

Article

The Effects of Three-Dimensional Scratch Geometry and Electrolyte Film Thickness on Galvanic Current Distribution in a Ni–W/SiC Coating–Q345B Steel System

Wenbo Li * and Zhengxu Zhao

Shandong Key Laboratory of Space Debris Monitoring and Low-Orbit Satellite Networking, Qingdao University of Technology, Qingdao 266520, China

* Correspondence: lwb@qau.edu.cn

Highlights

What are the main findings?

- Thicker surface films raise groove bottom net current and narrow the relative differences among the three groove shapes.
- Doubling the groove width raises integrated bottom current while lowering the mean bottom current density.
- Assigning the steel polarization response to the sidewalls lowers bottom current but raises total steel net current.

What are the implications of the main findings?

- Reporting bottom current alone can misread coupling strength, so current over all exposed steel should be reported alongside it.
- Integrated current and mean current density answer different questions, and either metric alone gives an incomplete description of the changed bottom response.
- Conditional oxygen coupling separates the measured net response from the reconstructed partial currents, which supports a stated reporting format for comparisons of damaged coatings.

Abstract

Through-coating scratches expose steel surfaces whose arrangement can alter galvanic current distribution. This study combines cross-sectional microscopy and polarization measurements with a three-dimensional finite element comparison of Ni–W/SiC-coated Q345B steel. Electrolyte properties and measured interfacial inputs both correspond to 3.5 wt.% NaCl. Linear, elliptical and circular grooves have a common prescribed bottom area and 180 μm depth, under surface films of 0.642–6.418 μm . Numerical checks include mesh refinement, charge conservation, interpolation ranges and an independently calculated limiting solution. A conditional reaction reconstruction further couples oxygen diffusion to the measured net response and tests source-condition recovery. In the net curve comparison, the linear groove carries the highest bottom current; its excess over the circular groove decreases from 174.2% to 77.3% as the film thickens. At 3.209 μm , doubling width increases bottom current by 32.4% while lowering mean density by 33.8%. Assigning steel kinetics to the sidewalls lowers bottom current by 62.7% and raises total steel current by 72.7%. Oxygen feedback is evaluated separately through net current, oxygen reduction reaction (ORR) consumption and minimum oxygen concentration. Connected partial filling at 3.209 μm retained the shape order. The results describe how scratch geometry and wetting redistribute the net electrochemical response.



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1. Introduction

In saline atmospheres, NaCl deposited on a metal surface can absorb moisture and form a local electrolyte, providing conditions for atmospheric corrosion [1]. The formation and persistence of a liquid electrolyte also depend on local relative humidity, the deliquescence conditions of deposited salt, and salt loading [2]. The size of droplets formed by salt particle deliquescence has been linked to corrosion initiation on steel [3]. Ambient relative humidity and the hygroscopic behavior of corrosion products affect subsequent corrosion development [4]. On coated steel, holes or scratches that penetrate the coating provide pathways for electrolyte contact with the substrate. In graphene-containing epoxy coatings, Sabet-Bokati and Plucknett distinguished galvanic corrosion risk from the effects of interfacial adhesion on delamination [5]. The local current imaging of steel protected by a polymer coating and scratched to the substrate showed anodic and cathodic activity across the defect and adjacent coated region. NaCl promoted delamination from the defect [6]. For artificially scratched epoxy/zinc-rich coatings on Q235 steel, the current distribution and protection process in the defect region differed between exposure under an atmospheric thin electrolyte film and immersion [7]. Local electrochemical measurements on reinforcing steel with an epoxy coating showed that microdefect size altered the initial corrosion response [8]. Mai et al. used a multiphysics model to examine the scratch-width-dependent loss of galvanic protection in damaged galvanized steel [9]. Corrosion assessment after coating damage needs to consider the exposed defect region, the adjacent coated region, and the actual wetting conditions.

Research on Ni–W/SiC composite coatings has focused mainly on deposition conditions, microstructure, and the performance of intact coatings. Yao et al. characterized the microstructure, mechanical properties, and corrosion resistance of electrodeposited Ni–W/SiC coatings [10]. Ma et al. examined how ultrasonic power density during pulse electrodeposition affected the structure and electrochemical performance of Ni–W–SiC coatings on Q235 steel [11]. Li et al. compared the effects of SiC concentration, current density, and deposition time on coating composition, corrosion resistance, and wear resistance [12]. Jia et al. combined electrodeposition simulations with experiments to examine how nano-, micro-, and dual-scale SiC particles affected coating growth, microstructure, and wear resistance [13]. Zhang et al. examined the effects of magnetic field direction on the microstructure, surface morphology, corrosion resistance, and wear resistance of coatings electrodeposited under a magnetic field [14]. Huang and Cheng combined sliding friction and electrochemical measurements to study the wear and corrosion of the composite coating in NaCl solution [15]. Work on artificially damaged Ni–W coatings is more limited. Li et al. studied a Ni–W/C110 steel system in a corrosive oilfield medium at high temperature and found that galvanic coupling at defects could promote substrate corrosion, accompanied by propagation along the coating–substrate interface [16]. These studies provide the materials and electrochemical basis for assessing the protective performance of damaged Ni–W coatings.

More broadly, the review of metastable austenite by Li et al. links transformation response to composition, grain size and morphology [17], illustrating why material state should be specified when constructing a controlled geometric comparison. Zhang et al. examine machined 7075-T6 aluminum surface integrity under microbiologically induced

corrosion [18], providing a complementary surface-condition perspective for describing damaged metallic systems.

Corrosion beneath thin electrolyte films is also affected by electrolyte film thickness and transport conditions. Nishikata et al. found that the initial corrosion rate of iron varied nonmonotonically with film thickness. Oxygen diffusion and oxygen dissolution at the interface between the gas and liquid phases contributed differently across the thickness ranges examined [19]. Dolgikh et al. used experiments with platinum electrodes and numerical calculations to analyze the combined effects of film thickness and NaCl concentration on the oxygen reduction reaction (ORR) current [20]. Liu et al. combined electrochemical tests with finite element calculations to examine how film thickness and cathode size affected the capacity of a galvanic system to supply cathodic current. They found that solution ohmic resistance was important in sufficiently thin films [21]. Thébault et al. incorporated film thickness and the electrode area ratio into a two-dimensional finite element analysis of an Fe/Zn system; both altered the regimes controlling galvanic coupling [22]. Measurements by Yadav et al. on a Zn/steel couple showed that relative humidity changed the spatial distributions of surface potential and pH beneath a thin electrolyte layer. Relative humidity also changed the extent of the steel surface affected by galvanic coupling [23]. These results show that the effect of film thickness on corrosion current depends on oxygen supply, solution resistance, electrode configuration, and wetting conditions.

Water activity is the water-vapor pressure over a solution divided by that over pure water at the same temperature; at vapor equilibrium, it equals fractional relative humidity [24]. Film thickness and solution composition affect different parts of the corrosion response [20,21]. Here, electrolyte composition is fixed at the concentration used for polarization measurements, while surface-film thickness is prescribed independently. The comparison addresses the effects of defect geometry and film thickness under a common electrolyte composition.

Numerical studies have incorporated electrode geometry and local current distributions into analyses of corrosion under thin electrolyte films. Liu et al. used a model based on the Laplace equation to study galvanic coupling beneath a thin film between a zinc plate and a stainless steel rod. They examined the effects of film thickness, conductivity, and electrode spacing [25]. Katona et al. evaluated finite element galvanic corrosion models against damage measurements for carbon steel/stainless steel and zinc/stainless steel couples while varying solution conditions, the anode:cathode ratio, and exposure time [26]. Du et al. combined droplet microarray experiments and finite element modeling to relate carbon steel corrosion morphology to droplet chemistry, oxygen transport, and corrosion-product coverage [27]. In a three-dimensional galvanic analysis, Zang et al. used electrochemical test parameters as interfacial inputs to models of 13Cr/9Cr or P110 components and calculated surface current density distributions [28]. Deshpande defined electrode boundaries using nonlinear polarization data and evaluated galvanic corrosion model predictions against scanning vibrating electrode technique (SVET) measurements and immersion tests [29]. In an AA2024/CFRP system beneath a thin electrolyte layer, Palani et al. compared calculated and experimental results for total current, local current density, and potential distribution [30]. For galvanized steel, Zhang et al. developed a peridynamic model that coupled oxygen transport, corrosion-product formation, and galvanic interactions during interface evolution, with comparisons against cut-edge and droplet benchmarks [31]. Van den Steen et al. used a droplet model to examine how droplet radius, contact angle, and size distribution affected atmospheric corrosion current [32].

Recent studies extend these approaches to time-dependent galvanic behavior. Tang et al. [33] coupled electrochemical dissolution and changing geometry in a transient finite

element model of an aluminum alloy/steel couple under mechanical loading. Shi et al. [34] combined galvanic current measurements with a thin-film model of a three-metal couple that included mass transfer, anodic deformation, and corrosion-product deposition. These studies relate calculated fields to changes in the reacting surfaces, whereas a fixed-geometry comparison can isolate the current redistribution associated with a prescribed scratch.

These models address different parts of the corrosion problem: electrolyte conduction, oxygen transport, evolving surfaces, and spatially resolved electrochemical reactions. The question considered here is how a through-coating groove of finite depth redistributes current when its planform shape and reactive surfaces are changed under common material inputs. A comparison at fixed prescribed groove bottom area separates shape from a simple increase in exposed bottom area. Width and sidewall comparisons then establish how integrated bottom current, mean bottom current density, and total steel current respond when the reactive area changes. For a Ni-W/SiC coating on Q345B steel, this distinction is needed to interpret a lower current at the groove bottom when steel sidewalls also participate in the reaction.

This study combines the experimental characterization of the coating and its polarization response with a steady-state simulation of three-dimensional grooves. Cross-sectional microscopy supplies a depth scale, and the measured coating and steel polarization curves define the interfacial kinetics. The contribution is a finite-depth comparison that distinguishes current at the groove bottom from current over all exposed steel, including reactive sidewalls. Equal-bottom-area shapes, groove width and sidewall assignments are evaluated separately. Mesh refinement, current conservation, interpolation range checks and prescribed input variations establish the numerical basis for interpreting these comparisons.

2. Materials and Methods

Sections 2.1 and 2.2 report experimental characterization and polarization inputs. Sections 2.3–2.6 define the electrolyte, three-dimensional model, current metrics and numerical checks. Section 2.7 specifies the conditional oxygen feedback analysis. The simulation results are reported in Section 3.

2.1. Coating Preparation and Cross-Section Characterization

Two coated specimens (specimens 1 and 2) with nominal dimensions of 10 mm × 10 mm × 10 mm supplied the coating polarization inputs. For bare Q345B steel, the polarization specimen had nominal dimensions of 20 mm × 10 mm × 10 mm. The scratches investigated in this study were defined in the numerical model. Q345B substrates were sequentially ground with 400-, 800-, 1200-, and 2000-grit abrasive papers, then polished, ultrasonically cleaned, treated with ethanol, and dried. Before electrodeposition, they were degreased, rinsed with hot and cold distilled water, activated by acid etching, and transferred to the plating bath.

