Considerations of the Role of the Cathodic Region in Localized Corrosion

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The overall goal of this study is to quantify the extent to which the rates of localized corrosion of a metallic surface can be supported by cathodic reactions within a thin electrolyte of limited lateral size. Such a situation is shown schematically for crevice corrosion in Figure 1. To accomplish this goal, the potential and current distributions on a wetted metal surface coupled to a localized corrosion site have been characterized, and the effects of various parameters, such as electrolyte layer thickness and composition, temperature, and the amount and nature of any particulate present. The figure of merit for the ability of an external cathode to support a localized corrosion site is the cathodic current capacity (I_{net}). Its value depends on the kinetic and physiochemical parameters of the interface and the electrolyte layer.

Although the primary focus of this work is on the role of the cathodic region in the localized corrosion of passive metals that are covered with thin layers of moisture or with layers of moist particulate, the general considerations are, however, also relevant to metals that are fully immersed in waters. For pitting or crevice corrosion to proceed, both anodic and cathodic processes are necessary. The metal loss and damage occurs at the anodic sites where metal atoms go into solution as soluble metal ions, and these oxidation reactions at the anode generate electrons. For the corrosion to proceed, the electrons must be consumed by reduction reactions at cathodic sites on the metal surface away from the anodes. For metals exposed to aqueous solutions in contact with air, the reduction of dissolved oxygen is the most prevalent reduction reaction to consume electrons. For natural conditions with no externally applied currents, the electrons generated at the anodes must be balanced by the electrons consumed at the cathode. Thus, the metal dissolution cannot proceed at a rate greater than the rate of the cathodic reactions.

In this paper, the factors that determine and control the capacity of the cathodic region to support anodic dissolution (maximum reduction current) are discussed. The information is drawn primarily from the results of computational analysis of the cathodic behavior associated with the crevice corrosion of a passive metal in thin layers of electrolyte [1, 2]. The computational analysis is continuing and experimental studies are also underway to validate the analytical results. Here, we discuss the controlling factors and identify scenarios where the propagation of localized corrosion is limited by the cathodic processes.

Metal surfaces that are not fully immersed in waters can be exposed to moisture in the form of thin layers of water and moist particulates that contain ionic species. These ionic species can originate from the water source (e.g., rain or dripping), dissolution of atmospheric gases, soluble species in any solids present, or from the deliquescence of hygroscopic salts. For passive metals in atmospheric corrosion, the localized corrosion processes of pitting and crevice corrosion are of the most interest. Pitting corrosion may initiate on a free surface if the potential is sufficiently oxidizing and the concentration of an aggressive species, e.g., chloride, is sufficiently high. Precipitates, metal oxide scales as well as geometrical crevices can generate occluded local geometries that trap electrolytes and thus promote crevice corrosion due to the development of acidic solutions by hydrolysis of dissolution products.

Corrosion cells under natural conditions, i.e., in the absence of an external applied current, can vary significantly from those in the most common laboratory experiments where electrochemical instruments (potentiostats) are used. The potentiostat ensures that sufficient cathodic current is provided to meet any anode demand; cathodic limitations are not observed. Furthermore, most experiments are conducted under fully immersed conditions with highly conductive solutions. This arrangement also favors conditions that avoid a regime of cathodic limitations on the corrosion propagation.

The important characteristics of the cathodic region associated with a thin layer localized corrosion cell include the water chemistry (i.e., ionic species and concentration), conductivity, geometry (thickness and area), temperature, and the electrochemical reduction reaction kinetics. Properties of the electrochemical reactions are reversible potential $E_{o,c}$, exchange current density $i_{o,c}$, Tafel slopes β_c, and limiting currents for mass transport control. Experimental kinetic data for the relevant electrochemical reactions as well as physiochemical data such as conductivity and diffusion coefficient of oxygen are needed to ground computations in reality.

Figure 2 shows the results of a set of calculations determining the cathode capacity as a function of cathode length and electrolyte layer thickness (1). For all electrolyte layer thicknesses, the cathode capacity saturates at long cathode length. This result implies that portions of cathode farther from the localized corrosion site than the length at which the I_{net} saturates (e.g., 10 cm for the 10 micron electrolyte layer) do not contribute significantly to maintaining an active localized corrosion site.

Another important consideration is the effect of particulates in the electrolyte layer. Particulates on the cathode surface can significantly reduce the cathode capacity (I_{total}) by (a) increasing the ohmic resistance to current in solution, (b) decreasing the electrode area, and (c) increasing the oxygen transport limitations. The particulate effects on the current distribution have been analyzed on the macroscopic scale by applying 'effective' properties to homogeneous electrolyte systems, and on the microscopic scale, using detailed distributions around single particles and particle arrays (2).

