Dissimilar engineering alloys in close proximity and in electrical contact are frequently encountered in the architecture of high-value structural assets in the transportation, aerospace, and marine industries. In service, these structures are often exposed to atmospheric environments, such as sea spray, that result in the formation of a thin electrolyte layer on the surface sufficient to allow the dissimilar alloys to form galvanic couples. Under atmospheric conditions, the electrolyte can also form via deliquescence of salt as either a droplet or a thin film on the alloy surface, leading to the establishment of a corrosion cell. The extent of galvanic corrosion on the anode that results depends on a number of environmental, physicochemical, and geometric variables, which include relative humidity, temperature, electrolyte conductivity, electrolyte film thickness, in addition to the electrochemical kinetics on the alloy surface.1–7 Different exposure conditions can be modeled by varying the thickness of the electrolyte film (also termed the water layer, WL), which in turn affects solution resistance as well as cathodic kinetics, thus having a direct effect on the total cathodic current available to support corrosion of the galvanic system. The effects of the electrolyte film thickness on corrosion rate were recognized initially by Tomashov;8 who qualitatively identified four regions of WL corresponding to different types of reaction control. As film thickness decreased, a transition from a plateau in corrosion rate when a constant diffusion layer was attained (conditions of full immersion) to cathodically controlled corrosion limited by diffusion of dissolved oxygen to the reaction surface (the corrosion rate increased as film thickness decreased under this condition, governed by Fickian mass transport behavior), before transitioning into reduced dissolution (termed anodic control) owing to lower corrosion product solubility in a smaller solution volume. Finally, an extreme region was reached which had the very low corrosion rate of dry chemical oxidation due to the lack of a continuous film. While useful conceptually, this outline lacked any quantitative, mechanistic description or validation of the relationship between electrochemical kinetics and the film thickness. Attempts to develop a rigorous study of this dependence have since been made by a number of researchers.9–22

Nishikata et al.,14,15 in their experimental studies on the oxygen reduction reaction (ORR) cathodic kinetics of both iron and platinum under an electrolyte thin film, observed a one-dimensional, Fickian relationship between the limiting current density for ORR and the film thickness over the range 20 μm to 1 mm. This study posited that a critical electrolyte film thickness exists in the vicinity of 1 mm. For films thicker than this critical value, the limiting current density would be constant, no longer obeying the inverse relationship of Fickian diffusion. This critical value thus defined the minimum thickness at which the boundary layer established by natural convection dictates mass transport. Experimental work by Stratmann et al.10–12 and Frankel et al.16 concurred regarding the presence of such a critical film thickness between 500 μm to 1 mm. However, the exact value for this critical electrolyte film thickness for natural convection is still unknown.

Recently there have been modeling studies18–24 that have focused on corrosion under an electrolyte thin film instead of full immersion. Dolgikh et al.24 performed a combined experimental and modeling study which incorporated the idea that convective flux could be expressed in terms of an analogous diffusion term.25 They proposed that the critical electrolyte film thickness for natural convection is on the order of 250 μm which is in line with the suggestion of Gileadi.26 It should be noted that the geometry used in that work consisted of a band electrode 1 mm × 10 mm, resulting in 2D diffusion which would inherently lead to higher currents and thus lower estimates for the natural convection layer termed the “micro-convection layer” by Dolgikh et al.24.

Galvanic corrosion under a thin film electrolyte is modulated by the WL thickness due to the impact of the WL on both diffusional kinetics at the cathode and ohmic drop in solution between the anode and cathode. Both of these aspects can affect the total amount of cathodic current available to drive dissolution at the anode. However, work to date has focused primarily on either one or the other of these two effects, which may often be synergistic. For instance, King et al.23 investigated the effect of electrolyte film thickness on the galvanic throwing power for a Mg-rich primer/AA2024-T351 couple, wherein an increase in electrolyte layer thickness was observed to lead to a smaller ohmic drop in solution and consequently a smaller potential difference between the anode and cathode sites. The effect of film thickness on mass transport-limited kinetics was not addressed in this study because in the potential range considered, as the cathodic kinetics accessible to the galvanic couple were in the activation-controlled region. Kelly and coworkers27,28 utilized a charge conservation-based argument to develop a model that permitted the numerical computation of the maximum current delivery capacity of a finite cathode under a thin electrolyte film as part of a model used to predict the maximum pit size that could form. The ohmic drop in solution delineated the potential gradient across the cathode, which in combination with kinetics information from experiment would then produce the
total current available to support corrosion on the coupled anode (i.e., the pit). The dependence of the current on the electrolyte film as a consequence of changes in relative humidity, loading density, and solution concentration was discussed. The experimental kinetics data used in this study were measured in full-immersion experiments and the value of the limiting current density in the simulations was modified assuming that the diffusion layer thickness was equal to the WL (all of which were below 1 mm). No studies have investigated the total cathodic current that a surface can supply over the range of WL spanning from thin films to full immersion.