Ni-W/SiC was deposited at 60 °C, 4 A/dm², and a pH of approximately 4 for 3 h. Bath circulation and mechanical stirring maintained the SiC suspension. The bath composition in Table 1 was selected from prior processing experience and specified in the earlier project task document. All reagents were of analytical grade and were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Its component concentrations were retained to give the specimens a common processing basis. The process follows the established route of electrodepositing Ni-W/SiC from a Ni-W electrolyte containing suspended SiC particles [10,12]. The commercial SiC powder (300–500 mesh) was supplied by Nangong City Lijia Metal Materials Co., Ltd. (formerly Nangong City Zhongmai Metal Materials Co., Ltd.), Nangong, Hebei, China.

Table 1. The plating bath composition of the Ni–W/SiC composite coating.

Component	Content
NiSO ₄ ·6H ₂ O	80 g/L
Na ₂ WO ₄	4 g/L
H ₃ PO ₄	7 g/L
SiC particles	10 g/L
Citric acid	33 g/L
Sodium acetate	13 g/L
H ₃ PO ₃	15.4 g/L
Thiourea	1 g/L
H ₂ SO ₄	As required to adjust pH
Deionized water	1 L

Cross-sectional morphology was characterized by scanning electron microscopy (SEM) using a Sigma 300 field-emission instrument (ZEISS, Oberkochen, Germany) equipped with an Ultim Max 40 energy-dispersive X-ray detector (Oxford Instruments, High Wycombe, UK) for local compositional analysis by energy-dispersive X-ray spectroscopy (EDS). Local EDS gave Ni, Si, W, and C mass fractions of 82.48%, 6.99%, 4.56%, and 5.96%, respectively. These semiquantitative values describe the analyzed region; overlap between the Si $K\alpha$ and W $M\alpha$ peaks limits the quantitative separation of Si and W. The full cross-section, higher-magnification view, spectrum, and local uncertainty estimates are retained in Figure S1 and Table S1.

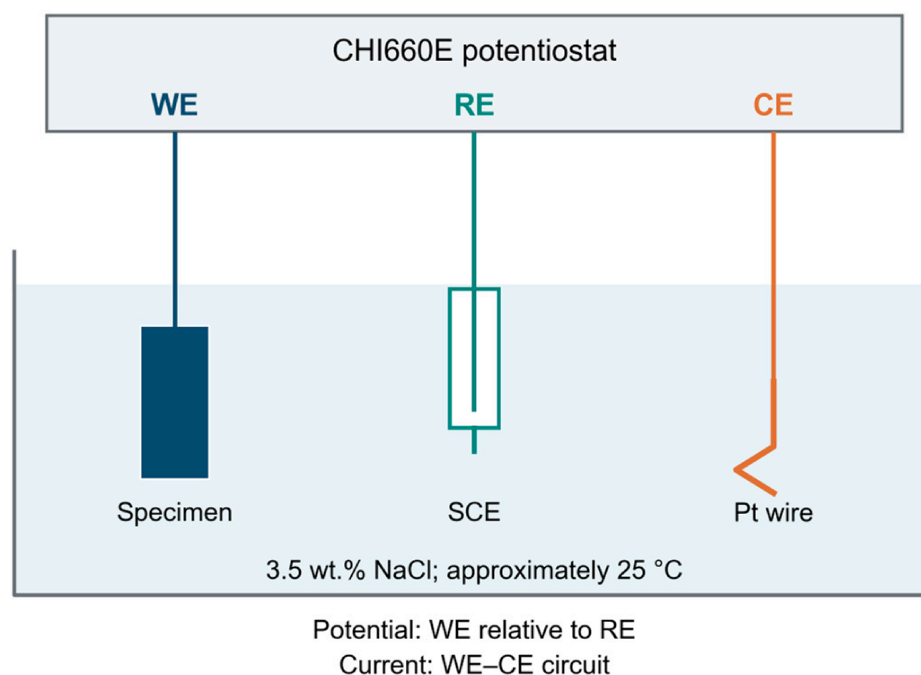
Ten lateral positions within one cross-sectional image from one specimen were analyzed. Image-plane distances were measured between the resolved composite-band boundaries, following the original line-gauge convention and using the native TIFF pixel calibration (Section S11). The within-field mean apparent thickness was 179.3 μm , with a positional standard deviation of 1.2 μm and a within-field range of 176.8–180.9 μm . The original 179.8 μm gauge label in the cross-section image remains a single local measurement. Figure S5 and Tables S12 and S13 give the ten measurement locations, values, and statistics.

2.2. Polarization Tests and Interfacial Inputs

Electrochemical tests were performed using a CHI660E workstation (CH Instruments, Inc., Austin, TX, USA), with the specimen, a platinum wire and a saturated calomel electrode (SCE) serving as the working, counter and reference electrodes, respectively (Figure 1). Tests used 3.5 wt.% NaCl at approximately 25 °C. The open-circuit potential was recorded for 1200 s, followed by electrochemical impedance spectroscopy (EIS) with a 5 mV perturbation and a programmed frequency range of 100 kHz to 0.01 Hz, then polarization scanning at 1 mV/s. A circuit fit with a series resistor and a parallel resistance–constant phase element (CPE) branch gave solution resistances of 13.8, 11.8 and 10.2 Ω for S1, S2 and Q345B, respectively; Section S2 reports the fit and voltage-drop diagnostics. The workstation controlled the working electrode potential relative to SCE and measured current through the working–counter electrode circuit.

For polarization measurements, the specimens were embedded in an insulating mounting material with an electrical lead brought out from the embedded part. An insulating mask around the test face defined the exposed window and its exposed area. The recorded exposed areas, rather than the nominal specimen-face area, were used to normalize current (Table 2).

Three-electrode connections



Connections only; electrode spacing is not to scale.

Figure 1. Three-electrode connections: the specimen working electrode, saturated calomel reference electrode and platinum wire counter electrode. The schematic shows electrical roles and is not drawn to the measured electrode spacing or specimen dimensions.

Table 2. Polarization inputs and their uses.

Input	Exposed Area (mm ²)	Interpolation Range (V vs. SCE)	Use
Coating specimen 1	51.8	−0.600 to 0.059	Coating input sensitivity comparison
Coating specimen 2	92.4	−0.600 to 0.103	Coating input sensitivity comparison
Q345B steel specimen	131.8	−0.800 to −0.304	Interfacial input for the steel reaction region
Coating reference curve	—	−0.600 to 0.059	Comparisons of shape, electrolyte film thickness, linear groove width, and sidewall reaction boundaries

The two Ni–W/SiC polarization curves were measured on specimens deposited from the bath in Table 1, with a SiC concentration of 10 g/L. Specimen 1 and specimen 2 distinguish these two measured inputs. Figure 2 shows the measured curves after normalization by exposed area and the arithmetic coating reference. For each measured curve, the valid scan segment before the abrupt current drop was retained. The plot uses absolute net current density on a logarithmic axis; the interpolation functions retain the signed values. The coating dataset comprises two specimens, with one measured polarization curve from each.

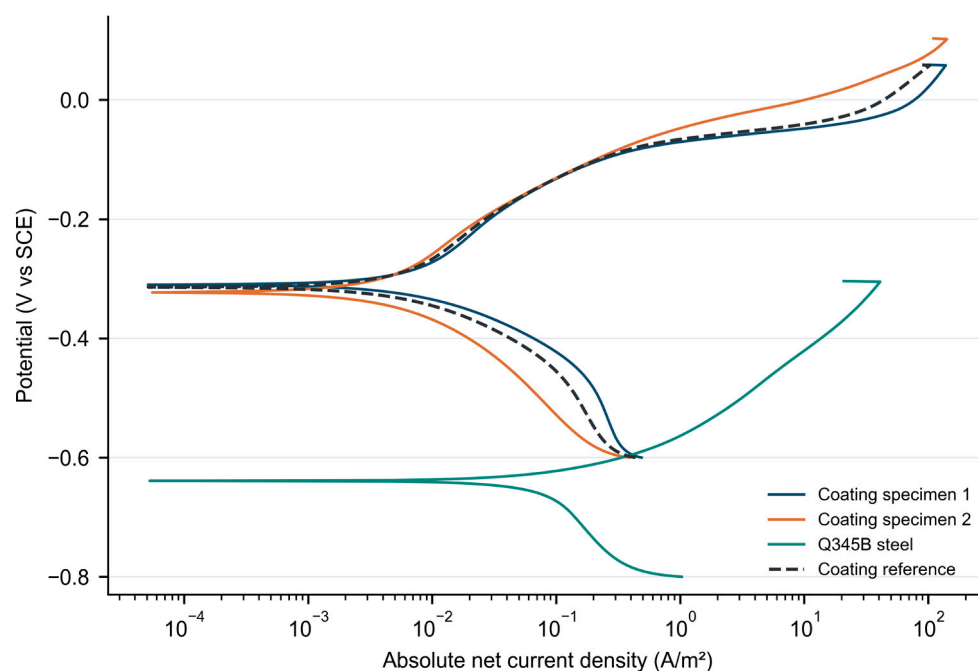


Figure 2. Measured polarization curves normalized by recorded exposed area and the arithmetic coating reference. Specimens 1 and 2 are the only two coating polarization specimens; the dashed reference is derived from these curves. Absolute net current density is plotted, whereas signed input values are used in the model.

The model used two polarization curves for the Ni–W/SiC composite coating and one for Q345B steel. The raw current was converted to net current density using the exposed area of each specimen, with anodic current defined as positive: $j = -I_{\text{raw}} / A$. The exposed area, valid interpolation range, and use of each input are given in Table 2.

A common coating input was constructed for the geometry comparisons by interpolating both measured coating curves onto their shared potential grid and taking the arithmetic mean of their signed net current densities. Equation (1) defines this reference curve; it is a data-processing definition rather than a separate experimental measurement:

$$j_{\text{coat,ref}}(E) = \frac{j_{\text{coat,1}}(E) + j_{\text{coat,2}}(E)}{2}. \quad (1)$$

The two measured coating curves were also applied separately to five configurations at a fixed electrolyte film thickness of 3.209 μm : the equal-area linear, elliptical, and circular grooves; the wider linear groove; and the linear groove with the Q345B response assigned to its sidewalls. The Q345B polarization curve remained unchanged. These comparisons assessed the sensitivity of the geometry-dependent current metrics to the selected coating input.

Polarization data processing comprised branch regression and model interpolation. The potential at zero current, E_0 , was first determined by linear interpolation between adjacent current points of opposite sign. The low-potential branch spanned $E_0 - 120$ to $E_0 - 40$ mV, and the high-potential branch spanned $E_0 + 40$ to $E_0 + 120$ mV. Eighty original scan points from each branch were used for an unweighted least squares regression of E against $\log_{10}(|I|/1 \text{ A})$. Figure S2a–c show the branch regressions for the three measured curves. Table S2 lists the regression metrics used to describe linearity within the selected intervals.

