative probability of stable pitting (*i.e.*, achieving 30 μA) to a higher value at each applied potential. The elevated local chloride concentration and acidity from the prior corrosion of the driven electrode has effectively lowered measured pitting potentials and, therefore, more electrodes pit at lower applied E values (as sensed at the remote RE).

This concentration effect was enhanced in the third experiment by pre-pitting an entire row of electrodes (see the inset in Fig. 2) for 10 min prior to applying a potential sweep to the remaining 20 electrodes. Figure 2 shows that the cumulative probability of achieving 30 μA was increased to even higher values, the highest values seen. Thus, the other 20 electrodes pitted more readily than in any of the other experiments when an entire row had just been corroded.

In the fourth potentiodynamic experiment, the central electrode was held at 1.0 V SCE, producing a current as large as 600 μA , while other 24 electrodes were simultaneously scanned from 0 to 1.0 V SCE at 1 mV/s. This allowed for the study of both the altered concentration field and the potential field. In Fig. 2, the cumulative probability of pitting was lower than when all 25 electrodes were swept individually (base case); the other 24 electrodes were less likely to pit. This indicates that when both the corrosion-inhibiting potential field effect (*e.g.*, ohmic potential drop) and the corrosion-enhancing concentration effect were both present, the potential field effect was stronger in raising the applied potential at which nearby electrodes would begin stable pitting.

In the last potentiodynamic experiment, an entire row of electrodes was simultaneously pitted at 1.0 V SCE while the remaining 20 electrodes were swept from 0 V to 1.0 V SCE. Once again, this enhanced the effects that were seen in the single electrode test. The five electrodes actively undergoing simultaneous localized corrosion caused the lowest cumulative probability curve for the other 20 electrodes (indicating the smallest probability of electrodes pitting at a given remotely sensed potential).

It was of interest to determine whether there was a distance component to these effects. Figure 3 shows the results from the experiment in which an entire row of electrodes was held at a higher potential using the bipotentiostat. A pronounced difference was present between the pitting behavior of the electrodes in the row closest to the actively corroding (1.0 V SCE) electrodes compared to those that were farthest away. The row of active pits emitting high current was row 0. Row 1 was closest to these active electrodes while row 4 was farthest away. The closest row was found to have only pitted during scans at higher remotely sensed, applied potentials than the ones that were farther away, indicating the extent of ohmic potential drop near row 0. Similar experimental results were found for the other types of experiments. However, the concentration-only experiments (with the actively corroding electrodes just turned off) yielded a smaller change in the cumulative probability of E_{pit} based on distance. Again, this indicates that the pit enhancing concentration effect is weaker than the inhibitive ohmic potential drop effect.

In addition to the potentiodynamic experiments, four types of potentiostatic experiments were conducted. Stable pitting induction times collected during potentiostatic experiments on the 25 electrode array were analyzed to determine what effect, if any, was seen due to the presence of concurrently driven electrode(s) or the prior-driven electrode(s) that underwent active pitting. The current emitted by a 1 V SCE driven electrode was typically between 100 and 600 μA resulting in a current density of 0.2 to 1.2 A/cm^2 , or an average of about 0.7 A/cm^2 . Induction times for the remainder of the electrodes in the array were defined to be the time at which their current exceeded 2.8 μA (their passive currents were often less than 0.02 μA or $4 \times 10^{-5} \text{A}/\text{cm}^2$). Figures 5 and 6 show schematics of the 5×5 electrode array at different elapsed times during potential hold

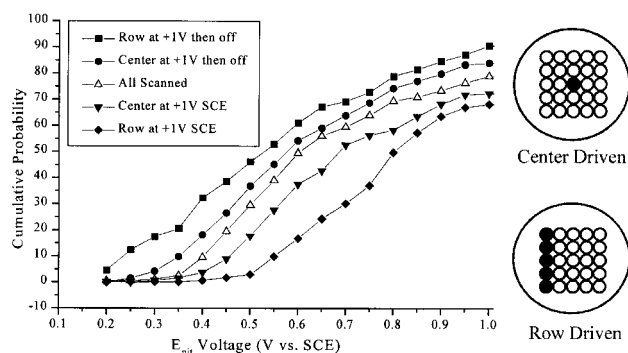


Figure 2. Remotely sensed pitting potentials from potential scans of 316 stainless steel in 0.05 M NaCl. Base case where all electrodes have been scanned together (middle curve) is compared to cases where either one or more electrodes undergoes active concurrent corrosion or prior corrosion. Each data point reflects the percent of active electrodes at that potential which is not equivalent to a single specimen run. Each curve was created using at least 144 specimens.

