

Modeling the Cathodic region in Crevice Corrosion under a Thin Electrolyte Film Including Particulates

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The present state of understanding of localized corrosion of passive metals is based primarily upon behavior under fully immersed solutions. There has been limited analysis of localized corrosion in moist layers of dust, particulate and deposits. This work is part of a multi-university Corrosion Cooperative of the DOE-OCRWM Science and Technology Program established to enhance the understanding of corrosion processes and materials performance¹. The objective of this project is to develop models to simulate localized corrosion.

The present analysis focuses specifically on the *cathodic region* near a corroding crevice with the objective of characterizing the effects of the critical process parameters on the required current to sustain the crevice corrosion. Previous related analytical^{2,3} and numerical⁴ studies have focused on galvanic corrosion where the rates of the anodic and cathodic processes are comparable, analyzing mostly the effects of the electrode kinetics and the thickness of the electrolyte layer. A recent study⁵ considers the cathodic region for crevice corrosion. The work here determines two and three dimensional current and potential distributions over the cathode. The analyzed cathodic oxygen reduction region adjacent to the crevice is depicted in Fig. 1. This region is modeled for the presence of extremely thin ($G_f = 1 - 2000 \mu\text{m}$) electrolyte film. The electrolyte film may become discontinuous thus limiting the cathode behavior. Spatial variation of pH affecting the oxygen reduction kinetics, and oxygen diffusion limitations in the film are analyzed. Additionally, the presence of particulates is considered. The effects of macroscopic scale parameters, including the extent of the cathodic region ($L = 0.1 - 30 \text{ mm}$), the crevice gap ($G_a = 1 - 25 \mu\text{m}$) and the film conductivity ($0.012 - 1.2 \text{ mS/cm}$) on the current and potential distributions were modeled using an electrochemical CAD software⁶. The total current which a specific cathode can provide to sustain the crevice corrosion, was calculated for limiting potential conditions (to prevent anode passivation) set at the crevice opening. Sample results are shown in Fig. 2. A range of electrode kinetics is explored including data typical to oxygen reduction kinetics on stainless-steel⁷ and on nickel based alloys. The time-dependent effects of the varying pH due to oxygen reduction were also simulated (Fig. 3).

The effect of solid particulate in the electrolyte layer was analyzed on both the macroscopic and microscopic level. The particulate effects on the current distribution were analyzed on the macroscopic scale applying Bruggeman's equation for average, 'effective' properties, and on the microscopic scale, using detailed distributions around single particles and particle arrays.

Experiments performed on cells emulating the simulated cathode region to validate the modeling data are reported. Both current distribution and changes in solution pH over the cathode were measured.

References

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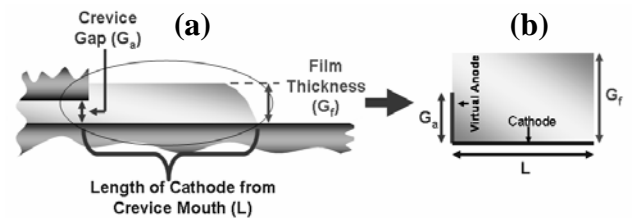


Fig. 1: Schematic diagram of (a) a Crevice with its adjacent cathodic region and (b) the decoupled cathodic region which is modeled.

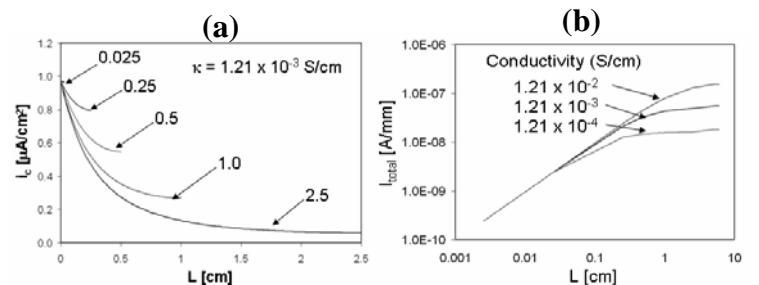


Fig. 2: Effect of varying the length of the cathode on (a) the current distribution, (b) the total current (per unit depth). The film and gap thickness were taken as $25 \mu\text{m}$. The potential at the crevice opening was set at -0.11 V . Modeled oxygen reduction kinetics⁷: $i_0 = 1 \times 10^{-9} \text{ A/cm}^2$; $\alpha_c = 0.59$.

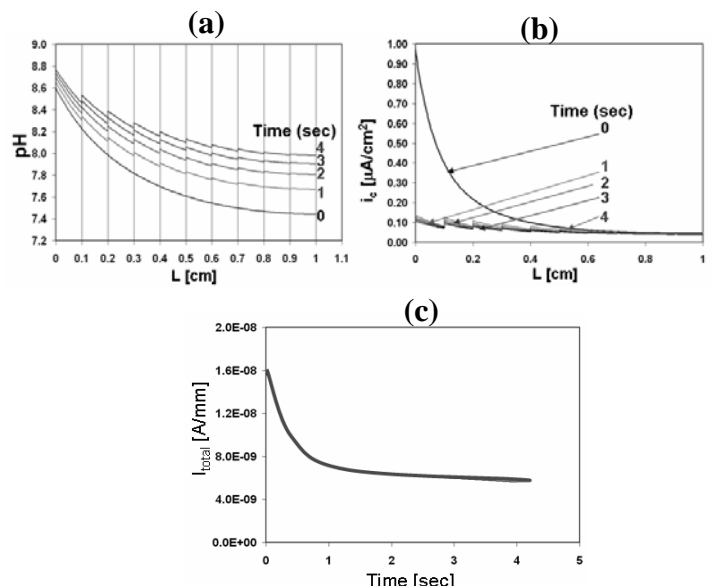


Fig. 3: Effect due to pH variations (a) time-dependent pH profile along the cathode, (b) time-dependent current distribution due to the pH effect on the reduction kinetics, and (c) total current as a function of time.