The finite element model directly used the piecewise linear interpolation of the complete net polarization curves after area normalization. The six branch regressions gave $R^2 = 0.9869\text{--}0.9990$ and potential RMSE = 0.739–2.64 mV (Figure S2 and Table S2); these

describe linearity in the selected scan windows, rather than agreement between simulated and measured galvanic currents. Values outside the full interpolation ranges were assigned the constant endpoint values by COMSOL Multiphysics 6.4. Local interfacial potentials in every saved solution were checked against the applicable measured range, as reported in Section 3.1.

2.3. Electrolyte Film Thickness and Electrolyte Parameters

All calculations use 3.5 wt.% NaCl at 25 °C, matching the polarization electrolyte. The Laliberté relation [35] and corrected Sen–Goode relation [36,37] give a solution density of $1.022 \times 10^3 \text{ kg/m}^3$ and a conductivity of 5.52 S/m, respectively. Both values apply to all prescribed film thicknesses. Section 2.7 and Section S14 specify the oxygen parameters for conditional coupling. Experimental conductance measurements and molecular calculations provide additional context for NaCl conductivity [38,39].

The mass fraction w and solution density ρ give the NaCl molar concentration through the mass-to-mole conversion:

$$c_{\text{NaCl}} = \frac{\rho w}{M_{\text{NaCl}}} \quad (2)$$

With $w = 0.035$ and $M_{\text{NaCl}} = 0.05844 \text{ kg/mol}$, Equation (2) gives $c_{\text{NaCl}} = 612 \text{ mol/m}^3$. Surface-film thicknesses of 0.642, 3.209 and 6.418 μm are prescribed geometric inputs spanning approximately one order of magnitude in a 1:5:10 ratio (Table 3). These levels retain the existing geometry cases for comparison and isolate the film thickness effect at a common electrolyte composition. The film occupies the region above the coating top surface; the filling of the finite-depth groove is specified separately.

Table 3. Prescribed surface-film thicknesses at a common electrolyte composition.

Case	Prescribed h (μm)
Thin	0.642
Intermediate	3.209
Thick	6.418

All cases use 3.5 wt.% NaCl at 25 °C. Film thickness is measured from the coating top surface; the electrolyte-filled groove depth is 180 μm .

Equation (2) is a unit conversion; density is supplied by the literature relation [35]. No relative humidity or deposited salt boundary is imposed in this comparison.

The common model inputs are molality 0.621 mol/kg H_2O , concentration 612 mol/ m^3 , density $1.022 \times 10^3 \text{ kg/m}^3$ and conductivity 5.52 S/m. Increasing the prescribed film thickness increases liquid volume and the cross-section available for lateral conduction while retaining the same composition.

The ratios of groove depth to surface-film thickness are approximately 280, 56 and 28. The film thickness specifies liquid above the coating, whereas the much deeper cavity can contain a locally retained reservoir. Complete filling defines an idealized retained-liquid configuration. At constant composition and density, the 1:5:10 surface-film volume ratio also changes the dissolved salt inventory. The thickness series therefore isolates geometry at a common composition; humidity-driven evolution at fixed deposited salt would involve concurrent changes in concentration and volume. Film thickness and groove filling are prescribed independently of relative humidity.

The main geometric comparisons apply the measured signed net polarization functions at this common concentration. A separate coupling analysis reconstructs nonnegative partial reactions and solves oxygen diffusion with feedback to the net interfacial current. This analysis tests selected reaction and transport assumptions at the same composition; it is described in Section 2.7 and reported in Section 3.7.

2.4. Defect Geometry and Comparison Design

The model used an idealized $200\text{ mm} \times 100\text{ mm}$ coated surface for controlled comparisons of scratch geometry. These dimensions specify the computational domain independently of the smaller specimens used to measure polarization inputs in Section 2.2. The cross-sectional image analysis in Section 2.1 supplied the approximately 0.18 mm depth scale, and a through-coating groove depth of $180\text{ }\mu\text{m}$ was prescribed for every baseline comparison. The groove bottom was assigned the Q345B response, and its sidewalls connected the bottom to the coating top surface. In the baseline comparisons, the groove was assumed to be completely filled with electrolyte and connected to a continuous surface film. Figure 3b shows these regions and the position of the groove within the modeled surface. Section 2.8 defines the additional partial-filling configurations.

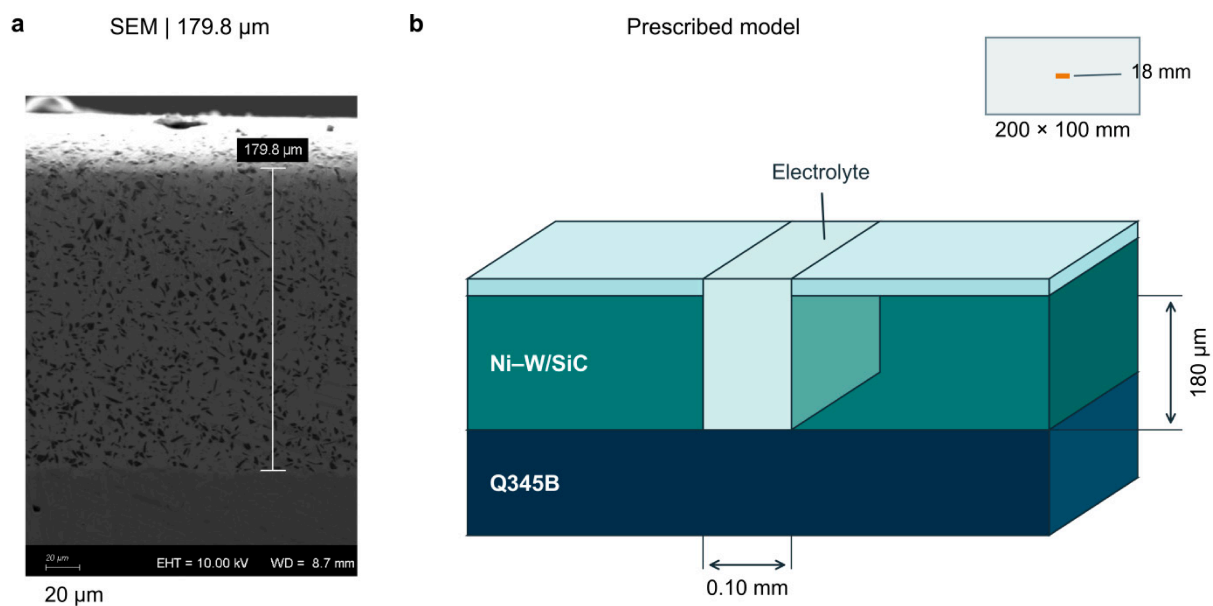


Figure 3. The cross-section of the Ni-W/SiC composite coating and through-coating groove model: (a) a scanning electron microscopy (SEM) image of the coating cross-section with the original single-point $179.8\text{ }\mu\text{m}$ gauge; (b) a schematic of the model geometry.

To compare the effect of planform shape, linear, elliptical, and circular defects were modeled, each with a prescribed groove bottom area of 1.80 mm^2 . The linear groove was 18 mm long and 0.10 mm wide. The elliptical groove had a ratio of the major axis to the minor axis of 2:1, with major and minor axes of approximately 2.141 and 1.070 mm ; the circular groove had a diameter of approximately 1.514 mm . Dimensions for the elliptical and circular grooves were rounded from the values calculated for equal areas. Discrete integration over curved domains introduced small area deviations. Under the baseline mesh condition with a $3.209\text{ }\mu\text{m}$ electrolyte film, the actual integrated groove bottom areas of the elliptical and circular grooves were 1.787 and 1.793 mm^2 , respectively. The mean current density for each was calculated using its actual integrated area.

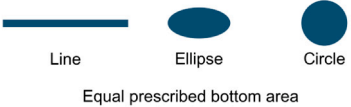
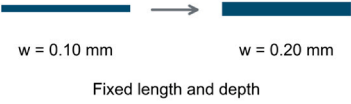
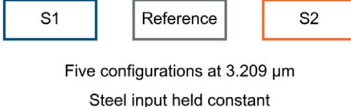
The prescribed surface film covers the projected domain, and the groove cavity contains additional electrolyte of the same composition. The baseline linear cavity volume is $0.324\text{ }\mu\text{L}$, equal to approximately 2.52% of the thinnest surface-film volume. This definition increases total electrolyte and salt inventory together without changing concentration. Equal-total-volume controls reduce the surface film to account for the filled cavity (Section S10).

The baseline case used an $18\text{ mm} \times 0.10\text{ mm}$ linear groove, a $3.209\text{ }\mu\text{m}$ electrolyte film, and the Ni-W/SiC polarization response assigned to the sidewalls. The comparison of

shape and film thickness used electrolyte film thicknesses of 0.642, 3.209, and 6.418 μm , forming a 3×3 calculation matrix. All cases used the coating reference curve and the Ni-W/SiC polarization response assigned to the sidewalls. The linear groove width comparison was conducted with a 3.209 μm electrolyte film. With the groove length fixed at 18 mm, the groove depth at 180 μm , and all other inputs unchanged, the width was increased from 0.10 to 0.20 mm and the groove bottom area from 1.80 to 3.60 mm^2 .

For the sidewall comparison, the 18 mm $\times$ 0.10 mm groove, 3.209 μm surface film, and coating reference input were held constant. The sidewalls were assigned either the Ni-W/SiC or Q345B polarization response. The steel reaction area was therefore either the 1.80 mm^2 bottom alone or the bottom plus 6.516 mm^2 of sidewalls, totaling 8.316 mm^2 . This prescribed boundary change varies both sidewall kinetics and the steel reaction area. Table 4 summarizes the comparison design; the diagrams identify the changed geometry or input.

Table 4. Comparison design and schematic diagrams. Dimensions and boundary assignments refer to the model; diagrams are not to scale.

Comparison	Varied Factor	Common Settings	Diagram
Shape $\times$ film thickness	Line/ellipse/circle; $h = 0.642, 3.209, 6.418 \mu\text{m}$	Bottom area 1.80 mm^2 ; reference input; coating walls	 Line Ellipse Circle Equal prescribed bottom area
Groove width	0.10 $\rightarrow$ 0.20 mm; bottom area 1.80 $\rightarrow$ 3.60 mm^2	Length 18 mm; $h = 3.209 \mu\text{m}$; reference input; coating walls	 $w = 0.10 \text{ mm}$ $w = 0.20 \text{ mm}$ Fixed length and depth
Sidewall assignment	Coating $\rightarrow$ steel response; steel area 1.80 $\rightarrow$ 8.316 mm^2	18 $\times$ 0.10 mm groove; $h = 3.209 \mu\text{m}$; reference input	 Coating walls Steel walls Bottom: steel in both cases
Coating input	Specimen 1/reference/specimen 2	Five configurations; $h = 3.209 \mu\text{m}$; common steel input	 S1 Reference S2 Five configurations at 3.209 μm Steel input held constant

The arrows indicate changes from the baseline condition to the comparison condition. All configurations use a prescribed groove depth of 180 μm and the Q345B polarization input on the bottom. Blue and orange in the sidewall diagrams denote coating and steel reaction assignments. The shape/width cartoons are plan views; the sidewall cartoons are cross-sections. The input comparison covers the three equal-area shapes, the wider line, and the line with steel sidewalls. The 3×3 shape–thickness matrix uses the reference coating curve.