The rotating disk electrode (RDE) technique provides a means to investigate the effects of WL thickness on the electrochemical kinetics under thin electrolytes. It utilizes hydrodynamic forces to create a constant diffusional boundary layer near the electrode surface. Thus, the rotation rate can be used to define a diffusional boundary layer thickness to represent the effect of the WL thickness on the diffusion of oxygen. This quantitative control of the diffusional boundary layer avoids some of the difficulties inherent in making electrochemical measurements in thin electrolyte layers.14,29 Panali et al.21 used electrochemical kinetics of both AA2024 and CFRP generated with RDE as boundary conditions in their modeling of galvanic corrosion between AA2024 and CFRP under a thin layer of electrolyte with varying thickness. In the present study, the RDE was utilized to achieve two goals: RDE testing on Pt was used to determine the critical water layer thickness beyond which natural convection controls the diffusional boundary layer; RDE testing of SS 316L at different rotation speeds was used to determine the effects of both water layer thickness and oxide film on cathodic limiting current density.

The galvanic couple between stainless steel (SS) Type 316L cathode and the aluminum alloy (AA) 7050-T7451 anode (hereafter referred to as AA/SS) formed the central focus of this study due to its widespread occurrence in aerospace repairs. This paper quantitatively determines and mechanistically interprets the effects of electrolyte film thickness on the total cathodic current available to support galvanic corrosion. The results of this study identify the exposure conditions under which the total cathodic current can be the controlling factor in the extent and distribution of dissolution on the anode.

### Experimental

**Sample preparation.**—The cathode sample used in the study was a rotating disk electrode (RDE) constructed from a cylinder of Type 316L stainless steel (McMaster-Carr Supply Company, Elmhurst, IL) of diameter 0.5 inches (1.27 cm) (embedded in a PTFE holder with an internal electrical contact) which resulted in an area of 1.27 cm² of diameter 0.5 inches (1.27 cm) (embedded in a PTFE holder with SiC paper). After grinding, the cathode surface was examined with an optical microscope to ensure that it was flush with the PTFE holder. The electrode surfaces were finally rinsed thoroughly with acetone and then with deionized water before use in the experiment.

**Electrochemical kinetics.**—Cathodic kinetics were determined in a three-electrode electrochemical cell with the stainless steel or platinum RDE as the working electrode actuated by a Pine Instruments ASR rotator (Pine Research Instrumentation, Inc., Durham, NC) with the electrode facing downward, saturated calomel reference electrode (SCE) and a platinum-niobium mesh as the counter electrode. The experiments were performed at a scan rate of 1 mV/s with the RDE at various rotation speeds ranging from 0 to 2000 rpm. Following 15 minutes of open circuit potential (OCP) measurement, the potential scan started 0.01 V above OCP, and ended at −1.6 V_SCE for Pt and −1.2 V_SCE for 316L. The current at a reference potential of −0.75 V_SCE was used to assess the relationship between cathodic limiting current density due to ORR and electrolyte layer thickness (δ) on each of Pt, and a reference potential of −0.85 V_SCE was used for the 316L polarization curves.

Electrochemical kinetics of AA7050 were measured by recording cyclic potentiodynamic polarization data of the coupons as working electrodes with a saturated calomel reference electrode (SCE) and a platinum-niobium mesh counter electrode. The experiments were performed in quiescent solution after 1 hour under OCP conditions. The potential was scanned at a rate of 1 mV/s from −0.05 V below OCP in the electropositive direction until a vertex current density of 1 mA/cm² was reached, at which point the scan was reversed until a final potential −1.55 V_SCE was reached.

All measurements were recorded in unbuffered 0.6 M NaCl. All experiments were performed on a Bio-Logic SP-200 (Bio-Logic SAS, Clai, France) potentiostat running EC-Lab (Version 11.01) software. The kinetics for the AA7050 were characterized quantitatively for the model via the Tafel fitting module of the anodic slope using the EC-lab software. The slope of the fitted curves was 23 mV/decade. Although active localized corrosion precludes any mechanistic interpretation of the slope, for determination of the current and potential distributions, such mechanistic information is not required. All that is required is the empirical relationship between potential and current density.

**Finite element method (FEM) modeling.**—The modeling framework is based on Laplace’s Equation,30,31 and the mathematical development of the modeling framework used has been described elsewhere.32,33 COMSOL Multiphysics v5.3 (COMSOL, Inc., Burlington, MA) software was used for two types of modeling work in this study. In this first type, the potential and current distributions along a 316L cathode coupled galvanically with AA7050-T7451 were modeled using a simplified two-dimensional geometry which represented the cross-section of the couple under a layer of electrolyte, as depicted in Figure 1. The anode-to-cathode area ratio of the system was varied by changing the length of the cathode with the anode length kept constant. The width of both electrodes was considered identical.

