

# **An Analytical Modeling Method for Calculating the Current Delivery Capacity of a Thin-Film Cathode and the Stability of Localized Corrosion under Atmospheric Environments**

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Corrosion resistant materials under atmospheric conditions can suffer from localized corrosion (pitting, crevice, stress-corrosion cracking). The stability of such a localized corrosion site requires that the site (anode) must dissolve at a sufficiently high rate to maintain the critical chemistry while a wetted surrounding area (cathode) provides matching cathodic current. The objective of this study was to computationally characterize the stability of such a local corrosion site and explore effects of physiochemical parameters and electrochemistry, and therefore to contribute to the establishment of a scientific basis for the prediction of the stabilization of localized attack. An analytical method for evaluating the stability of localized corrosion of corrosion-resistant alloys under thin-layer (or atmospheric) conditions is presented. The method uses input data that are either thermodynamic in nature or easily obtained experimentally. The maximum cathode current available depends on the cathode geometry, temperature, relative humidity, deposition density of salt (*i.e.*, mass of salt per unit area of cathode), and interfacial electrochemical kinetics. The anode demand depends on the crevice geometry, the position of attack within the crevice, and the localized corrosion stability product. By coupling these two approaches, the stability of a crevice can be determined for a given environmental scenario. The method has been applied to the atmospheric localized corrosion of Type 316L stainless steel.

## **Introduction**

Many structures are exposed to atmospheric conditions under which thin layers of moisture exist on the surface. The presence of soluble salts leads to the creation of a thin electrolyte layer whose characteristics, including its corrosivity, are a function of the nature of the salt(s), the temperature, and the relative humidity. For a given metal, the characteristics of this electrolyte layer and the interfacial electrode kinetics have a controlling influence on the evolution of corrosion damage. For corrosion resistant alloys, such as stainless steels, the rates of uniform corrosion are very low due to the formation

and maintenance of a passive film. However, these materials are susceptible to localized corrosion under atmospheric conditions. For these alloys, it has been difficult to quantitatively characterize conditions under which localized corrosion (e.g., pitting, crevice corrosion, intergranular corrosion) can occur to an extent that impacts the function of the structure. While many localized corrosion sites may initiate, consideration of the conditions for long-term stability under atmospheric exposures has received little attention. This work derives analytical expressions for the calculation of bounding conditions for localized corrosion stability under atmospheric conditions.

The localized corrosion stability of a freely corroding system can be analyzed in terms of the galvanic couple formed by the localized corrosion site, which serves as the dominant anode, and the surrounding freely exposed surface, which serves as the dominant cathode. In order for the localized corrosion site to remain active, it must sustain a sufficiently high dissolution rate to maintain the critical chemistry at the corroding surface site. In addition, the external cathode must be able to supply the current needed by the anode to maintain its critical chemistry. If either site fails to maintain the required current, the site must begin to stifle because the conservation of charge requires the total anodic current to equal the total cathodic current. Localized corrosion stability can thus be analyzed from two perspectives: the needs of the localized corrosion site anode to dissolve, which we will term the *anode demand* ( $I_{LC}$ ), and the ability of the surrounding cathode to supply current, which will be referred to as the *cathode current capacity* ( $I_{net,max}$ ). Thus, for system stability  $I_{net,max} \geq I_{LC}$ .

This work describes analytic expressions that result in values for  $I_{LC}$  for a crevice and  $I_{net,max}$  for a thin-film cathode characteristic of atmospheric exposure. The expression for  $I_{LC}$  considers both the anodic dissolution behavior of the material and the geometry of the crevice. The expression for  $I_{net,max}$  considers the atmospheric conditions (relative humidity), the amount and nature of the salt(s) present on the surface, and the cathodic interfacial electrode kinetics of the surface external to the crevice. In both expressions, temperature and other variables express their influence through effects on the parameters listed for each expression. A rectangular system is considered, but the concepts can be extended to other regular two-dimensional geometries.

#### Expression for Anode Current Demand ( $I_{LC}$ )

A stability criterion for the anodic behavior of pits has been developed by Galvele. [1,2] Galvele based his criterion on the concept that in order for a pit to remain active, the solution chemistry at the corroding pit surface must be sufficiently aggressive as to prevent repassivation by oxide formation. The aggressive solution is created by the hydrolysis of metal cations produced by dissolution. Diffusion out of the pit acts to dilute this solution chemistry, but the geometry of the pit serves as a diffusion barrier. Thus, the dissolution rate (and subsequent hydrolysis which was assumed to be very rapid) must exceed the rate at which mass transport could sufficiently dilute the solution. Galvele showed that for a one-dimensional pit of depth  $x$ , the product  $x \cdot i$  could be used to determine stability, where  $i$  is the dissolution current density at the base of the pit. This parameter has become known as the pit stability product. The deeper a pit, the lower the

current density at the base of the pit required to maintain the acidic electrolyte needed to prevent repassivation. Numeric values for the parameter  $x \cdot i$  have been established for a range of metals and alloys [3,4], and the concept has been validated in its ability to predict the transition of pits from metastable to stable [5].