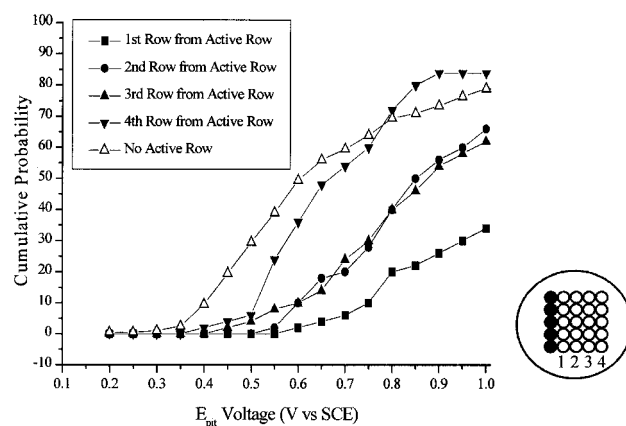


Figure 3. Active pitting of electrodes on row 0 is seen to effect the distribution of apparent pitting potentials for electrodes on other rows. These are also compared to the base case where the potential field is not altered by an active pitting electrode row. Each curve was created using at least 50 specimens.

experiments (which are described below). The electrodes shown in black were driven (either prior to or simultaneously during the data collection on the remaining electrodes); the electrodes in gray developed a stable pit by the time indicated and are actively emitting current. As time progressed, more stable pits were formed on the electrodes, as can be seen in all of the figures. Note that there will be an additional effect of these stable pits on subsequent pitting, but this secondary effect is much smaller than that of the higher potential electrode(s) under the conditions of these experiments because the current emitted is smaller; such secondary interactions will be considered in future work.

The base case (with no driven pitting electrodes) was established in the first potentiostatic experiments by using a single potentiostat to hold all 25 electrodes at the same potential, either 200, 250, or 300 mV SCE, while the current signal was collected at 20 Hz. When the locations of pitting sites on the array are examined, no apparent pattern can be seen in these experiments. In the next experiments, the concentration effect was isolated from the electric potential field effect by using a single potentiostat to drive the central electrode at 1.0 V for 10 min. This potential was then turned off while a constant potential was maintained on the remaining 24 electrodes. Potentials of 200, 250, and 300 mV SCE were applied for these concentration

experiments. Figure 4 shows the resulting pattern of pit locations from an applied potential of 300 mV. It is obvious that the closest electrodes pitted more readily, indicating the detrimental effect of a local concentration change.

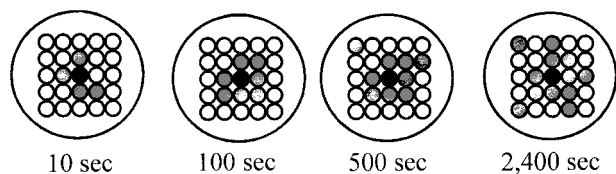


Figure 4. Sites of stable pit formation at various times during a concentration-effect potentiostatic experiment. The central electrode (black) was driven at 1 V SCE, stopped, then the other 24 were held at 300 mV SCE. Gray shading indicates active pits after a given time.

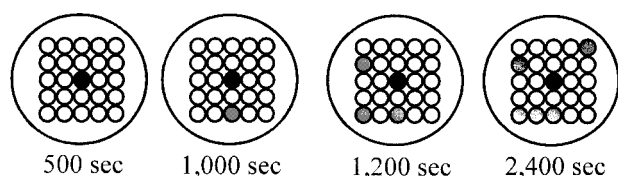


Figure 5. Sites of stable pit formation at various times during a bipotential potentiostatic experiment. The central (black) electrode was driven at 1 V SCE and the other 24 were held at 300 mV SCE. Gray shading indicates active pits after a given time.

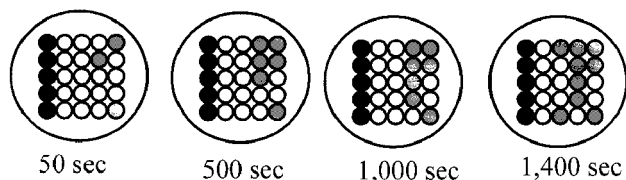


Figure 6. Sites of stable pit formation at various times during a bipotential potentiostatic experiment. One row of electrodes was driven at 1 V SCE (the black electrodes) and the other 20 were held at 500 mV SCE. Gray shading indicates active pits after a given time.

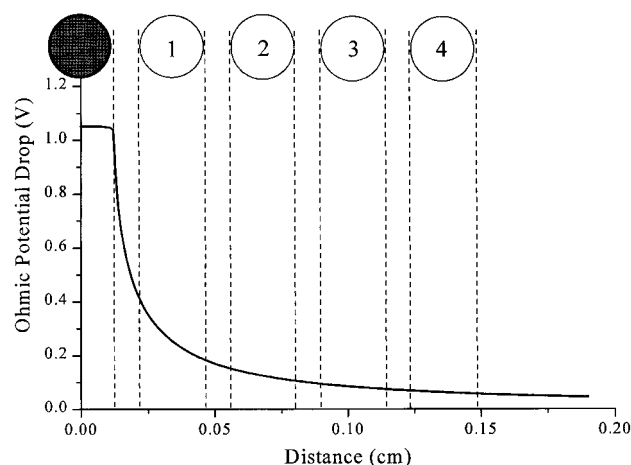


Figure 7. The ohmic potential field distribution in solution just above the electrode surface for a flush mounted circular electrode of 0.025 cm diam with 0.7 A/cm² current density using Newman's solution in Ref. 7. The active current emitting electrode is centered at the origin and the remainder of the surface is considered to be ideally passive (no current). The positions of the passive electrodes in the array are indicated.