2.5. Governing Equations, Interfacial Boundaries, and Solution

For uniform electrolyte conductivity, the potential field follows current continuity and Ohm's law, as used in conduction-based galvanic models [25,29,30]:

$$J_1 = -\kappa \nabla \phi_1, \quad \nabla \cdot J_1 = 0, \quad (3)$$

Here, J_1 is the electrolyte current density vector, κ is conductivity, and ϕ_1 is the electrolyte potential. All external boundaries other than the electrode reaction interfaces were electrically insulating.

The coating and steel substrate shared a floating metal potential. A zero-potential constraint at a single electrolyte point fixed the potential reference. The local interfacial po-

tential, referenced to SCE, was determined from the difference between the metal potential and electrolyte potential:

$$E_{\text{int}} = V_{m,\text{SHE}} - \phi_1 - 0.2444\text{V} = V_{m,\text{SCE}} - \phi_1. \quad (4)$$

Here, SHE denotes the standard hydrogen electrode. The adopted 0.2444 V offset is the tabulated SCE potential versus SHE at 25 °C [40], used in the saved model to convert the metal potential reference. The measured interpolation inputs remain on the SCE scale. The net current density at the steel interface was given by $j_{\text{steel}}(E_{\text{int}})$ and the raw net current density at the coating interface by $j_{\text{coat,raw}}(E_{\text{int}})$. Both were obtained from the polarization interpolation functions described in Section 2.2.

The three groove shapes have the same prescribed bottom area of 1.80 mm² and different sidewall areas. On the 200 mm × 100 mm computational surface, a common effective coating area is used to compare geometries at fixed nominal coating participation:

$$A_{\text{coat,target}} = L_x L_y - A_{\text{bottom,target}} = 0.0199982 \text{ m}^2.$$

Let the geometric coating reaction area be $A_{\text{coat,geo}}$. The area factor and the coating boundary current density applied in the model were as follows:

$$s_A = \frac{A_{\text{coat,target}}}{A_{\text{coat,geo}}}, \quad j_{\text{coat}} = s_A j_{\text{coat,raw}}. \quad (5)$$

The three groove shapes with the same prescribed groove bottom area therefore used the same raw polarization function, while their respective area factors kept the effective coating area constant. For the widened linear groove, calculation based on its groove bottom area of 3.60 mm² gave an effective coating area of 0.0199964 m².

Equation (4) defines the potential used with measured polarization data [29,30]. In Equation (5), the geometric coating area is integrated over the same coating selection to which the single global area factor is applied. Section S9 and Table S10 provide the native read-back areas and coefficients for the three reference shapes. The factor has no spatial coordinate dependence; local current varies with local interfacial potential. Coating top surfaces and coating-assigned sidewalls receive the same weight, whereas steel-assigned sidewalls enter the steel integral. For oxygen coupling, the weight multiplies both coating net current and its ORR partial current. Effective participation is varied through $q = 0.01$, 0.1 and 1 at fixed electrolyte geometry (Section S12), corresponding to nominal coating-to-bottom area ratios of approximately 111, 1110 and 11,100.

For the electrically coupled coating and substrate, the floating metal potential was determined by zero net current over all reaction surfaces, the charge conservation condition used in galvanic coupling models [29,30]:

$$\int_{\Gamma_{\text{steel}}} j_{\text{steel}} \, dA + \int_{\Gamma_{\text{coat}}} j_{\text{coat}} \, dA = 0. \quad (6)$$

Here, Γ_{steel} and Γ_{coat} denote the interfaces assigned the steel and coating polarization responses, respectively. In the case with steel sidewalls, Γ_{steel} included both the groove bottom and sidewalls.

The model was built in COMSOL Multiphysics 6.4, and the potential field at steady state was solved using the PARDISO solver with a relative tolerance of 1×10^{-7} .

Linearized interfacial responses were used to initialize the potential field, followed by the complete measured polarization functions. The floating metal potential was adjusted through an external root search to satisfy the current balance criterion. Initialization settings are documented in Section S4.

2.6. Current Metrics and Numerical Checks

The signed integrated groove bottom current I_{bottom} and mean groove bottom current density $\bar{j}_{\text{bottom}}$ were defined as follows:

$$I_{\text{bottom}} = \int_{\Gamma_{\text{bottom}}} j_{\text{steel}} dA. \quad (7a)$$

$$\bar{j}_{\text{bottom}} = \frac{I_{\text{bottom}}}{A_{\text{bottom}}}. \quad (7b)$$

Equations (7a,b) and (8) define the surface-integrated outputs used in this study. For the case with steel sidewalls, the total steel current includes both the groove bottom and sidewalls:

$$I_{\text{steel,total}} = \int_{\Gamma_{\text{steel}}} j_{\text{steel}} dA = I_{\text{bottom}} + I_{\text{sidewall}}. \quad (8)$$

Current signs were retained during integration. Field plots show the positive component of bottom net current density, $\max(j_{\text{bottom}}, 0)$. The area-weighted 99.5th percentile characterizes the upper tail: a threshold is located by bisection at which the cumulative bottom area fraction reaches 0.995. The metric is evaluated from the continuous finite element field rather than by counting mesh nodes.

The reported current is a net interfacial current. With nonnegative magnitudes for the partial anodic and cathodic currents, $j_{\text{net}} = j_a - j_{\text{ORR}} - j_{\text{c,other}}$. A positive local value indicates a net anodic response, and $\max(j_{\text{net}}, 0)$ is its positive part, not the anodic metal dissolution partial current. The bottom integral and mean density quantify net current distribution under the prescribed conditions. These net current metrics describe electrochemical response; quantitative penetration or mass-loss rates require the anodic dissolution current.

Shape span at each film thickness was defined as $(I_{\text{max}} - I_{\text{min}})/I_{\text{min}} \times 100\%$. Changes with linear groove width were calculated relative to the 0.10 mm case. Currents over the groove bottom, sidewalls, and all exposed steel surfaces were reported separately for the sidewall comparison. The 3×3 matrix of shape and film thickness was summarized by a descriptive decomposition of sums of squares for two factors, without replication. The modeled variation was separated into components associated with film thickness, shape, and the residual nonadditive term. This decomposition was descriptive; no significance test was applied.

The cavity and surface film use swept meshes built from triangular source faces on the bottom and coating top. The primary mesh uses in-plane division parameter 6 and four layers through each liquid domain. Successive primary refinements and their actual settings are listed in Sections S4 and S8. Conditional oxygen calculations use their own refinement sequences, documented in Section S15.

Primary model refinement covers the elliptical groove at all three film thicknesses and the circular and linear grooves at the thinnest film, giving five representative sequences and twelve adjacent-level comparisons. Oxygen-coupled refinement covers all nine shape–thickness combinations for the representative reaction scenario. Equation (9) defines the symmetric relative mesh difference:

$$\delta_x = \frac{2|x_{\text{baseline}} - x_{\text{refined}}|}{|x_{\text{baseline}}| + |x_{\text{refined}}|} \times 100\%. \quad (9)$$

Here, x_{baseline} and x_{refined} denote the values obtained with the baseline and refined meshes, respectively.

Acceptance limits are 1% for integrated bottom current, 1% for mean density, 5% for its 99.5th percentile and 0.5 mV for metal potential. The representative electrolyte potential drop is the difference between area averages over the bottom and coating top, excluding

sidewalls; its mesh difference limit is 0.1 mV. Oxygen-coupled checks additionally require a relative mesh difference below 1% in the minimum c/c^* . ORR integral changes are retained as a supplementary diagnostic.

Additional checks cover equal-total-electrolyte-volume controls, effective coating participation and the negligible ohmic drop limit (Sections S10, S12 and S13). Conditional oxygen boundaries are checked against one-dimensional analytical solutions, source-condition recovery and signed flux balances (Section S14). Relative changes and mesh differences are calculated from unrounded outputs; displayed values are rounded independently. An external CS/SS benchmark compares calculated junction recession with published corrosion depth measurements [26], using the source geometry and electrochemical parameters (Section S16).

Polarization interpolation ranges and current balance were checked for every saved solution. The minimum and maximum local interfacial potentials over each reaction region, including reactive sidewalls, were compared with the complete potential range of the corresponding polarization curve. The current balance residual was calculated as the absolute sum of the signed integrated currents over all steel and coating reaction surfaces, normalized by the larger absolute value of the integrated steel and coating currents. A residual below 10^{-6} was required. The signed currents were also integrated separately over the bottom, sidewalls, and coating top surface to check their reconstruction of the total current.

2.7. Conditional Coupling of Oxygen Transport

The net polarization curves do not separately identify oxygen reduction and other partial reactions. We therefore use a conditional reconstruction that preserves each measured net curve at a defined calibration state. Let $r(E) = f j_{c,cal}(E)$ be the nonnegative calibration cathodic component assigned to the ORR and $L_{cal} = M L_{base}$ its specified transport limit. The source-condition transport contribution is removed before solving transport in the new film [41,42]:

$$K(E) = \frac{r(E)}{1 - \frac{r(E)}{L_{cal}}}, \quad 0 \leq r(E) < L_{cal}. \quad (10a)$$

$$j_{net}(E, c) = j_{meas}(E) + r(E) - K(E) \frac{c}{c^*}. \quad (10b)$$

At $\frac{c_{cal}}{c^*} = 1 - \frac{r}{L_{cal}}$, Equation (10b), with K from Equation (10a), recovers j_{meas} . The coating reference averages the reconstructed S1 and S2 components. Steady-state oxygen diffusion obeys $\nabla \cdot (-D \nabla c) = 0$. Using the outward liquid normal, electrode consumption is $\mathbf{n} \cdot (-D \nabla c) = \frac{Kc}{4Fc^*}$, and gas supply is $\mathbf{n} \cdot (-D \nabla c) = -k_g(c^* - c)$. All remaining outer boundaries have zero oxygen flux. The ORR is counted on both the coating and steel, including locations where the steel net current is anodic. The coating area factor multiplies its net current and oxygen consumption terms consistently.

The prescribed oxygen parameters are $c^* = 0.214 \text{ mol/m}^3$, $D = 2.23 \times 10^{-9} \text{ m}^2/\text{s}$ and $4F k_g c^* = 3.0 \text{ A/m}^2$, with a four-electron, first-order oxygen reaction. The c^* value follows the saline-solubility calculation [43]; D and k_g are fixed scenario inputs. Three reaction scenarios use $(f, M) = (1, 1)$, $(0.5, 1)$ and $(1, 10)$, with the reference coating input and coating sidewalls. Section S14 gives parameter origins, partial current construction, units and one-dimensional analytical/source-recovery checks. Each coupled case is compared with a no-feedback solve on the same mesh. The reported outputs are bottom net current, total steel net current, total ORR consumption $I_{ORR}/(4F)$ and minimum oxygen concentration; Section S15 gives the full results.