The concept of the pit stability product can be extended to other forms of localized corrosion such as crevices or intergranular fissures. Kehler [6] has discussed its use in determining conditions under which metastable pits within crevices can stabilize sufficiently to coalesce and lead to crevice corrosion. In the case of materials which undergo widespread depassivation within a portion of the crevice, an alternative approach is required. In engineering applications, one often wants to know whether or not a crevice of given geometry can corrode stably anywhere within the crevice. The 1-dimensional pit geometry used by Galvele can be adapted for crevice corrosion as shown in Figure 1. In this approach, the distance  $x$  of interest is the distance from the mouth of the crevice to the position of interest.

In order to calculate  $I_{LC}$  from  $i$ , one needs an area. For the purposes of the present work, we will assume that the area of high rate dissolution is equal to the product of the width of the crevice (perpendicular to the direction of  $x$ ) and the gap,  $g$ . In general, the area of crevice attack is substantially larger than this, *i.e.*, stainless steels undergoing crevice corrosion with gaps of several microns often exhibit attacked regions with widths of 100 microns or more. However, it is not clear that the entire attacked region observed after the test was active at the same time. As the objective of the present work is a bounding calculation, the use of  $g$  in calculation of the anode area seems appropriately conservative in that larger areas would result in larger currents, making stability more difficult. The resulting expression for the anode current demand is shown in Equation 1.

$$I_{LC} = i \cdot g \cdot w = \frac{(xi)_{crit}}{x} \cdot g \cdot w \quad (1)$$

where  $(xi)_{crit}$  is the experimentally determined value of the critical pit stability product,  $g$  is the crevice gap, and  $w$  is the width of the crevice.

#### Analytical Expression for Maximum Current from a Thin-Electrolyte Cathode

For stability analysis, only the total current delivered from the thin-electrolyte cathode is of interest and detailed information concerning the spatial distributions of the potential and current are not required. Under these conditions, a cathode covered with a thin electrolyte can be considered in terms of an equivalent electrode as shown by Cui *et al.* and as shown in Figure 2 [7]. Briefly, an equivalent electrode to a thin film cathode would be one that would supply the same current if placed at the mouth of the crevice. The analysis of Cui *et al.* considers a thin-electrolyte cathode with constant water layer thickness,  $WL$ , and conductivity,  $\kappa$ , the mouth of which is held at the repassivation potential of the material in question under the conditions of interest. Given the current-potential behavior of the external cathode appropriate to the conditions of interest, and

considering only ohmic drop, the maximum net cathode current can be shown to be given by Equation 2 [7].

$$I_{\text{net}} = W \cdot \sqrt{2 \cdot \kappa \cdot WL \cdot \int_{E_{\text{rp}}}^{E_{\text{corr}}} (i_c - i_p) \cdot dE} \quad (2)$$

Where  $W$  is the crevice width,  $E_{\text{rp}}$  is the repassivation potential, and  $i_c$  and  $i_p$  are the cathodic and passive currents.

By integrating the cathodic current from the repassivation potential to the corrosion potential of the cathode, the maximum current can be calculated without consideration of cathode length (*i.e.*, wetted area). Any portion of the wetted surface that is sufficiently far from the crevice mouth that the potential has fallen to  $E_{\text{corr}}$  cannot supply net cathodic current for support of the crevice propagation because all of its cathodic current is used locally to support the passive dissolution current density. Thus, the expression describes the maximum current a surface of any size could produce.

Note that this expression is bounding because as the cathodic reactions proceed, the production of  $\text{OH}^-$  from either water reduction or oxygen reduction will increase the pH in the thin electrolyte, which for passive corrosion resistant alloys leads to a slowing of the electrochemical kinetics. Thus the total current from a cathode would tend to decrease with time in the absence of a substantial change of one of the other parameters. Although the hydroxyl will act to increase the conductivity, we are considering rather concentrated solutions already, and precipitation of any dissolved metal ions will tend to counteract the increase in conductivity by decreasing the cross-sectional area. [8]

Validation of the analytical expression can be shown by comparison to full numeric simulations using a finite element method code [7]. As shown in Figure 3 for a wide variety of cases, the comparison between the two approaches is very good.

Although the analytical expression of Eqn 2 is an improvement over the need for full numeric simulations, it has limitations with regards to its application to actual atmospheric corrosion scenarios. Measurements and/or control of all of the parameters in Eqn 2 is very difficult, especially  $WL$  and  $\kappa$ . In addition, it implicitly assumes that  $WL$ ,  $\kappa$ , and  $\text{O}_2$  solubility (needed for calculations of  $i_{\text{lim}}$ ) are independent, but in reality, two other physiochemical parameters control these.