### Table I. Composition of the SS316L disk used (all values in weight percent).

|   | C  | Mn | P  | S  | Si | Cr | Ni | Mo | N  | Cu | Fe |
|---|----|----|----|----|----|----|----|----|----|----|----|
|   | 0.019 | 1.750 | 0.039 | 0.028 | 0.460 | 17.03 | 10.160 | 2.050 | 0.071 | 0.440 | Balance |

### Table II. Composition of the AA7050-T7451 used (all values in weight percent).

|   | Si | Fe | Cu | Mn | Mg | Cr | Zn | Ti | Zr | Al |
|---|----|----|----|----|----|----|----|----|----|----|
|   | 0.12 | 0.15 | 2.6 | 0.1 | 2.6 | 0.04 | 6.7 | 0.06 | 0.15 | Balance |

![Figure 1. Schematic configuration of the interaction between thin film electrolyte and galvanic couple (316L cathode with AA7050 anode in this study). Width of anode/cathode is normal to x-y plane.](image)
obviating the necessity for a three-dimensional model. For the major modeling study in which cathodic current availability was the focus, the anode length was fixed at 0.01 m, and the range of cathode lengths considered in this study varied from 0.01 m to 0.4 m, corresponding to an area ratio of 1:1 to 1:40, respectively. The thickness of the WL was varied across four orders of magnitude from 13.8 μm to 5 cm in order to provide a sufficiently wide range to capture exposure conditions representative of thin film and full immersion at either limit. The second type of modeling was carried out to investigate the effect of area ratio of anode to cathode, in which cathode length was fixed at 0.1 m with constant WL = 1 mm on the surface, and the area ratio of anode to cathode varied from 0.1 to 10. Simulations using the model geometry were run to convergence such that differences in calculations from consecutive iterations were less than the error tolerance limit of 0.1%.

The model results shown here are based on the use of the Laplace equation as the governing equation rather than implementing the full Nernst-Planck equation with consideration of ion-ion interactions. The latter is extraordinarily computationally expensive, and for the goals of this work, unnecessary. The Laplace approach provided a straightforward framework to calculate the spatial distribution of electrochemical variables on the cathode surface, relying instead on the knowledge of the physicochemical characteristics of the electrolyte such as the conductivity estimated from thermodynamic solution modeling. The value used for solution conductivity (κ) throughout this study was that of 0.6 M NaCl, 5.5 S/m. Boundary conditions (B.C.) were anodic kinetics of AA7050 (anodic B.C.) and cathodic kinetics of SS 316L (cathodic B.C.). All the calculations assumed steady state.

The absolute value of the total cathodic current per unit width (iCW) from a surface surrounding a finite anode under thin film conditions is dependent on the WL thickness, solution conductivity (κ), cathodic and anodic kinetics, and length of cathode (Lc). WL thickness and κ affect the ohmic resistance of the electrolyte per unit length of cathode, WL thickness and κ affect the current-potential behavior of the galvanic couple, and Lc fixes the maximum cathode length available for current supply. The WL thickness is a function of both loading density (LD = amount of salt deposited per unit area), and the relative humidity (RH). The calculations of cathodic current availability were performed for electrolyte properties corresponding to 0.6 M NaCl, which would be in equilibrium with a RH of 98% at 25°C as representative of atmospheric exposure conditions. Different WL thicknesses modeled in the study therefore correspond to different amounts of NaCl deposited on the metal surface. Furthermore, a constant RH values fixes the equilibrium concentration of salt thus decoupling κ from its dependence on varying WL thickness.

Results

The total cathodic current available to support galvanic corrosion across different cathode lengths under varying WL thicknesses was computed from the solution of the Laplace equation for the model geometry with the boundary conditions described previously. The experimental RDE cathodic kinetics data were analyzed to extract the value of the critical boundary layer thickness due to natural convection as well as identify any effects on the diffusion limited current density due to the presence of a native oxide film. In order to evaluate the effects of both mass transport-limited kinetics as well as the ohmic resistance in solution on the total current delivery capacity of the finite cathode, the simulated data were assessed in terms of the total cathodic current output versus the electrolyte film thickness for a range of cathode lengths.

**Determination of critical electrolyte layer thickness for natural convection.**—The RDE technique provides an experimental methodology to study the effect of varying the thickness of the diffusional boundary layer on kinetics. The Levich Equation quantitatively describes the convective motion at a RDE, utilizing hydrodynamic forces to control the boundary layer thickness, which is related to the angular velocity of rotation as shown in Equation 1:

$$i_{lim} = \frac{nFD_{O_2}(C_{O_2,\text{bulk}} - C_{O_2,\text{electrode\_surface}})}{\delta} \left(\frac{2\pi}{60}r\sigma\right)^{1/2}$$