Over the same steel selection, the conditional anodic current equals the net current plus the ORR and remaining cathodic partial currents. The remaining term is zero for

$f = 1$. For $f = 0.5$, the integral of $(1 - f)j_{c,cal}$ must also be included. These integrals were evaluated from the saved fields using the original reaction parameters. Section S18 reports the conditional decomposition separately for the final representative meshes and the normal-mesh scenarios.

2.8. Prescribed Partial Groove Filling

Groove filling sensitivity was examined at a surface-film thickness of $3.209\ \mu\text{m}$ for the three reference shapes. In addition to full filling, the prescribed groove liquid volume fraction, $F_v = V_{\text{liquid,groove}}/(A_b d)$, was 0.50 or 0.25. The $180\ \mu\text{m}$ depth, nominal $1.80\ \text{mm}^2$ bottom area and coating sidewall response remained unchanged. A bottom liquid pool was connected to the film over the intact coating by a sidewall liquid layer of thickness $\delta = 3.209\ \mu\text{m}$. The central air region extended through the groove mouth to the atmosphere, with no liquid lid. The steel bottom and coating sidewalls remained fully wetted (Figure S7).

The air-core cross-section was obtained by a true inward normal offset of thickness δ from each groove perimeter. If its area is A_{core} , the pool height H measured from the groove bottom is

$$H = d\left[1 - \frac{(1 - F_v)A_b}{A_{\text{core}}}\right]. \quad (11)$$

Equation (11) includes liquid in the sidewall layer, so $F_v = 0.50$ does not generally give $H = d/2$. The flat interfaces and filling fractions define a prescribed wetting sensitivity comparison; predicting their evolution would require contact angle, salt deposition and humidity-dependent liquid balance models. Both the net curve and representative oxygen-coupled branches ($f = 1$, $M = 1$) retain the original interfacial inputs, coating area factors and transport parameters. All gas–liquid interfaces adjoining the open air region receive the original Robin supply condition. The gas boundary uses a uniform prescribed atmospheric oxygen activity.

The two center-plane symmetries permit a quarter-domain calculation with zero normal charge and oxygen flux on the cut planes. Extensive outputs are multiplied by four; local densities and concentrations are unchanged. Full-domain pilot comparisons and successive mesh refinement are reported in Section S17. The numerical criteria in Section 2.6 also apply here, with a 1% refinement limit for the additional steel ORR and conditional anodic integrals. The corresponding results are reported in Section 3.8.

3. Simulation Results

3.1. Input Sensitivity and Model Reliability

For the baseline linear groove at $3.209\ \mu\text{m}$, the two measured coating inputs gave bottom currents of 17.78 and $13.25\ \mu\text{A}$ and mean bottom current densities of 9.88 and $7.36\ \text{A}/\text{m}^2$ (Figure 4). The simulated currents differed by $4.53\ \mu\text{A}$ or 34.2% relative to specimen 2.

The reference input gave a bottom current of $15.99\ \mu\text{A}$, between the two specimen-specific results (Figure 4a). Floating metal potentials were -309.8 , -314.2 and $-322.7\ \text{mV}$ vs. SCE for S1, the reference and S2, respectively (Figure 4b). Sections 3.2–3.5 use the reference; Section 3.6 compares all three inputs at $3.209\ \mu\text{m}$.

All five primary refinement sequences met the unchanged acceptance limits on their final adjacent-level comparison. The largest final differences were 0.033% in bottom current, 0.100% in mean density, 0.099% in the 99.5th percentile, 0.0104 mV in metal potential and 0.0677 mV in representative potential drop (Figure 5; Tables S3 and S4).

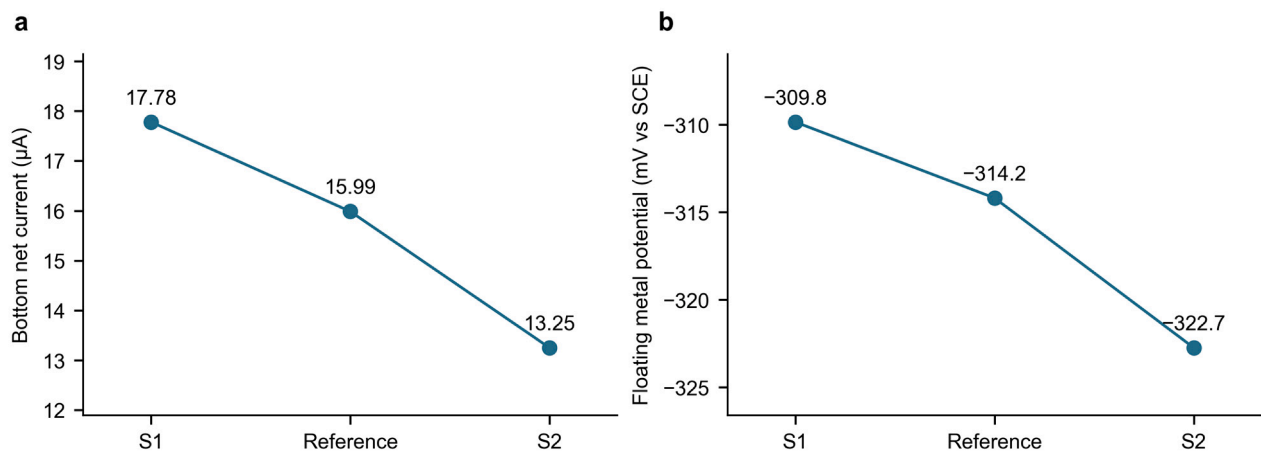


Figure 4. Simulated responses to the two measured coating curves and their arithmetic reference: (a) integrated groove bottom current; (b) floating metal potential. All cases use the baseline linear groove, a $3.209\ \mu\text{m}$ electrolyte film, coating-assigned sidewalls, and the baseline mesh. Lines connect three deterministic input cases; they do not represent a fitted relation.

Mesh change / acceptance limit (%)					
Values above 100 exceed the specified limit					
Circle · $0.642\ \mu\text{m}$ · N→F	3.1	19.9	4.0	2.1	111.1
Circle · $0.642\ \mu\text{m}$ · F→FF	3.3	9.6	1.9	2.1	53.2
Ellipse · $0.642\ \mu\text{m}$ · N→F	2.2	28.0	5.6	1.9	162.0
Ellipse · $0.642\ \mu\text{m}$ · F→FF	2.6	29.7	6.0	0.5	170.9
Ellipse · $0.642\ \mu\text{m}$ · FF→FFF	1.6	10.0	2.0	0.2	57.2
Ellipse · $3.209\ \mu\text{m}$ · N→F	2.8	23.0	4.7	1.1	164.4
Ellipse · $3.209\ \mu\text{m}$ · F→FF	4.7	22.4	4.7	1.1	159.8
Ellipse · $3.209\ \mu\text{m}$ · FF→FFF	2.6	9.0	1.8	0.3	64.4
Ellipse · $6.418\ \mu\text{m}$ · N→F	2.9	22.9	4.5	0.7	155.7
Ellipse · $6.418\ \mu\text{m}$ · F→FF	5.1	22.0	4.4	0.0	148.5
Ellipse · $6.418\ \mu\text{m}$ · FF→FFF	1.6	10.0	1.9	0.8	67.7
Line · $0.642\ \mu\text{m}$ · N→F	0.2	0.2	0.1	1.9	1.6
	Bottom I	Mean j	99.5% j	Metal E	Representative Δp

Figure 5. Twelve adjacent-level comparisons in five representative primary model refinement sequences. Values show the mesh difference as a percentage of its unchanged acceptance limit. Coral cells exceed 100%; N, F, FF and FFF identify successive meshes within this primary model family.

Figure 5 retains every adjacent-level comparison, including early exceedances. Each value is the mesh difference divided by its acceptance limit and multiplied by 100%; values above 100% exceed the criterion. These normalized percentages differ from the mesh differences themselves.

The initial elliptical groove comparisons exceeded the $0.1\ \text{mV}$ potential drop criterion. Continuing from in-plane parameter/layer pairs 8/5 to 12/7 and 18/10 reduced the final differences to 0.0572, 0.0644, 0.0677 mV at 0.642, 3.209 and $6.418\ \mu\text{m}$. The thin-film circular groove also required an additional refinement. The principal geometry results use

the selected saved solutions listed in Supplementary Data; failed earlier pairs remain in Tables S4 and S9.

The 36 matched-concentration configurations satisfied the 10^{-6} current balance criterion, with a maximum residual of 2.71×10^{-7} . Saved interfacial potentials remained inside their measured interpolation ranges. The reported integrals were checked after saving and reloading the native models (Tables S7 and S8). Table S21 lists the configuration families.

Equal-total-volume controls at the thinnest film reduced surface-film thickness to approximately $0.626 \mu\text{m}$. Bottom current changed by -0.81% for the linear, -1.30% for the elliptical and -1.33% for the circular groove relative to their corresponding uncorrected controls (Table S11). These values quantify the effect of accounting for cavity filling in the liquid inventory; they do not change the prescribed $180 \mu\text{m}$ depth or the electrolyte concentration.

At $3.209 \mu\text{m}$, reducing uniform effective coating participation to $q = 0.1$ or 0.01 changed bottom net current by -61.6% to -25.5% in the net curve controls and -60.3% to -26.3% with the representative conditional oxygen boundary (Tables S14 and S15). Each value compares the same shape and reaction setting with $q = 1$. The coefficient changes participation within the retained electrolyte domain; it does not change the physical coupon dimensions or represent spatially patchy wetting. At $q = 0.01$, the refined ellipse/circle separation is only 0.87% without feedback and 0.95% with feedback. Both orderings are retained through refinement, while the area comparison primarily distinguishes the line from the two compact defects (Section S12).

A separate piecewise linear calculation gives the negligible ohmic drop limit of the net current model. The finite element check uses imposed conductivities of 1.708×10^3 and $1.708 \times 10^5 \text{ S/m}$; these are mathematical limiting inputs. At the higher value, steel current and metal potential differences from the independent limit were no greater than 0.0662% and 0.0161 mV (Section S13). The reused six limit cases retain the same measured interpolation tables and source geometries, verified by their saved hashes.

An external carbon steel/stainless steel benchmark compared the conduction-and-reaction framework with published corrosion depth measurements [26]. The Laplace equation with nonlinear electrode boundaries was solved for anode/cathode lengths of $7/12.1$ and $5.9/22.2 \text{ mm}$ in 0.1 mol/L NaCl , retaining the published kinetic parameters. Local anodic dissolution current was converted to recession at the electrode junction using Faraday's law. Mean absolute percentage errors were 20.7% and 25.3% , with mean absolute errors of 0.98 and $3.56 \mu\text{m}$, respectively. Both calculations and measurements showed greater steel loss at the larger cathode-to-anode ratio. Section S16 reports the observation definition, parameter values, numerical checks and pointwise errors (Figure S6; Tables S22 and S23).

3.2. Current Magnitude and Spatial Distribution for Defects with the Same Area

At $3.209 \mu\text{m}$, integrated bottom currents were 15.99 , 8.16 and $8.00 \mu\text{A}$ for the linear, elliptical and circular grooves, respectively (Figure 6d). The linear value exceeded the elliptical value by 96.0% and the circular value by 99.7% . The compact shapes gave similar currents despite their different planforms.