The relative humidity (RH) and the amount of salt(s) present on the surface determine the electrolyte thickness, conductivity, and  $\text{O}_2$  solubility. The RH determines the equilibrium concentration of salt in solution through the deliquescent behavior of the salt(s) of interest [9]. The amount of salt (referred to herein as the deposition density (DD) in units of mass per unit area) can be used to determine the electrolyte layer thickness when combined with the concentration. Thus, Eqn 2 can be replaced with Eqn 3 which emphasizes the dependence of  $\kappa$  and  $WL$  on RH and DD. The value of  $i_{\text{lim}}$  is also

affected by RH and DD in that the diffusion boundary layer thickness is equal to the WL for thin electrolytes less than 200 microns.

$$I_{\text{net,max}} = W \cdot \sqrt{2 \cdot \frac{\kappa(\text{RH}) \cdot \text{DD} \cdot (1 + m_{\text{salt}}(\text{RH}) \cdot \text{MW}_{\text{salt}})}{\rho(\text{RH}) \cdot m_{\text{salt}}(\text{RH}) \cdot \text{MW}_{\text{salt}}} \cdot \int_{E_{\text{rp}}}^{E_{\text{corr}}} (i_c - i_p) dE} \quad (3)$$

Data exist for each of these relations for many salts and fitting can be done for any salt or combination of salts, if sufficient thermodynamic data are available or can be calculated [10]. The application of Eqn 3 to any given case allows calculations of  $I_{\text{net,max}}$  with a knowledge of two easily measurable parameters (RH, and DD) and the interfacial kinetics (obtainable from measurements in bulk solution and corrected for enhanced mass transport of oxygen).

### Calculation of Anode Demand and Maximum Cathode Current for Type 316L

We apply the expressions developed above to the case of a Type 316L crevice exposed to atmospheric conditions with NaCl deposited on its external surface in order to demonstrate its advantages and limitations.

The anode demand calculation is straightforward. For Type 316SS, Pistorius and Burstein [3] and Newman [4] have shown the  $x \cdot i$  value to be between 0.3 and 0.6 A/m at room temperature. For convenience, we will assume a value of 0.5 A/m. Thus, for a 10 micron deep pit to be stable, the current density at the base must be at least  $5 \times 10^4 \text{ A/m}^2$  ( $5 \text{ A/cm}^2$ ), whereas for a 1 mm deep pit, a current density of only  $50 \text{ mA/cm}^2$  would be required. Crevice corrosion on Type 316L is generally thought to require a crevice gap of less than 6 microns [11], so for this example, we will choose a value for  $g$  of 1 micron. The insertion of these values into Equation 1 results in the following set of cases for  $I_{LC}$  shown in Table 1.

Table 1: Examples of  $I_{LC}$  calculated for SS 316L at room temperature, assuming  $x_i = 0.5 \text{ A/m}$  [2,3];  $i = 0.5/x \text{ (A/m}^2\text{)}$ ;  $\text{Area} = 10^{-8} \text{ m}^2$ .

$x \text{ (mm)}$	$I_{LC} \text{ (}\mu\text{A)}$ <i>for a 1-cm wide crevice</i>
0.1	50
0.5	10
1	5
5	1

Calculation of the cathode current capacity requires information on the chemical characteristics of the salt(s) of interest as well as the cathodic kinetics. The deliquescence behavior of NaCl is well known, and the equilibrium concentration of NaCl in solution in contact with air of different RH is shown in Figure 4a. There are

excellent reference sources for the dependence of conductivity, density, and O<sub>2</sub> solubility on the concentration of NaCl [9] which can be combined with the data in Figure 4a to produce Figures 4b-4d. In addition to the data, the figures show fitted functions. The functions selected were chosen based on the ability to produce a good fit. No other meaning is attached to their form or values of the constants. Their utility is that they allow a fully analytic expression for  $I_{net,max}$  for Type 316L exposed to atmospheric conditions with deposited NaCl to be developed as shown in Equation 3.

Combining all the results showed in the above discussions, the net cathodic current can be calculated according to the following equation:

$$I_{net} = W \times \sqrt{2} \times \sqrt{\int_{E_{rp}}^{E_{corr}} (i_c - i_p) \cdot dE} \times \sqrt{\frac{DR \cdot (2.5 - 0.0146RH)}{2636 - 37.5RH + 0.113RH^2}} \times \sqrt{48150 - 2876RH + 69RH^2 - 0.82RH^3 + 4.85 \times 10^{-3}RH^4 - 1.2 \times 10^{-5}RH^5} \quad (4)$$

$\sqrt{\int_{E_{rp}}^{E_{corr}} (i_c - i_p) \cdot dE}$  can be calculated for any given polarization curve and choice of  $E_{rp}$ .

Thus,  $I_{net,max}$  can be calculated according to equation 4 at given RH and NaCl deposition rate. This expression is specific for the case of Type 316L exposed to atmospheric conditions at room temperature and NaCl as the deposited salt. Room-temperature cathodic polarization data from Sridhar [12] were used to determine Type 316L. A repassivation potential of -0.4 V<sub>SCE</sub> was used for Type 316L at room temperature [12].