where δ is the thickness of hydrodynamic boundary layer or diffusional layer, D is the diffusivity of dissolved oxygen at 25°C (D = 9.2E-7 m²/s, calculated by OLI Analyzer Studio 9.2), ν is the kinematic viscosity of 0.6M NaCl solution (ν = 9.2 E-7 m²/s, calculated by OLI Analyzer Studio 9.2), and rpm is the rotation speed of the RDE. δ can be obtained for corresponding rotation speed by using Equation 1 (e.g., 0, 10, 50, 200, 720, and 2000 rpm represent full immersion, and δ equal to 200 μm, 89 μm, 44.5 μm, 23.5 μm, and 13.8 μm, respectively). Figure 2 shows cathodic polarization curves of Pt RDE in 0.6 M NaCl as a function of rotation speed. According to the expression of the steady state, one-dimensional diffusion limited current density, the limiting current density is inversely proportional to δ. However, the diffusional layer thickness cannot continue to increase without bound, because at some thickness, natural convection will cause mixing and thus terminate the concentration gradient. Otherwise, there would be zero current at steady state in full immersion because δ would go to infinity if it were not bounded.

**Electrochemical kinetics of SS 316L and AA7050-T7451.**—Polarization curves of SS 316L using the RDE are displayed as a function of rotation speed from 0 to 2000 rpm in Figure 4. The cathodic limiting current density on 316L increased with increasing rotation speed, showing the same tendency as the Pt RDE data. Figure 5 compares the Levich plots for the Pt (iₜₘᵦᵣ = 0.75 V SCE) and 316L (iₜᵦᵣ = −0.85 V SCE) data. For δ thicker than 36.4 μm, the limiting current densities for 316L were almost identical with those for Pt. For thinner δ, there was discrepancy between limiting current densities for Pt and 316L,
Figure 3. (a) Limiting current density ($i_{lim}$) at $-0.75 \text{ V}_{\text{SCE}}$ vs $1/\delta$; (b) Zoom-in of thick WL regime to exhibit critical natural convection electrolyte layer thickness ($\delta_{nc}$). Blue dash line represents the value for cathodic limiting current density of Pt in full immersion condition.

A cyclic potentiodynamic polarization (CPP) curves of AA7050 is shown in Figure 6a. The reverse scan portion of the AA7050 curve (Figure 6b) was selected for the modeling study because localized corrosion of AA7050 was already established in this part, with the Tafel fit to the anodic branch of AA7050 shown in the same figure. AA7050 had fairly flat anodic kinetics with the anodic pseudo-Tafel slope of 23 mV/decade, indicating the low polarizability of active localized corrosion.

Effect of area ratio of anode to cathode on total cathodic current.—The majority of the modeling results for the galvanic couple between AA7050 and SS316L used a fixed length of the anode (AA). However, it is of importance to demonstrate the application of this modeling study is not applicable only to the length of anode used here (i.e., 0.01 m), but rather is applicable as long as the anodic materials has electrochemical kinetics with limited polarizability and the galvanic coupling potential for a 1:1 cathode: anode ratio is located in the region of diffusion controlled cathodic kinetics of the cathode. Under these conditions, the variation in area ratio has a negligible effect on total cathodic current per width. An example for a WL of 1 mm is shown in Figure 7, in which a fixed length of cathode (SS) equal to 0.01 m was coupled with different lengths of anode (AA). It is clearly seen that total cathodic current per unit width was invariant to the change in the length of anode over an area ratio range of at least 0.1 to 10. Although varying the exposure area of anode changed the potential at the SS/AA interface slightly, it was still located in the diffusion-controlled kinetics region of 316L, so the current was almost a constant in this scenario due to the fixed length (surface area) of the 316L (cathode). The almost non-polarizable electrochemical kinetics of AA7050 led only a subtle change of the galvanic couple potential when varying the area ratio. As a result of these two effects, the total cathodic current per length of SS316L was a constant regardless of the length of the coupled AA7050.

$IC/W$ on SS 316L coupled with AA7050 versus WL as a function of LC.—In this section, results from studies of a galvanic couple between AA7050 and SS316L with fixed length of the anode (AA). However, it is of importance to demonstrate the application of this modeling study is not applicable only to the length of anode used here (i.e., 0.01 m) and 316L with length ranging from 0.01 to 0.4 m are described. In addition to the experimentally determined cathodic kinetics, simulated cathodic kinetics with an equivalent WL of 400 μm were created, as the minimum rotation speed available experimentally was 10 rpm, which implies that the maximum equivalent was 200 μm. The boundary conditions are shown in Figure 8.

The total cathodic currents per width ($IC/W$) for a 316L cathode versus WL as a function of the length of cathode ($LC$) are plotted in Figure 9. The linear scale of Figure 9a shows that the $IC/W$ became a
constant after a critical WL for each LC, and this constant total current increased with LC. A semi-log scale plot allows better inspection of the IC/W in the thin electrolyte layer (<1 mm) region, shown in Figure 9b. For short LC (< 0.0925 m), the IC/W initially increased with WL, then decreased to an intermediate minimum at δ(nc) = 800 μm before reaching a plateau. For a cathode length of 0.0925 m, IC/W grew before reaching a first plateau with WL from 400 μm to 800 μm, and then again increased with WL until reaching a second plateau. For cathode lengths larger than 0.0925 m, the total IC/W did not have an intermediate minimum, instead it increased with increasing WL until reaching a plateau albeit with an inflection point at 800 μm. Figure 9c shows that for sufficiently thick WL (0.05 m), there was a linear relationship between IC/W and LC, the criterion for considering a galvanic couple to be under full immersion conditions. The IC/W over a range of WL smaller than 1 mm for four cases in which cathode length is equal to 0.01, 0.05, 0.0925, and 0.1 m is displayed in Figure 10, showing the existence of this intermediate minimum for LC less than 0.0925 m.