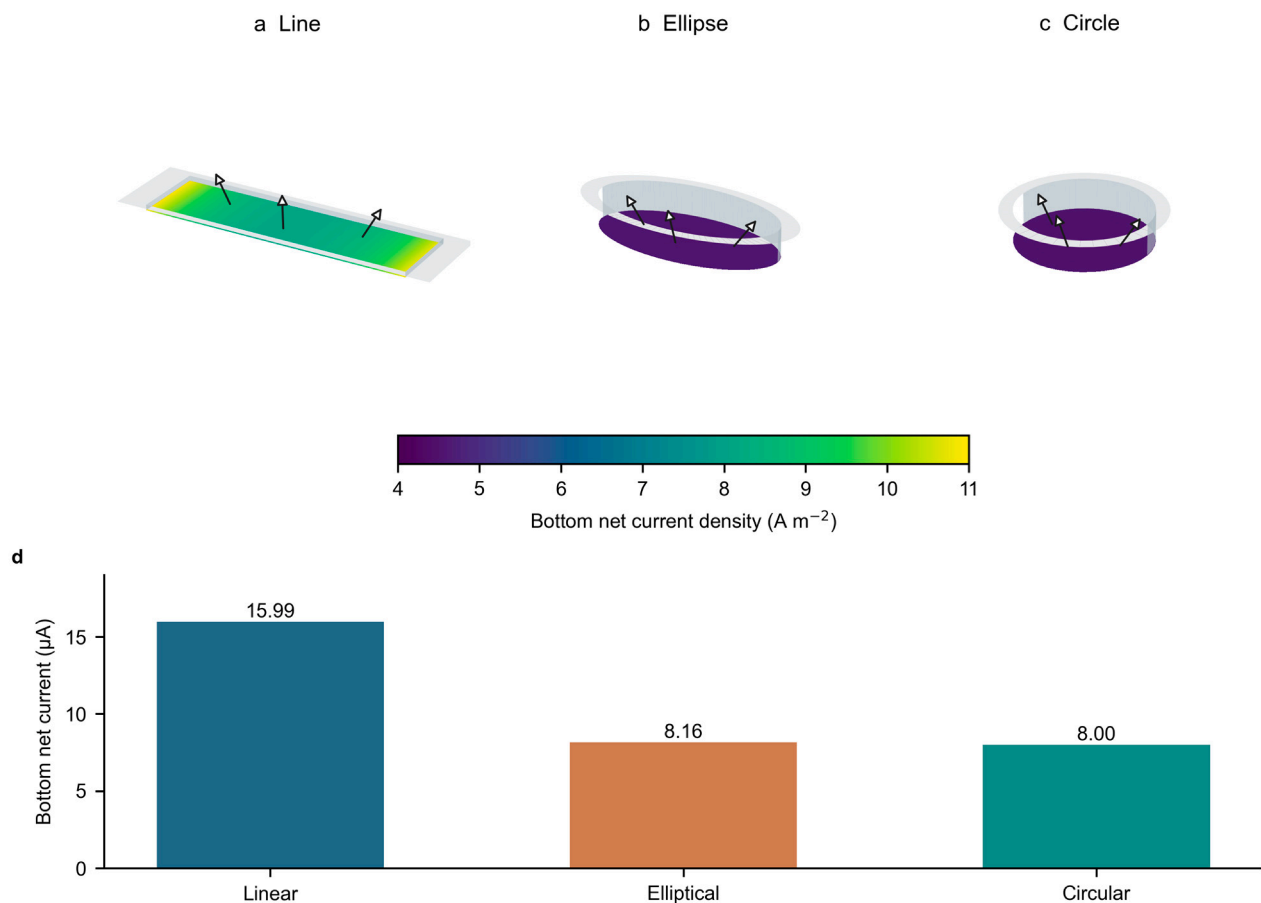


Figure 6. Reference input results at $3.209 \mu\text{m}$ with coating sidewalls: bottom net current density for (a) line, (b) ellipse and (c) circle; (d) integrated bottom net current. Cutaway dimensions use the magnifications stated in the text. Arrows indicate sampled, normalized computed electrolyte current directions, not fluid velocity.

Figure 6a–c show bottom net current density under the reference input. Native-field ranges are approximately $8.13\text{--}10.90 \text{ A/m}^2$ for the linear groove, $4.51\text{--}4.58 \text{ A/m}^2$ for the elliptical groove and $4.45\text{--}4.48 \text{ A/m}^2$ for the circular groove. The linear bottom carries both a higher density and greater spatial variation.

Local cutaways omit the near-sidewalls to expose the bottom fields. Gray surfaces provide the geometric context. The line is magnified transversely by 50 and all three depths by 2; circle and ellipse share the same physical projection scales. Arrows sample the computed conventional electrolyte current $\mathbf{J}_1 = -\kappa \nabla \phi_1$, with normalized display lengths and the same coordinate transformation.

3.3. Effect of Electrolyte Film Thickness on Differences Among Shapes

Figure 7a represents the linear groove bottom field at $3.209 \mu\text{m}$. Surface height and color both show net current density, while $\xi = x/(9 \text{ mm})$ and $\eta = y/(0.05 \text{ mm})$ normalize the physical coordinates. Triangulation is constructed in physical coordinates before the display transformation.

Table 5 and Figure 7b show the groove bottom currents for the three defects at different electrolyte film thicknesses. As electrolyte film thickness increased from 0.642 to $6.418 \mu\text{m}$, the currents increased for all three shapes, and the linear groove current remained higher than those for the elliptical and circular grooves. Values in Figure 7b were obtained from the global integration of the model and are reported to two decimal places; the current density in Figure 7a and the integrated current in Figure 7b use separate color scales and units.

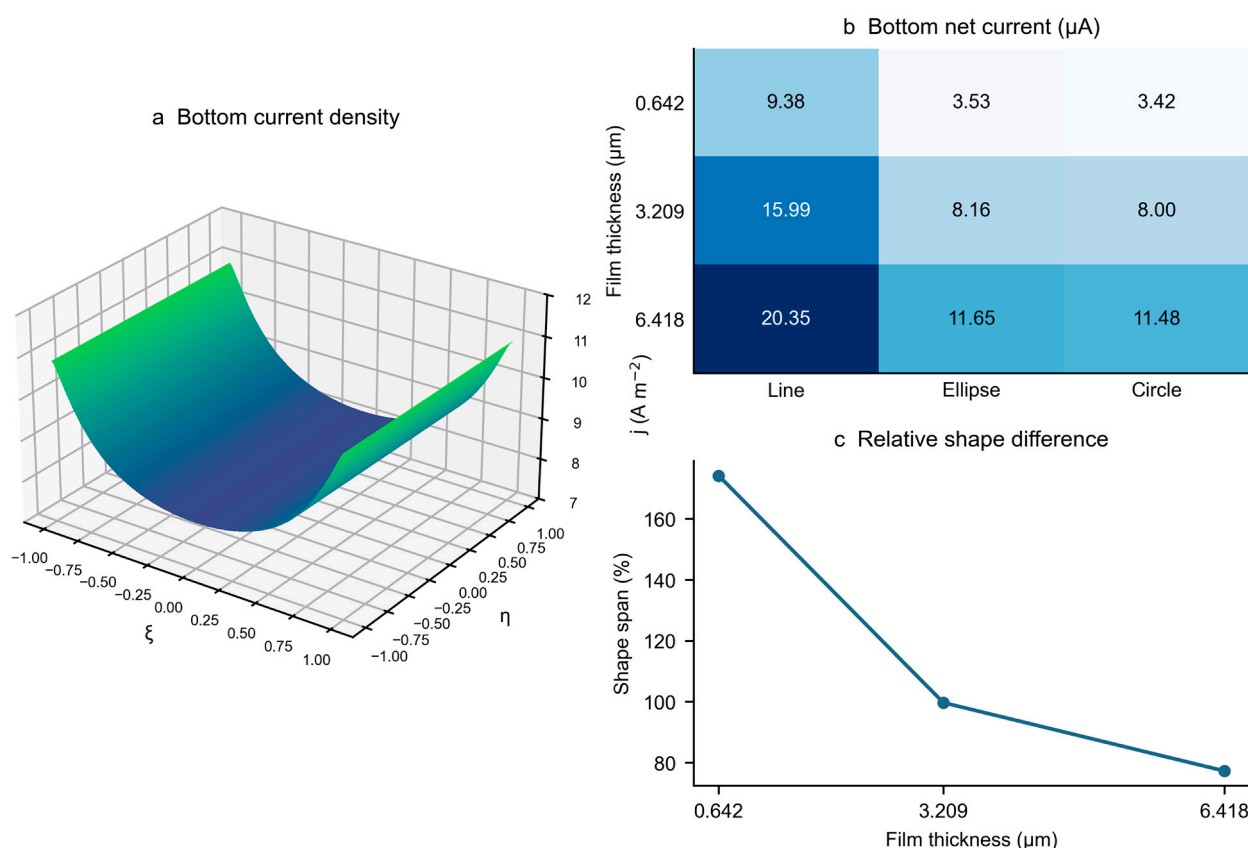


Figure 7. Effects of defect shape and electrolyte film thickness on groove bottom current: (a) current density surface plot for the linear groove bottom, where the colour scale shows the net current density; (b) matrix of integrated groove bottom current; (c) relative shape span.

Table 5. Groove bottom currents at different electrolyte film thicknesses.

h (μm)	Line I (μA)	Ellipse I (μA)	Circle I (μA)	Shape Span (%)
0.642	9.38	3.53	3.42	174.2
3.209	15.99	8.16	8.00	99.7
6.418	20.35	11.65	11.48	77.3

Primary model meshes for line/ellipse/circle are F/FFF/FF at 0.642 μm and N/FFF/N at 3.209 and 6.418 μm . Section S4 defines the mesh settings, and Section S8 documents ellipse refinement. The Main_Table5 dataset in Supplementary Data identifies each saved case. Table S5 uses N meshes throughout for paired coating input comparisons.

From 0.642 to 6.418 μm , bottom current increased by 116.9%, 230.1% and 235.4% for the linear, elliptical and circular grooves. The larger proportional increases for the compact shapes reduced shape span from 174.2% to 99.7% and 77.3% across the three film thicknesses (Figure 7c).

Current density surfaces for the linear groove at the three electrolyte film thicknesses are shown in Figure S3a–c, with the corresponding integrated groove bottom currents in Figure S3d.

In the descriptive sum-of-squares decomposition of the 3×3 matrix, film thickness, shape and the remaining nonadditive term accounted for 51.6%, 47.2% and 1.2% of total variation. These proportions describe this prescribed matrix; they are not estimates of random error or interaction significance.

3.4. Groove Bottom Current and Mean Groove Bottom Current Density with Increasing Linear Groove Width

At an electrolyte film thickness of $3.209\ \mu\text{m}$, the groove length and depth were held at 18 mm and $180\ \mu\text{m}$, respectively, while the linear groove width was increased from 0.10 to 0.20 mm. The groove bottom area increased from 1.80 to $3.60\ \text{mm}^2$. The two geometries in Figure 8a use the same lateral display magnification, and the schematics are not drawn to the true ratio of length to width.