Figure 5 shows the surface for  $I_{net,max}$  as a function of the two important variables, RH and DD. The effects of DD are far stronger than those of RH as shown in Figure 6. The RH has limited effects at a constant DD due to the fact that although increasing the RH increases the WL, it does so at the expense of conductivity for a given DD due to the relation between NaCl concentration and RH.

The analyses of maximum cathode capacity can be coupled with the Galvele criterion for localized corrosion stability to gain insights into the conditions under which localized corrosion can propagate under atmospheric exposures. Figure 7 shows  $I_{net,max}$  for two RH as a function of DD. Superimposed as horizontal lines are the currents required to maintain stable localized corrosion for Type 316SS of the indicated depths according to the Galvele criterion and the geometry assumed. Intersections of an  $I_{net,max}$  line and a Galvele criterion line are critical points. For a localized corrosion site of that depth exposed to an atmosphere of the given RH, the DD must be at least that indicated by the intersection for the site to be stable. For example, a localized corrosion site of 500 microns in depth, exposed to an atmosphere at 96% RH, requires that at least 271.7  $\mu\text{g}/\text{cm}^2$  of NaCl be present in order to be stable. Less NaCl than that would lead to repassivation. The other intersections illustrate the decreasing demand required for deeper localized corrosion sites.

An additional application of the approach would consider a set DD, and determine the critical RH at which a localized corrosion site of a given depth could be stabilized. Such an analysis could be of use for determining storage conditions (e.g., dehumidification strategies) or for investigating the role of diurnal cycles in atmospheric localized corrosion. As shown in Figure 8, 316SS requires an RH of above 92.2% for a DD of 90  $\mu\text{g}/\text{cm}^2$  and a site depth of 1000  $\mu\text{m}$ . Higher RH are required as DD increases, and for DD less than 51.7  $\mu\text{g}/\text{cm}^2$ , no RH satisfies the condition.

## Discussion

Most previous modeling of atmospheric corrosion has focused on uniform corrosion, with a limited amount of study of galvanic corrosion. Uniform corrosion modeling typically has involved empirical fitting of dose-response functions for metals exposed to various pollutant gases [13], although Graedel and Tinblad developed and demonstrated a framework for a more fundamentally based approach referred to as GILDES [14]. Galvanic corrosion in thin electrolytes has been modeled using both analytical [15] and numeric modeling [16-19]. Most of these focused on determining the distributions of current and potential across the surface as a function of presumed electrolyte layer thickness and composition as well as interfacial kinetics. None of these studies focused on determining bounding solutions for the problem of interest.

Cui *et al.* [20] focused on determining the total net current available from a cathode covered with a thin-electrolyte of uniform thickness and composition with a known length, but it did not represent a *bounding* solution for the conditions more relevant to atmospheric corrosion in service or laboratory experiments: a known salt deposition density and a fixed relative humidity and temperature. A tacit assumption in that work was the independence of electrolyte layer thickness, solution conductivity, and oxygen solubility which in actual atmospheric exposures is not correct.

More recently, Cui *et al.* [7] developed an analytic expression for the maximum net current from a thin-electrolyte cathode without the need for knowledge of cathode size. The assumption that *WL* and *RH* and NaCl concentration are independent parameters was maintained, however, as did the difficulty in relating the results to actual service or to experimental results from laboratory exposures. That work did introduce the idea of coupling the results of a calculation of the total net cathode current available to the anodic current demands of a crevice via consideration of the galvanic coupling between the thin-electrolyte cathode and the occluded crevice anode.

Atmospheric localized corrosion is essentially a galvanic corrosion problem in which the anode and cathode are linked by the potential at the mouth of the localized corrosion site. For a stability analysis, one should assume that the potential at the mouth is the repassivation potential. It has been shown by Sridhar *et al.* [12] that when properly determined, a repassivation potential represents a threshold for stable localized corrosion. The linking via the repassivation potential allows computational decoupling. By holding the end of the cathode nearest the localized corrosion site at the repassivation potential, the details of the conditions inside the localized corrosion site are unnecessary for

analysis of the ability of the cathode to supply current. Using the Galvele criterion [2], one can assess the stability of the atmospheric localized corrosion by comparing the anode's need for current to the cathode's ability to provide it.

The approach can be used for a reasonable bounding analysis of the stability of localized corrosion on materials exposed to thin-electrolyte layer conditions, such as in atmospheric exposure. Its advantages include its form as two analytical expressions that require limited inputs, all of which are available in the literature (*e.g.*, deliquescence behavior) or easily measured (*e.g.*, relative humidity). Note that it also has utility as a guide for experimental measurements of localized corrosion under thin electrolyte conditions as it can be used to determine what combinations of DD and RH (at a given temperature) will lead to stable localized corrosion. Both the RH and DD are easily controlled in a laboratory and determined under service conditions. Cathodic kinetics can be determined in the electrolyte of interest under bulk solution conditions, and then implemented into the model as the diffusion-limited oxygen diffusion reduction is taken into account.