Discussion

This work presents the results of a finite-element based modeling approach to understand the effects of electrolyte layer thickness (WL) on galvanic corrosion between AA7050-T7451 and SS 316L with different area ratios in thin film electrolyte conditions, as might be expected during atmospheric exposure of many structures. The critical question of when an electrolyte layer can be treated as a thin film, a thick film and full immersion is addressed. The first section describes the experimental determination of the thickness of the natural convection layer, δ(nc), which defines the WL thickness above which the diffusion-limited current density becomes independent of WL thickness. It can also be considered the WL thickness below which true thin film electrolyte conditions occur. The second section describes the dependence of the total cathodic current from a surface exposed to an electrolyte film available to drive galvanic corrosion. The dependences of this total current on WL thickness and cathode length are quantified and rationalized. The effects of WL thickness can be viewed as a competition between the ohmic resistance of the electrolyte and diffusion-controlled cathodic kinetics of the cathode as will be discussed in detailing in the following section. The results as a function of cathode length can be parsed into two categories according which parameter controls the available cathodic current capacity. Both modeling and experiment data in the literature are also compared to validate our simulated results. The logarithmic relationship between the WL thickness and the total cathode current is shown to be independent of cathode length under thin film conditions. There also exists an ohmic-resistance affected thin
film condition above which true full immersions are realized in that the total cathode current scales linearly with the size of the cathode. Finally, the implications of the work as well as its limitations are discussed.

**Determination of the thickness of the natural convection layer.**—Natural (or free) convection is the spontaneous fluid flow created by density gradients. In the present case, this flow prevents the oxygen concentration gradient from extending to large distances away from the electrode. The most obvious manifestation of the presence of a natural convection layer is the presence of a non-zero diffusion-limited current density at steady state under quiescent conditions, as illustrated in Figures 2 and 4 for the 0 rpm case of ORR on Pt and 316L, respectively. In the absence of natural convection, the diffusion boundary layer would continuously increase with time, lowering the diffusion-limited current density continuously as well. Instead, a well-defined, diffusion-limited current for oxygen reduction is found of approximately 22 μA/cm². Either through the use of Equation 2, or the construction of the intersection of the lines in Figure 3, a natural convection boundary layer of approximately 800 μm was observed for the system studied here. Although natural convection in electrochemical systems has been discussed in texts, there has been a limited amount of experimental work aimed at determining the actual thickness of this layer. Wragg et al. did study free convection under stagnant conditions, producing correlations between dimensionless parameters involving the diffusivity, density difference between the bulk and the surface, the viscosity, and a characteristic dimension of the electrode. Fenech and Tobias did related work. In both cases, a knowledge of the density difference of the solution at the interface versus the bulk is required to determine the dimension of the natural convection layer. In the case of oxygen reduction, that information is not available. Nonetheless, the literature cites values of δnc from 250 μm to 1 mm. Tomashov estimated that thin film conditions could be considered to apply for WL < 1 mm. Amatore et al. described a micro-convection approach in which a diffusion-like term was used to account for natural convection. They estimated a δnc of 230 μm, which Dolgikh et al. also used in their extension of this approach from consideration of a single species to multi-ion environments. This value is also similar to that stated in Gileadi’s text. The present work describes both a rigorous experimental method for measurement of δnc and data demonstrating its use. It should be noted that different systems (i.e., electrolytes, temperatures, diffusing species, geometries) may have other values of the natural convection layer, but the method used in this work provides a means to determine the value unambiguously.

**Different regimes of dependence of cathodic current on film thickness are clearly distinguishable.**—Based on LC, distinct regimes arise that delineate the dependence of cathode current on film thickness. The potential along the cathode rose from that at the AA/SS

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**Figure 9.** (a) IC/W vs. WL as a function of cathode length (LC) in linear scale; (b) IC/W vs. WL as a function of LC in semi-logarithm scale; (c) IC/W vs. LC as a function of WL.
interface toward the open circuit potential of the cathode (SS). The extent of potential rise and its distribution is determined by the ohmic drop in solution along the cathode. This ohmic drop is determined by the $WL$ thickness, the current/potential relationship and the cathode length. The net effects of these variables is the existence of four regimes of behavior for $WL$, with the particulars of the regimes depending on the cathode length.

$L_C < 0.0925$ m.—In the small cathode-to-anode area ratio region, the total cathodic current available exhibited four distinct $WL$ thickness regimes. This behavior is illustrated using the results for the 0.05 m long cathode (Figure 11).