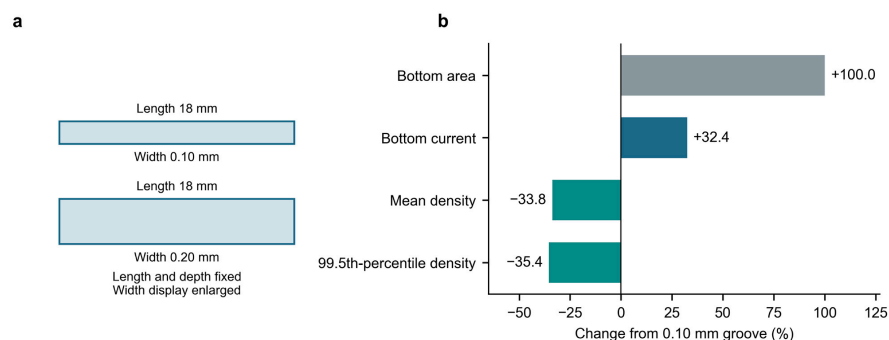


Figure 8. Changes in groove bottom current and current density with increasing linear groove width: (a) comparison of geometries with different groove widths; (b) relative changes in area and current metrics.

Doubling width increased bottom current from 15.99 to $21.17\ \mu\text{A}$ (32.4%), while mean bottom current density decreased from 8.88 to $5.88\ \text{A}/\text{m}^2$ (33.8%). The 99.5th-percentile density decreased from 10.89 to $7.04\ \text{A}/\text{m}^2$ (35.4%; Figure 8b). Changes use the narrow groove as the denominator and unrounded outputs for calculation.

3.5. Effect of Sidewall Reactions on Current Partitioning over Exposed Steel Surfaces

With the baseline linear groove geometry and electrolyte film thickness held constant, the polarization function assigned to the model sidewalls was changed from Ni-W/SiC to Q345B. The two boundary cases are shown in the upper and lower schematics in Figure 9a. Thin colored lines indicate the reaction boundary assignments on the sidewalls, and the schematics are not drawn to scale. The steel reaction area increased from $1.80\ \text{mm}^2$, comprising only the groove bottom, to $8.316\ \text{mm}^2$, comprising the groove bottom and sidewalls, as shown in Figure 9c.

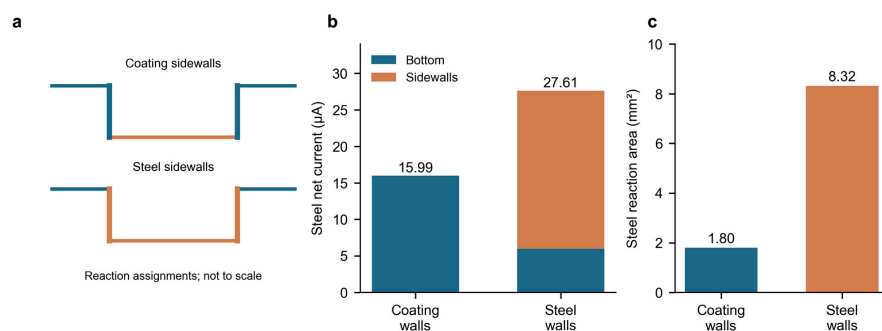


Figure 9. Current partitioning over exposed steel surfaces under the two sidewall reaction boundary conditions: (a) sidewall reaction boundaries; (b) groove bottom and sidewall currents; (c) steel reaction area.

Assigning steel to the sidewalls reduced bottom current from 15.99 to $5.96\ \mu\text{A}$ (62.7%), while total exposed steel net current increased to $27.61\ \mu\text{A}$ (72.7%). The sidewalls carried

21.65 μA or 78.4% of total steel current (Figure 9b). Independently integrated bottom and sidewall contributions reconstructed the total (Table S6).

3.6. Sensitivity of Geometry Comparisons to Coating Inputs

Both measured coating inputs retained the directions of the reference geometry comparisons at 3.209 μm (Table 6; Figure S4). The linear bottom current exceeded the circular value by 86.5%–106.9% and the elliptical value by 83.6%–102.9% (Table S5). Elliptical currents exceeded circular currents by 1.6%–1.9%.

Table 6. Changes in current metrics under the three coating inputs at a film thickness of 3.209 μm .

Coating Input	Line/Circle ΔI (%)	Width ΔI (%)	Width $\Delta \text{mean } j$ (%)	Steel Walls $\Delta \text{bottom } I$ (%)	Steel Walls $\Delta \text{total } I$ (%)
S1	106.9	33.6	−33.2	−62.2	75.4
Reference	99.7	32.4	−33.8	−62.7	72.7
S2	86.5	30.7	−34.6	−63.5	68.9

Each percentage uses the corresponding comparison case with the same coating input as its denominator. The shape comparison uses the circular groove; width and sidewall comparisons use the 0.10 mm linear groove with the coating response on its sidewalls. Reference denotes the arithmetic mean polarization curve. Positive and negative values indicate increases and decreases, respectively. The ranges described in the text span these three deterministic inputs.

Widening increased bottom current by 30.7%–33.6% and reduced mean bottom density by 33.2%–34.6%. Steel sidewalls reduced bottom current by 62.2%–63.5% while increasing total steel net current by 68.9%–75.4%. The opposing bottom and total steel responses thus persisted across the two measured inputs and their derived reference.

3.7. Conditional Oxygen Feedback Across Film Thicknesses

The 27 normal-mesh scenarios changed bottom net current by −0.80% to +19.79% relative to their same-mesh no-feedback controls (Figure 10a–c). The maximum local oxygen depletion ranged from 7.4% to 53.6% (Figure 10d–f). These percentages describe different quantities: oxygen concentration is an input to a partial reaction, whereas net current follows the balance of reaction components and the floating potential. An increase from the no-feedback control can result when the new-film supply exceeds the defined source supply after source-transport removal. Table 7 reports the four principal outputs on the final accepted representative meshes; Table S19 gives the complete normal-mesh scenario matrix.

The bottom net current ordering is line > ellipse > circle in each tested reaction scenario and film thickness and remains so on the final representative meshes. The minimum oxygen concentration does not give one invariant shape ordering. All sidewalls in this matrix use the coating response, so total steel net current equals bottom current. The width and steel sidewall results in Sections 3.4–3.6 belong to the net curve comparison; the oxygen matrix does not extend those particular boundaries.

The reconstructed anodic current exceeds steel net current by 0.0902%–1.2470% in the nine final representative full-groove cases. Across the 27 normal-mesh scenarios, including the remaining cathodic contribution where $f = 0.5$, the range is 0.0902%–1.8499% (Section S18). The net and reconstructed anodic currents retain the same line > ellipse > circle ordering in each of the twelve shape comparison groups. These differences quantify the contribution of the reconstructed cathodic partial currents to the steel current balance.

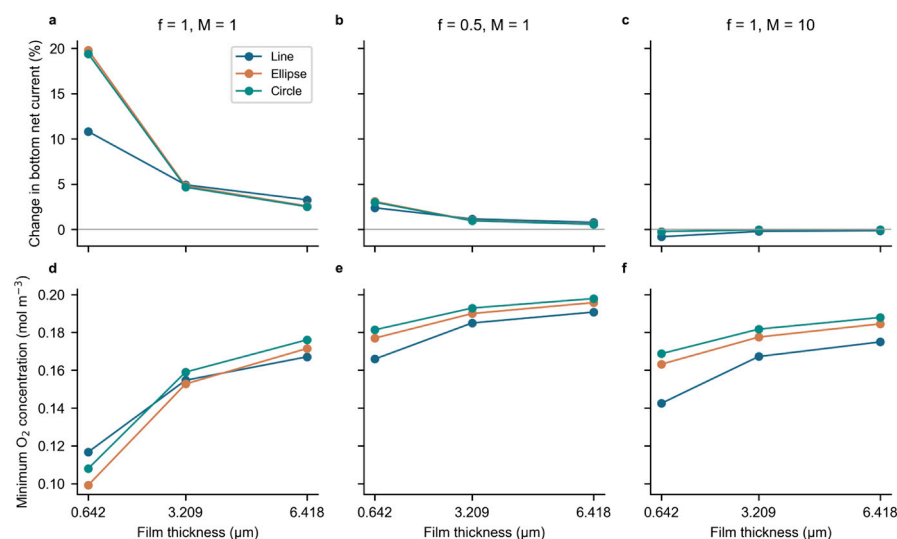


Figure 10. Conditional oxygen feedback under three prescribed reaction scenarios. Panels (a–c) give the change in bottom net current from a same-mesh no-feedback control; panels (d–f) give minimum oxygen concentration. Symbols are discrete N-mesh calculations. f is the calibration cathodic fraction assigned to the oxygen reduction reaction (ORR), and M is the calibration limit multiplier; fixed transport parameters are listed in Section S14.

Table 7. Four outputs on the final accepted meshes for the $f = 1, M = 1$ scenario.

h (μm)	Shape	Bottom Net I (μA)	Total Steel Net I (μA)	ORR (nmol/s)	Min. O_2 (mol/ m^3)
0.642	Line	10.39	10.39	0.5694	0.1167
0.642	Ellipse	4.22	4.22	0.5554	0.1012
0.642	Circle	4.08	4.08	0.5550	0.1082
3.209	Line	16.77	16.77	0.5818	0.1546
3.209	Ellipse	8.55	8.55	0.5637	0.1537
3.209	Circle	8.39	8.39	0.5634	0.1591
6.418	Line	21.01	21.01	0.5896	0.1670
6.418	Ellipse	11.95	11.95	0.5701	0.1722
6.418	Circle	11.77	11.77	0.5697	0.1761

All cases use the reference coating input and coating sidewalls. ORR consumption includes coating and steel. Table S20 identifies the final mesh comparisons used here; Table S19 retains N-mesh values for the full scenario matrix. The Oxygen_Selected_Representative dataset in Supplementary Data identifies the selected cases and unrounded outputs.

The nine representative refinement sequences met all six criteria. The largest accepted charge and oxygen closure residuals were 6.09×10^{-7} and 3.68×10^{-14} , respectively, below 10^{-6} . The source reconstruction and one-dimensional checks in Section S14 establish the defined numerical baseline. The stable current ranking supports comparison within the selected reaction scenarios and fixed transport parameters.

3.8. Sensitivity to Prescribed Partial Groove Filling

The nine wetting configurations at 3.209 μm retain the numerical line > ellipse > circle ordering in both electrochemical branches (Figure S8 and Tables S25 and S26). The smallest ellipse/circle separation is 1.87%; each adjacent shape difference exceeds the sum of the observed successive mesh current changes by at least a factor of 18.9. The rebuilt full-groove currents differ from their original matching results by no more than 0.357%. The rebuilt full-groove cases provide the reference for the filling comparisons.