As with all models, this approach to localized corrosion stability has important limitations due to the assumptions invoked. The calculation implicitly assumes no physical limitations to cathode length (*e.g.*, due to imperfect wetting), constant chemical conditions ( $\kappa$ ), electrochemical conditions (kinetics), and physical conditions (DD, temperature). It represents a bounding condition – other factors can reduce the current capacity such as decreased kinetics with increasing pH. Thus, the time evolution of the cathodic current is not calculable analytically. More importantly, it does not consider transient currents available from discharge of the interfacial capacitance of the cathode [21]. As these currents are short-lived, they would be expected to be of limited effectiveness in stabilizing a localized corrosion site, although they may be of importance in supporting metastable sites at early times when the demands are highest.

Three other limitations should also be noted. The approach ignores any effects of chemical interactions between the localized corrosion site and the cathode. For example, one might expect that anolyte exiting the localized corrosion site would lead to precipitation of solids as it encountered the higher pH of the catholyte. Although this no doubt occurs, it should be noted that the precipitation would serve as a *limiter* of effective cathode capacity by imposing an additional resistance in the current path. The method does require knowledge of the relevant interfacial cathodic kinetics, although such measurements are generally straightforward, including in thin electrolytes. As presently constituted, the method assumes that kinetics are independent of salt concentration, although that is not inherent – if data are available, the dependence can be included by using different polarization data for different DD/RH. Finally, the method assumes the absence of localized corrosion on the cathode which would reduce the net cathodic current available for the crevice.

## Summary



Crevice corrosion stability under freely corroding conditions requires a cathode outside the crevice that is capable of providing the current needed by the occluded anode. The occluded anode must continue to be sufficiently active that the critical crevice solution can be maintained against the diluting action of diffusion. In the present work, an analytical method has been developed to predict the maximum cathodic current available from a metal exposed to a thin-layer electrolyte given only a limited number of input parameters, the values of which are straightforwardly obtained. These calculations of the maximum cathode current can be coupled to an extension of the pit stability product ( $x \cdot i$ ) which predicts the anode current required to maintain an active crevice. This coupling allows an analysis of the stability of crevice corrosion under thin-electrolyte conditions. By doing so, it allows quantification of compatibility requirements between anode and cathode for a given set of exposure conditions.

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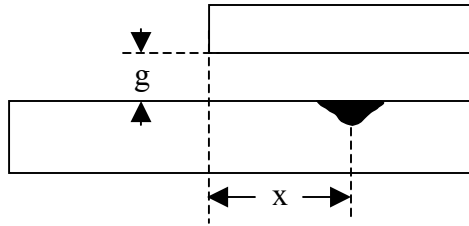


Figure 1. Schematic diagram for the crevice used to apply the pit stability criterion.

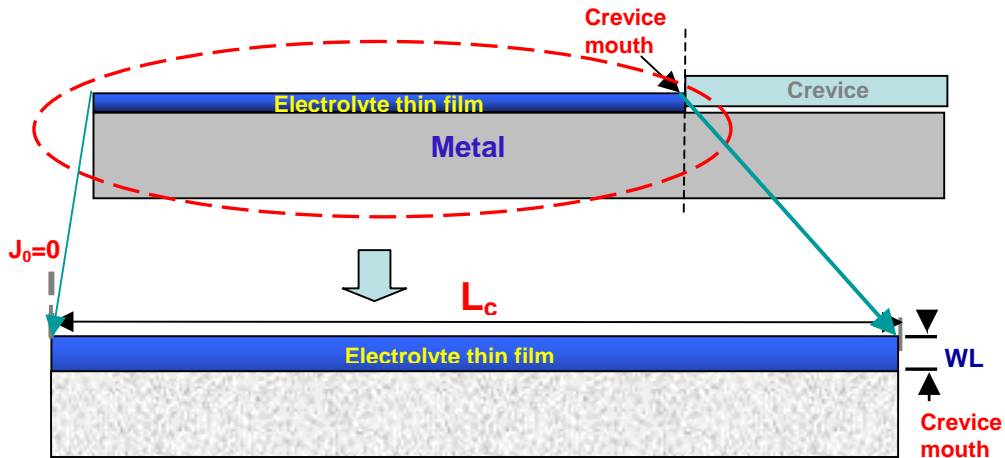


Figure 2. Schematic of a typical crevice corrosion system under atmospheric environment. The cathode is extracted by keeping the potential at the crevice mouth constant.  $WL$  is the electrolyte thickness and  $L_c$  is the length of the cathode.

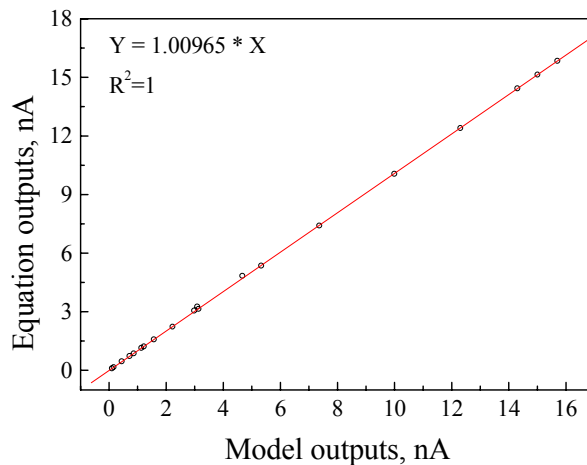


Figure 3. Comparison of the net cathodic current results obtained from finite element model calculations and from Equation 2 calculations. The difference between these two methods is lower than 1%.