Next, the simulated pit potentiostatic experiments were performed with the central electrode held at 1.0 V SCE while the remaining 24 electrodes were simultaneously held at constant potentials of either 100, 200, 300, 400, or 500 mV SCE in separate experiments. Here, stable pits tended to form more readily on the electrodes farthest away from the active central pit (Fig. 5). Another interesting effect can be seen when comparing Fig. 4 to Fig. 5; there are fewer electrodes with stable pits forming during the experiment reported in Fig. 5, further demonstrating that the potential field was dominant in its suppression of further stable pits.

Row experiments were similarly conducted by driving an entire row of electrodes at 1.0 V SCE while the remaining 20 electrodes were held at a second potential (200, 300, 400, and 500 mV). The row of actively pitting electrodes appeared to severely inhibit the formation of pits on the electrodes in the nearest row (Fig. 6). In fact, none of the five nearest electrodes ever underwent stable pitting in any of the experiments, demonstrating the repeatability of this result.

Discussion

It has been shown experimentally that an actively pitting corrosion site changes the pitting conditions for the other electrodes in the array. The potential field near an active site can change and such changes can be estimated. Newman's analytical solutions of the potential fields above a corroding disk were obtained from the solution of the Laplace equation;⁷ more complete simulations can be carried out. Figure 7 shows the calculated ohmic potential change as a function of distance along the surface near a flush-mounted electrode embedded in an insulator. In Newman's calculation, the remaining surface is considered to be an insulator.⁷ Here, the remaining surface is the passively dissolving 316 stainless steel. However, the passive current density can be ignored because it is five to six orders of magnitude below the current of the active pit. Effectively it is equal to the expectations for an insulator. The parameters used here correspond to the system used for the above experiments: an electrode 0.025 cm in diam in an electrolyte with a concentration of 0.05 M NaCl. A representative active pit current density of 0.7 A/cm² was chosen. Figure 7 shows a total of four neighboring electrodes for an array of 0.025 cm diam electrodes with 0.009 cm between electrodes (the same configuration as our array). The first nearest neighbor would be strongly affected by ohmic potential drop while the effect begins to diminish for the fourth nearest neighbor. As can be seen from Fig. 7, the ohmic potential drop within a radial distance of 0.025 cm from the active pit site (at 0 cm) can be as large as 400 mV and is still 200 mV at a distance of 0.05 cm. Thus, the true interfacial potential at these positions is 200-400 mV below the applied potential that is remotely sensed by the controlling RE [when all electrodes are passively dissolving and ohmic (IR) drop is negligible, the potential sensed by the RE is equal to the interfacial potential]. This theoretical potential field calculation helps to explain the basis for the deviation in pitting potentials and incubation times seen in the experimental results. As seen in Fig. 2 and 3, a 200-400 mV decrease in the true interfacial potential significantly affects the probability of pitting. The remotely sensed potential must be scanned to more positive potentials to induce pit stabilization when a nearby active electrode emits a high current.

An analogous argument can be constructed for the concentration field change. It is well known that pits grown at +1.0 V SCE exhibit kinetics that are mass-transport controlled with a supersaturated salt solution formed at the pit bottom (*i.e.*, approximately 5 M NiCl₂).⁸ As shown by Harb and Alkire for nickel, this leads to development of a concentration field outside the pit.² The radial concentration gradient can be expected to extend from a concentration near 5 M at the pit to the bulk solution concentration of 0.05 M NaCl within a distance of about 0.1 cm. Since the IR corrected mean pitting potentials of many materials decreases on the order of 100 mV with every order of magnitude increase in [Cl⁻],^{9,10} it is clear that the mean pitting potential could easily be decreased by approximately

200 mV due to the enhanced chloride concentration near a just deactivated pit site. A 200 mV decrease in median E_{pit} significantly increases the risk of pitting at any applied potential investigated. This effect is seen when an actively pitting electrode or row is turned off and the remaining electrodes are scanned.

The experiments discussed in this paper were all done under potentiodynamic or potentiostatic conditions. Similar experiments can (and will) be done under freely corroding conditions. Thus, the role of cathodic protection on pitting could be studied separately from ohmic shielding by using electrically coupled electrodes at their mixed potential. In this case, actively pitting electrodes would be coupled to many other electrodes that supply cathodic current. The actively pitting electrode would be selected for activation either mechanically or electrochemically or would be designed to be more susceptible by materials selection.

Conclusions

Both the concentration and potential field gradients in solution were found to affect the pitting potentials and induction times at nearby electrodes over the distances studied (less than 0.15 cm). These results agree with theoretical estimations of the distance over which the concentration and potential fields are altered. Ohmic potential drop on electrodes near active pits (driven electrodes) resulted in the raising of remotely sensed (measured) pitting potentials and increased pit induction times. Enhancement of pitting was

observed when the local solution composition was concentrated by prior pitting.

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