Regime 1: $WL \geq 4$ mm.—For the large $WL$ thicknesses in this regime, the couple was essentially under full immersion conditions, and the ohmic drop across the entire cathode was negligible. Thus, the two electrodes were not polarized appreciably from the coupling potential predicted from Mixed Potential Theory ignoring ohmic drop, but taking into account the cathode-to-anode area ratio. Consequently, the cathodic current density at all points is equal to the coupling current density (for the AA/SS couple, this is the mass transport-limited cathodic current density when $WL = 800 \mu m$) and $I_C$ is simply $i_{\lim} \cdot L_C$. As shown in Figure 9c, the total cathode current scales linearly with $L_C$. In this regime, the system behaves as if it is fully immersed in the electrolyte.

Regime 2: $800 \mu m \leq WL < \delta_{nc}$.—The role of the ohmic drop in this second regime was small, but not completely negligible, causing only minor polarization from the coupling potential. Moreover, polarization of the cathode away from the coupling potential resulted in a current density still in the mass transfer-limited region shown in Fig. 11b. Therefore, the $I_C/W$ available was only marginally smaller than that available under very thick $WL$ conditions (Regime 1). Kinetics data generated in quiescent full immersion conditions informed the calculation of the potential distribution and the cathodic current density at each point on the cathode. The diffusion distance controlling the cathodic kinetics in this regime was the hydrodynamic boundary layer associated with natural convection ($\delta_{nc}$). The value of $\delta_{nc}$ will determine at what $WL$ thickness the transition occurs, but will not qualitatively affect the existence of such behavior. It should be noted that the more noble portion of the potential range associated with mass transfer limitation was, in fact, mixed activation/diffusion control, so the current density was slightly lower than the limiting current density, especially for longer cathodes. A decrease in total cathodic current can be resulted if the potential range associated with mass transport control is narrow, and consequently even a low ohmic drop can result in the sufficiently distant points on the cathode displaying kinetics associated with the mixed activation/diffusion-limited region.

Regime 3: $400 \mu m \leq WL < \delta_{nc}$.—In Regime 3, the diffusion distance controlling the cathodic kinetics was the water layer thickness ($WL$) itself. Calculations of the cathodic current density in this regime used kinetic information obtained from RDE studies in which decreasing $WL$ thickness was simulated by the increasing the rotation speed of the RDE to reduce the diffusional boundary layer in a calculable manner. Although the effect of ohmic resistance was still significant, it did not become the dominant factor controlling the relationship between $I_C/W$ and $WL$ as long as the percentage of the cathode length under mass-transfer (M-T) limited kinetics was above 50%, as illustrated in Figure 11b. As a result, the total cathodic current showed a sharp rise with decreasing $WL$ thickness because of the inverse relationship between the cathodic limiting current density and the $WL$ thickness.

Figure 10. $I_C/W$ over a range of $WL \leq 1$ mm for $L_C = 0.01$ m; (b) 0.05 m; (c) 0.0925 m; (d) 0.1 m.
Regime 4: WL < 400 μm.—At sufficiently thin WL thicknesses, the ohmic drop was substantial, with less than 10% of length of cathode within the M-T limited kinetics portion of the polarization in this regime (see Figure 11b). The vast majority of the cathode experienced potentials in the mixed or activation region of the polarization curve. A precipitous drop in the total cathodic current occurred at smaller potentials in the mixed or activation region of the polarization curve. If the WL was sufficiently small, the ohmic drop would be so large such that every point on the cathode would be at its OCP and there would be no net current to the anode. Under the conditions studied here, even a 13.8 μm WL allowed some interaction between the cathode and anode, as demonstrated by a non-zero value of IC/W.

To better understand the competitive nature of relationship between ohmic drop and M-T limited kinetics on IC/W in thin electrolytes, Figure 12 compares the result in Figure 11a with IC/W vs. WL affected by either only ohmic drop or only M-T limited kinetics. To do so, the ability of computational studies to isolate individual parameters was exploited by performing one set of calculations in which the M-T kinetics were made very rapid, allowing the effects of ohmic drop (and IC/W) alone to be studied, and performing another set of calculations in which the ohmic drop was maintained at a low level, allowing the effects of IC/W on M-T (and IC/W) alone to be studied. The circular symbols are the results for ohmic drop control, whereas the triangles are the results for the M-T limited kinetics control. The line with the circular symbols assumed that the cathodic kinetics for WL = 13.8 μm applied to the calculation of IC/W for all WL cases, and thus changing the thickness of electrolyte layer only varied the amount of ohmic drop. As for the line with triangle symbols, it was assumed that the WL during the simulation was equal to 800 μm to fix the ohmic resistance, and the M-T limited kinetics was varied to test the effects of the diffusion layer alone.