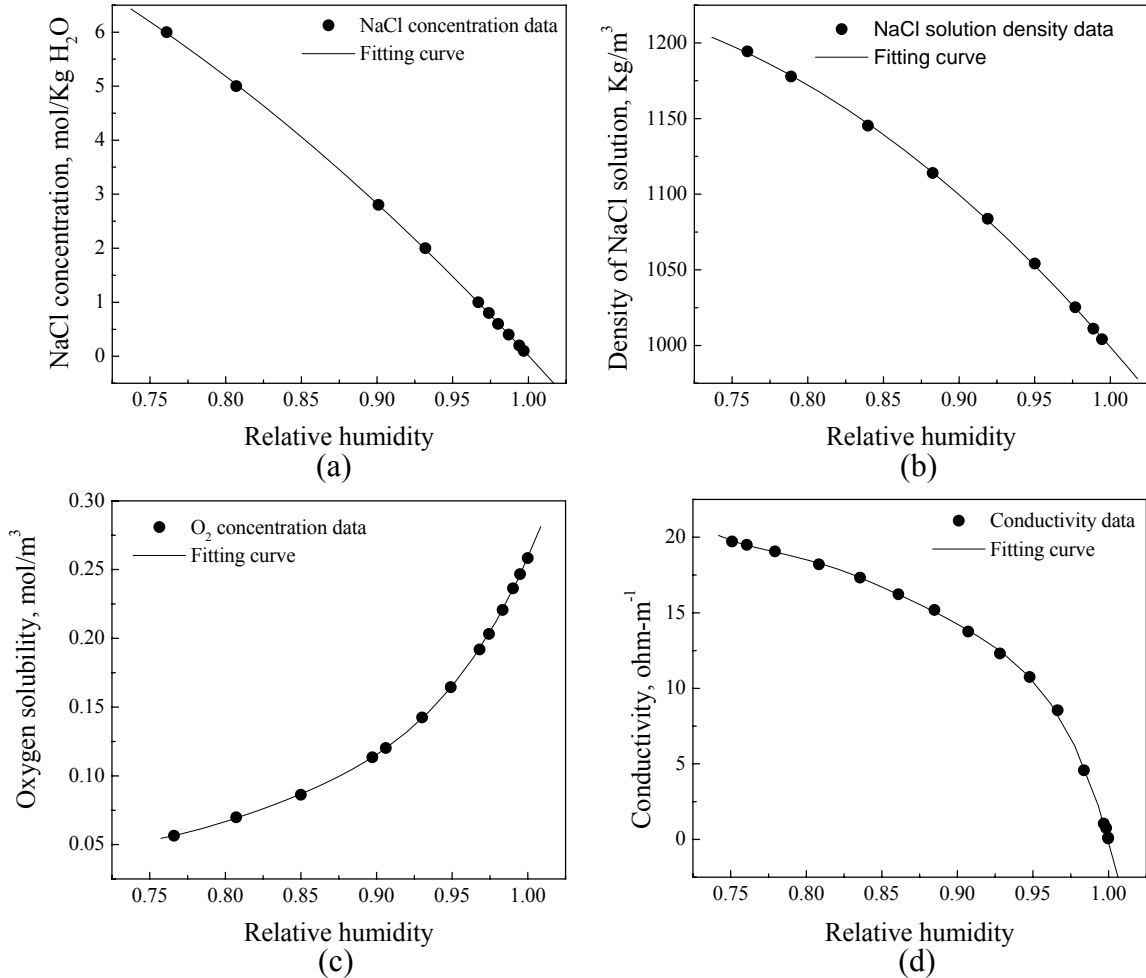


Figure 4. NaCl concentration, density of NaCl solution, oxygen concentration, and electrical conductivity of the solution formed on NaCl deposited metal surface exposed in atmospheric environments as functions of relative humidity. [9]