This work will produce a quantitative evaluation of conditions under which cathodic limitations control the stability and propagation rate of localized corrosion on corrosion resistant alloys under atmospheric conditions which lead to the formation of thin electrolyte layers.

References
1. F. Cui, F. J. Preseul-Moreno, R. G. Kelly, "Computational Modeling of the Stability of Crevice Corrosion of Wetted SS316L, Proceedings - Multiscale Simulations of Electrochemical Systems - Computational Aspects, Electrochemical Society, October, 2005.
2. Arun S. Agarwal, Uziel Landau, Xi Shan and Joe H. Payer, "Modeling the Cathodic Region in Crevice Corrosion under a Thin Electrolyte Film Including Particulates", Proceedings - Multiscale Simulations of Electrochemical Systems - Computational Aspects, Electrochemical Society, October, 2005.
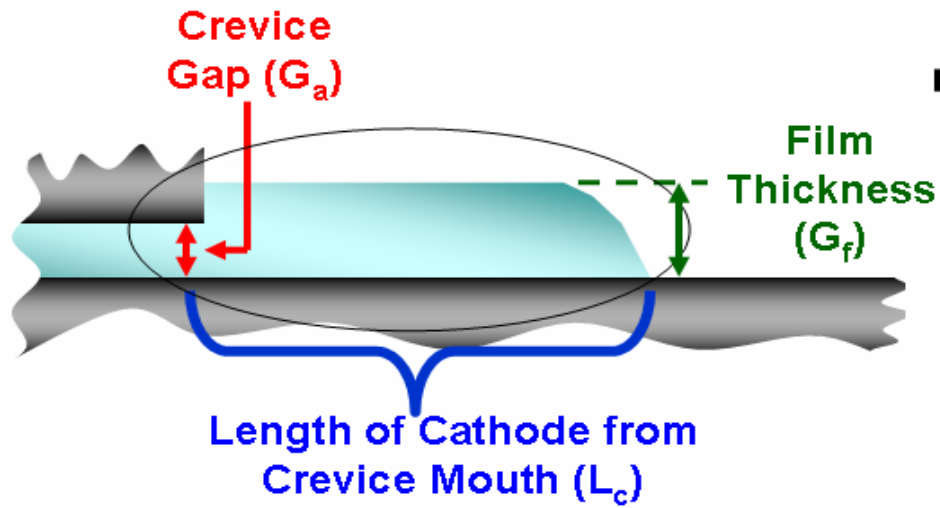
Figure 1-Schematic diagram of the cathodic region on a metal surface outside of an anodic crevice corrosion region. [2]
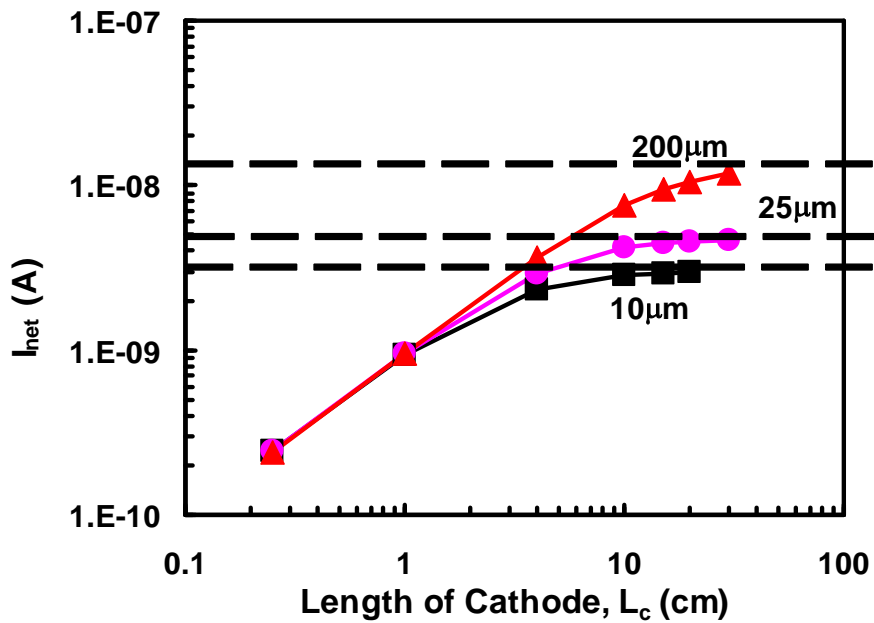

Figure 2: Cathode capacity (I_{net}) as a function of length of cathode for electrolyte layers of different thicknesses showing limiting behavior at long cathode lengths. Current normalized to 1-cm wide cathode. Assumed solution composition 1 M NaCl. [1]