As shown in Figure 12, as the WL thickness increased, the ohmic drop decreased linearly, and thus the total cathodic current increased linearly. Conversely, the M-T controlled current decreased with increasing WL thickness as the increasing boundary layer increased the diffusion distance until the natural convection WL thickness was achieved. For WL thickness larger than δnc, the current did not change as the current density was limited by δnc.

The behavior of the combined system (illustrated by the squares) can be understood by noting that the ohmic and M-T processes occur in series. At low WL thickness, the current was controlled by the ohmic drop; the M-T limited kinetics at these WL thicknesses were very high and would thus allow much larger currents than those allowed by the ohmic drop limitation. At large WL thicknesses, the current was controlled by the M-T kinetics. In the intermediate region, both processes were important and their resistances effectively added, suppressing the current to values below either limiting behavior.

As the length of the cathode increased, the total current in Regimes 1 and 2 increased due to the larger area. The ohmically-controlled Regime 4 was unchanged with increasing cathode length as for these small WL, only the small portion of the cathode nearest the anode/cathode interface contributed current. Regime 3, in which the transition from ohmic to M-T control occurred, also shrank until it disappeared as the length increased to the critical value = 0.0925 m.

Critical LC = 0.0925 m.—The results for LC of 0.0925 m also show 4 different regimes in Figure 13 like what are shown in Figure 11 for the shorter cathodes. The dominant factors controlling the patterns in Regime 1’ (WL ≥ 8 mm) and Regime 2’ (δnc ≤ WL < 8 mm) were the same as Regime 1 and 2 for smaller cathode scenario in Figure 11, respectively. However, there was difference between Regime 3’ (Figure 13) and Regime 3 (Figure 11) within the same range of WL (400 μm ≤ WL < δnc). For Regime 3’, although the M-T limited cathodic kinetics at a WL thickness of 400 μm was twice as large as at a WL thickness of 800 μm, these faster cathodic kinetics covered only about 20% of the length of cathode for WL = 400 μm compared to 60% of the length covered by smaller kinetics for WL = 800 μm. Thus, the effect of the larger ohmic resistance of the smaller WL (400 μm)
nullified the effects of enhanced M-T limited cathodic kinetics at the same WL. As a result, $I_c/W$ at $WL = 400 \mu m$ was identical to $WL = 800 \mu m$ in Regime 3’, which did not show the same pattern in Regime 3. Regime 4’ was identical to Regime 4 (Figure 11) for the case of smaller cathode, which has been discussed above.

$L_c > 0.0925 m$.—For large cathodes, four regimes were observed, but some were qualitatively different than observed for shorter cathodes. Results from a cathode length of 0.4 m are shown in Figure 14. Regime 1” ($WL \geq 3.2 \text{ cm}$) was similar to Regime 1 in Figure 11 and Regime 1’ in Figure 13, and Regime 2” ($2 \text{ cm} \leq WL < 3.2 \text{ cm}$) is similar to Regime 2 in Figure 11 and 2’ in Figure 13, in which potential range across the entire cathode length was within M-T limited region (as demonstrated in Figure 14b), but the average cathodic current density was closer to the value at the beginning of mass-transfer limited region, making $I_c/W$ slightly smaller. In Regime 3” ($\delta_{oc} \leq WL < 2 \text{ cm}$), the dominant controlling factor was the same as Regime 2”, except that the percentage of $L_c$ within M-T limited kinetics was reduced with decreased WL, causing the rate of decrease in $I_c/W$ with deceasing WL to be larger than in Regime 2”. Regime 4” ($WL \leq \delta_{oc}$) was similar to Regime 4 (Figure 11) and 4’ (Figure 13) as the ohmic drop was so dominant, that cathode length was irrelevant.

The linear dependence of total current on the logarithm of the WL thickness for small WL and its independence of cathode length.—As shown in Figure 9b, the data of total cathodic current per width versus the logarithm of WL thickness for very thin films fit a straight line with a slope that was independent of cathode length over this range of WL thicknesses. The WL range across which this linear dependence was observed expanded when more cathode was available, reaching nearly the value of the boundary layer for natural convection ($\delta_{nc}$) for the largest cathode length studied. Similar trends have been reported from experiment as well as modeling.8,21,40 The particular values of the slope and the intercept for this linear fit vary from study to study as the quantitative parameters are determined by the specific kinetics considered. For instance, Palani et al.21 considered ORR kinetics on carbon fiber reinforced polymer in contrast to this work on 316L stainless steel. This linear relationship between $I_{cath}$ and log WL was also present across similar film thicknesses in the work of McCafferty data40 as well as the finite element modeling study by Morris and Smyrl;8 however, the polarization parameters...
considered in those studies were extracted in the linear limit of kinetics near the open circuit potential. This analysis therefore yields another important insight; the nature of the kinetics itself does not affect the observation of a linear relationship between total cathodic current and logarithm of the WL thickness across a certain range of WL thicknesses lower than the boundary layer for natural convection (δ∞). However, the particular numerical values that the slope and the intercept of the linear fit assume are dependent on the specific polarization kinetics chosen.