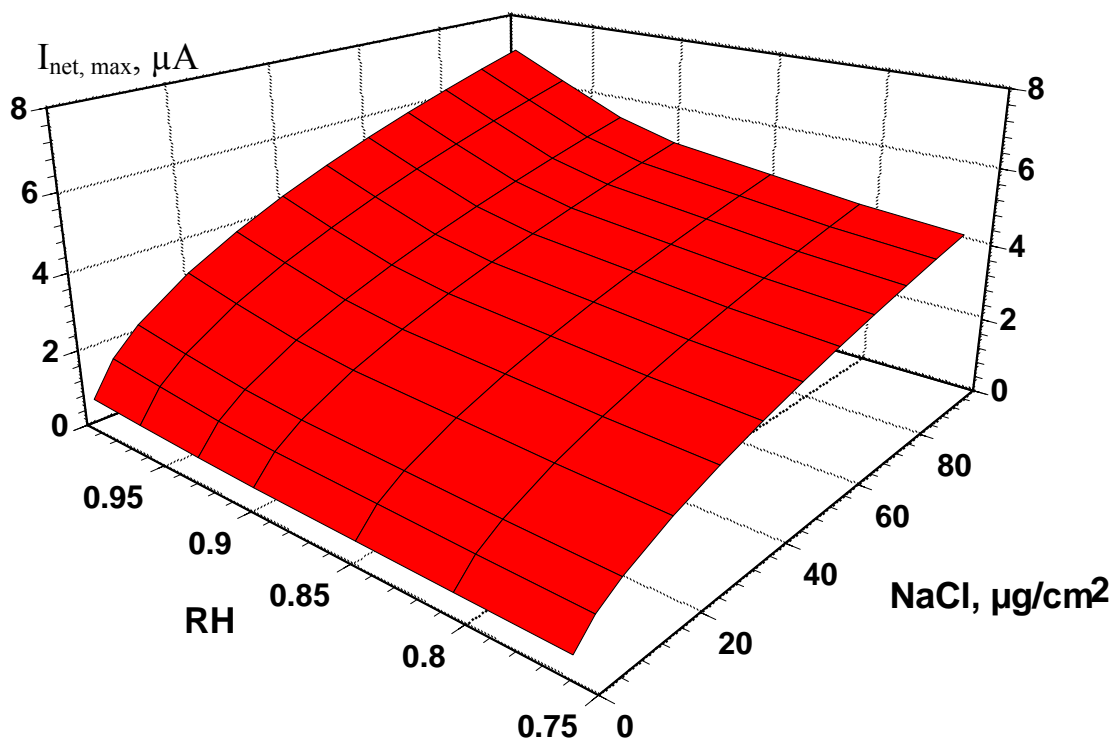


Figure 5. The effects of relative humidity and amount of deposited NaCl on the cathode capacity of SS 316L under atmospheric environments. The width of the cathode for calculation is 1 cm and temperature is 25 °C.

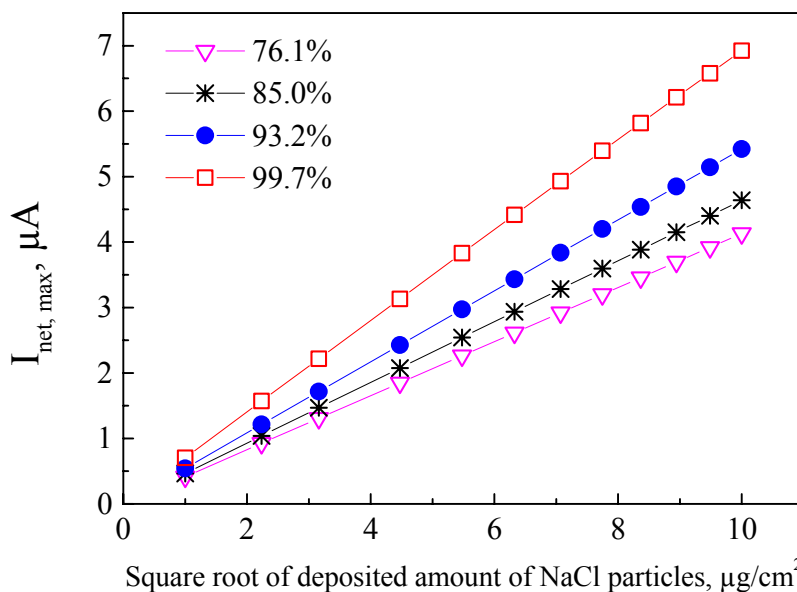
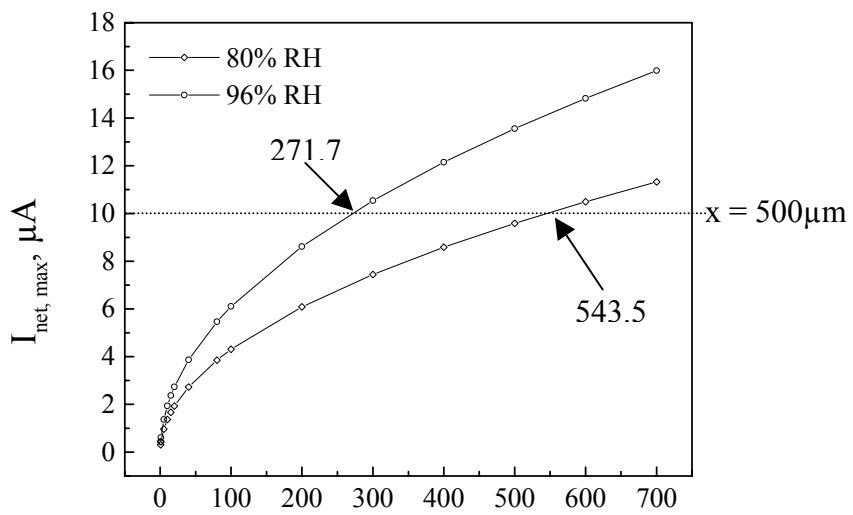
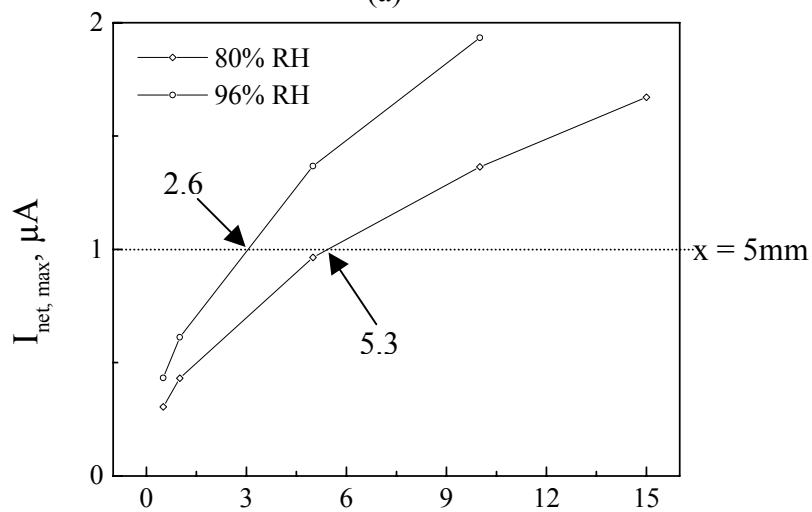


Figure 6. Calculated cathode capacity of SS 316L surface covered with thin electrolyte layer increases linearly with the square root of amount of deposited NaCl particles at different relative humidity.



Amount of deposited NaCl particles,  $\mu\text{g}/\text{cm}^2$   
(a)



Amount of deposited NaCl particles,  $\mu\text{g}/\text{cm}^2$   
(b)

Figure 7. Calculated cathode capacity for SS 316L as a function of the amount of deposited NaCl at 80%, 96% RH and 25 °C. (a) Overall behavior, (b) Behavior at low DD.

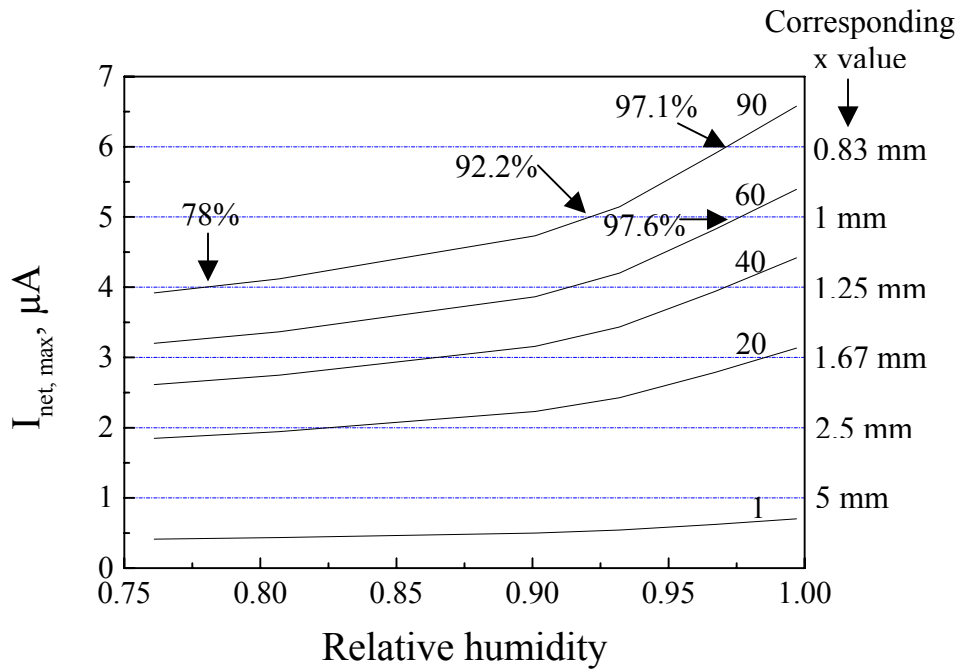


Figure 8. Calculated cathode capacity of SS 316L surface covered with thin electrolyte layer as a function of RH and amount of deposited NaCl in  $\mu g/cm^2$ . For a crevice, the cross area of the crevice will be  $10^{-8} m^2$  if the gap is  $1 \mu m$  and the width of the crevice is 1 cm. If x is  $1000 \mu m$ , then I is  $5 \mu A$ , an RH of above 92.2% for a DD of  $90 \mu g/cm^2$  is required. For DD less than  $51.67 \mu g/cm^2$ , no RH satisfies the combined conditions.