In order to justify the independence of $I_c/W$ on $L_c$ for a limited range of WL, comparisons of current density distributions along the length of cathode for cathodes ranging from 0.05 to 0.4 m when WL = 89 μm are presented in Figure 15. Cathodic current densities were highest and stayed as a constant along the first 3 mm of the cathode from the interface because this region on all of the cathodes was under M-T controlled kinetics, before decaying at almost the same rate along the rest of the cathode for all four cases. Analysis shows that for the $L_c$ studied, more than 90% of the $I_c/W$ resulted from the first 0.05 m of the cathode (shown in Table III). In addition, the current densities over the first 800 μm from the AA/SS interface along the length of the cathode were virtually identical for all $L_c$ in Figure 15, thus it is not surprising that the total current at low WL thicknesses was independent of the cathode length.

**Implications and limitations.—**As with all models, the modeling approach used here has several limitations. The most important are: 1) the assumption of a uniform thin layer of electrolyte across the entire galvanic couple, which is not always the case due to imperfect wetting, especially at the edge of the cathode/anode. This imperfect wetting would lead to a shorter effective length of cathode available. The effect on the total current would depend on what regimes are sampled by the droplet and will be the reported in future work, 2) the assumption of a static, stagnant, and uniform electrolyte layer with constant chemical concentration and conductivity neglects the fact of changes in chemical (solution chemistry, corrosion products), electrochemical (corrosion kinetics) and physical (evaporation, temperature) conditions can and do occur in reality, 3) the current work focused on the contribution from cathode, using an anode that is largely non-polarizable, 4) the assumption of steady-state is made in the study, neglecting the time-evolution of cathodic current available and 5) only ohmic drop is considered, which is an intrinsic limitation of the use of Laplace’s Equation-based modeling, with diffusion effects being captured through the effects on cathodic kinetics.

Despite these limitations the implications of the work should be noted. The method for determining the natural convection layer should be applicable to any system for which the hydrodynamic boundary layer can be controlled (e.g., rotating disk, rotating cylinder, flow channel, etc.). In this way, the effects of solution composition and properties on the natural convection process can be determined, and physics models of natural convection can be quantitatively assessed. The presence of the different regimes of cathode length and WL thickness represent a key element in understanding the factors controlling galvanic interactions under atmospheric conditions. In particular, the fact that cathode length matters for $WL > 800$ μm is surprising; intuition might lead one to believe that current would not be thrown through an 800 μm WL from a cathode surface 0.05 m away (a $L_c$: WL of 125), but in fact, the current is $\sim 5 \times$ higher than that of a 0.01 m long cathode. These longer throwing distances have important implications for the sizing of samples for chamber or outdoor testing, as samples that are too small will be non-conservative results. The decrease in total current that occurs for small cathodes (<0.0925 m in the present case) at larger WL highlights the importance of considering the interplay between ohmic drop and mass transport for cathodic reactions when considering galvanic interactions under atmospheric conditions. In addition, the observation of oxide film effects on the diffusion limited current density at thin (<40 μm in the cases studied here) is important as otherwise, the amount of cathodic current available will be overestimated under these conditions, which would lead to substantial errors, particularly in cases of wetting and drying.

**Conclusions**

This study assesses how the total cathodic current capacity of a surface on the electrolyte film thickness and cathode size in a galvanic couple. It spans the range of WL thickness from full immersion conditions (where the total cathode current scales with cathode size) to the thin film regime in which the WL is the diffusion boundary layer thickness. In order to fully assess the transition from thin film to thick film condition, an understanding of the natural convection layer thickness is required. The natural convection layer defines the upper limit for true thin film behavior for atmospheric corrosion, and it can be experimentally determined by combining RDE experiments with data from quiescent conditions. For the conditions studied here, the natural convection boundary layer was found to be close to 800 μm. For very thin electrolyte layers, it was shown that oxide films can limit cathodic kinetics which will have important implications for galvanic corrosion productions under wetting and drying. The WL thickness, cathode length and electrochemical kinetics interact to create four regimes of total cathode current as a function of WL thickness. The prediction of a decrease in total available cathodic current upon an increase in WL thickness for small ($L_c < 0.0925$ m) is unique and has implications both for corrosion testing and corrosion prediction. The dependences can be understood by considering the competitive effects of ohmic drop and mass transport of oxygen on the total current for different cathode lengths.

**Table III. Percentage of ratio of $I_c/W$ for the first 0.05 m of $L_c$ to that for the entire cathode for $L_c = 0.05, 0.1, 0.2, 0.4$ m.**

| $L_c$ (m) | Percentage (%) |
|-----------|----------------|
| 0.05      | 100            |
| 0.1       | 94.2           |
| 0.2       | 93.5           |
| 0.4       | 92.5           |

**Acknowledgments**

The financial support from Office of Naval Research (ONR) via Grants N00014-14-1-0012 and N00014-17-1-2033, Sea-Based Aviation Program, William Nickerson, Program Manager is gratefully acknowledged.
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