With oxygen feedback, reducing the groove liquid volume fraction from 1.00 to 0.50 lowers steel bottom net current by 1.42%, 4.03% and 4.11% for the line, ellipse and circle, respectively. At a fraction of 0.25, the corresponding reductions are 2.26%, 6.14% and 6.26%. The net curve branch also gives lower currents, with reductions of 2.47%, 5.72% and 5.81% at 0.25. The decrease in the net curve branch shows the contribution of the changed conducting geometry.

The open air core increases oxygen availability and steel ORR consumption in the tested partial configurations even as steel net current decreases. For example, the line groove minimum c/c^* increases from 0.724 at full filling to 0.945 at a fraction of 0.25. The conditional anodic partial current also retains the same shape ordering across these connected wall-film/pool configurations at 3.209 μm .

4. Discussion

4.1. Combined Effects of Defect Shape and Electrolyte Film Thickness

At electrolyte film thicknesses of 0.642, 3.209, and 6.418 μm , current at the groove bottom was higher for the linear groove than for the elliptical and circular grooves; the latter two were similar (Figures 6 and 7). All three defects had the same prescribed groove bottom area, and the effective coating reaction area was held constant as described in Section 2.5. Local current depends on the material polarization functions and interfacial potential. Defect geometry affects the electrolyte potential field and the relative positions of the steel and coating reaction surfaces. The linear groove extends the exposed steel surface along its long axis. Across its width, the groove bottom lies closer to the coating interfaces on either side, giving a shorter electrolyte conduction path between the reaction regions. This spatial arrangement is consistent with the higher current calculated for the linear groove. Van den Steen et al. [32] also found that droplet radius and contact angle altered calculated current density, indicating that spatial configuration within a liquid electrolyte affects atmospheric corrosion response. The present comparison did not isolate individual geometric variables. Perimeter, aspect ratio, and boundary curvature changed together, so the calculated ranking represents their combined effects.

Current at the groove bottom increased for all three geometries with increasing film thickness, while the relative differences among shapes decreased. Conductivity and interfacial polarization functions were fixed across the three film thickness cases. Within this formulation, the increase in current is consistent with a larger cross-section for lateral conduction and lower lateral ohmic resistance. Liu et al. [21] also reported higher total cathodic current when film thickness was increased while cathodic kinetics were held fixed. The larger proportional increases for the elliptical and circular grooves reduced the excess of the linear groove current over the circular groove current from 174.2% to 77.3%. Under the specified inputs, the contrast between elongated and compact defects was the greatest at 0.642 μm , the thinnest film examined.

The thickness response also depends on the reaction and transport assumptions. Section 3.7 tests oxygen feedback while retaining the three prescribed geometries. Tang et al. [33] treated transient dissolution, Du et al. [27] linked droplet experiments with oxygen transport and product coverage, Zhang et al. [31] incorporated evolving surfaces, and Shi et al. [34] compared a thin-film model with galvanic current measurements. These exposure-dependent processes can change the current path and active surface with time.

For quantitative context, Zhang et al. [7] measured defect wire currents in an epoxy/zinc-rich coating–Q235 system under 750 μm absorbent paper kept wet with 3.5 wt.% NaCl. At 1 h, two 1.77 mm² defect wires carried -130.46 and -345.98 $\mu\text{A}/\text{cm}^2$ (-1.30 and -3.46 A/m²); one wire became anodic at $+16.59$ $\mu\text{A}/\text{cm}^2$ ($+0.166$ A/m²) after 2231 h. These are signed wire-average measurements under sacrificial protection and

subsequent protection loss. The present 3.209 μm net curve fields span approximately 4.45–10.90 A/m^2 on the steel bottom. The different polarities, coating systems, exposure times and liquid geometries matter: the wetted paper thickness is not a free-film thickness, and a wire average is not a local finite element value. The comparison places the calculated currents in an experimental context without using the other system as a validation target.

4.2. Changes in Reactive Area and Current Partitioning over Exposed Steel Surfaces

Changing the linear groove width tested how exposed area relates to integrated net current and mean net current density at the groove bottom. When the width doubled, the groove bottom area increased by 100%, net current at the groove bottom increased by 32.4%, and mean current density decreased by 33.8% (Figure 8). The current density at the 99.5th percentile also decreased. Mean current density fell because current increased by less than area. Wan et al. [8] also found that the diameter of circular microdefects altered the initial electrochemical response, although exposed area varied in that experiment. In the present comparison, widening changed both the steel reaction area and its position relative to the adjacent coating. Integrated current also depends on material polarization and current balance across all reaction surfaces. Under the specified inputs, a larger exposed area carried a higher net current at the groove bottom but a lower mean current density. Mai et al. [9] also linked scratch widening to changes in the current path and exposed steel cathodic demand in a zinc–steel system. That sacrificial protection setting differs from the net steel current evaluated here, so its width-dependent response provides a mechanistic comparison rather than validation of the present current changes.

Sidewall reactions extend the steel reaction region without changing the planform opening. At the same groove geometry, assigning the Q345B rather than Ni–W/SiC polarization function to the sidewalls reduced current at the groove bottom by 62.7% (Figure 9). Net current over all exposed steel surfaces increased by 72.7%, and the sidewalls carried 78.4% of that current. The new assignment changed the sidewall polarization characteristics and extended the region with a steel response from the bottom alone to the bottom and sidewalls. Currents at the bottom, sidewalls, and coating surface together satisfy overall current balance. In this case, current at the groove bottom decreased, while the sidewalls became the main region carrying net current over the exposed steel.

The width and sidewall comparisons require distinct current metrics. Integrated current and mean current density at the groove bottom describe the magnitude and spatial concentration of the bottom net response, whereas current integrated over all exposed steel surfaces describes the net current carried by the exposed steel region. For defects with reactive steel sidewalls, reporting this total together with the separate bottom and sidewall contributions shows how current is partitioned and prevents a lower bottom current from being interpreted as a decrease in the total net current over exposed steel.

4.3. Experimental Basis, Input Sensitivity, and Model Applicability

The coating polarization input changes the magnitude of the calculated current. For the baseline linear groove, specimen 1 gives a bottom current 34.2% higher than specimen 2; the arithmetic reference gives an intermediate value (Figure 4). Across five configurations at 3.209 μm , both measured inputs retain the higher bottom current of the linear groove, the increase in integrated current and decrease in mean density upon widening, and the decrease in bottom current accompanied by an increase in total steel current for steel-assigned sidewalls (Table 6). The coating dataset consists of two measured specimens, with one curve from each. Their arithmetic reference supplies a common comparison input; it is neither an additional specimen nor an estimate of a population distribution. The input comparison establishes the stated directions at 3.209 μm . The full shape–thickness matrix

uses the reference curve. Differences between the two specimens are retained without assigning them to an unmeasured structural or processing cause [11,13].

Using 3.5 wt.% NaCl for both the electrolyte properties and the measured polarization inputs aligns the solution composition. Transfer from an immersed polarization cell to a thin film additionally depends on oxygen supply [20,21]. The conditional analysis retains the measured net response at its defined calibration state, then varies the ORR share and calibration transport strength while resolving the film oxygen field. The resulting changes measure sensitivity to these specified assumptions; the two net curves alone do not determine a unique ORR decomposition.

The connected partial-filling comparison preserves the steel bottom and coating sidewall reaction areas while changing the conducting liquid geometry and oxygen access. The lower net currents in both branches are consistent with the narrower liquid paths, while the increased steel ORR reflects improved oxygen access. Full filling gives the highest net current in this tested family at 3.209 μm . Atmospheric deposits can produce locally thick liquid, partially wetted sidewalls and disconnected patches [2,3,32]. Relative humidity, salt deposition, capillary retention and surface wetting determine the occurrence and persistence of those states. Applying the comparison to an exposure history would require measured wetting and liquid inventory information, including changes in liquid connectivity, bottom wetting and electrolyte composition.

The coupled scenarios resolve steady-state oxygen diffusion and current redistribution in a fixed geometry. Steel dissolution and hydrolysis can change local pH, while cathodic reactions can create alkaline regions. Product precipitation, coverage and active/passive transitions can then alter reaction kinetics, accessible area and electrolyte resistance; accumulation may also produce occluded or differentially aerated regions. Dissolution and deposition change groove depth, width and sidewall area with time [27,31,34]. These processes require evolving chemistry and geometry for exposure history predictions. The external CS/SS benchmark provides an output-level test of the conduction-and-reaction framework (Section S16). The quantitative validation of local currents and evolving damage in the Ni-W/SiC defects will require matched-defect exposure measurements [26,34].

5. Conclusions

The three-dimensional calculations show that the interpretation of galvanic coupling depends on both scratch geometry and the surface over which current is evaluated:

1. Equal exposed bottom areas need not carry equal net currents. The elongated groove carried more bottom current than the compact grooves at each film thickness in the full-groove comparison. Their relative separation decreased as the film thickened. At 3.209 μm , the tested connected partial-filling configurations retained the shape order while reducing oxygen-coupled bottom net current by 1.42%–6.26% relative to the corresponding full groove.
2. Increasing exposed area can raise integrated current while lowering mean current density. Doubling groove width produced this combination, so either metric alone gives an incomplete description of the changed bottom response.
3. Reactive steel sidewalls can redirect current away from the groove bottom while increasing total steel current. In the reference case, the sidewalls carried 78.4% of the total. A decrease in bottom current therefore does not imply weaker galvanic coupling over all exposed steel surfaces.

For electrochemical comparisons under matched conditions, the calculations support reporting planform and depth, wetting configuration, sidewall reaction assignment, bottom net current density and net current integrated over all exposed steel. These descriptors distinguish a local bottom response from redistribution toward sidewalls. The two measured

coating inputs test the shape, width and sidewall directions at 3.209 μm ; the conditional oxygen matrix separately tests the reference shapes over three film thicknesses. ORR consumption, oxygen minima and reconstructed partial currents retain their separate meanings. The results support comparisons of net electrochemical response within the specified scenarios. Extending these comparisons to quantitative steel loss requires independently supported dissolution currents and exposure histories.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/coatings16101153/s1>. The Supplementary Materials contain Sections S1–S18. Figure S1: Cross-sectional and local energy-dispersive X-ray spectroscopy (EDS) characterization of Ni–W/SiC composite coating; Figure S2: The branch regressions of the measured polarization curves; Figure S3: Current density and integrated current for the linear groove at different electrolyte film thicknesses; Figure S4: The sensitivity of the geometry comparisons to the coating input at 3.209 μm ; Figure S5: A ten-position apparent-thickness analysis of the cross-sectional image in the manuscript; Figure S6: The external CS/SS depth benchmark in 0.1 mol/L NaCl at 298.15 K; Figure S7: Cross-sectional definition of the line-groove configurations; Figure S8: Dependence on prescribed groove liquid-volume fraction at 3.209 μm ; Table S1: Semiquantitative composition of local energy-dispersive X-ray spectroscopy (EDS) field of view shown in Figure S1c; Table S2: Branch regression metrics for the three measured polarization curves; Table S3: Final mesh differences for five representative primary-model sequences; Table S4: All twelve adjacent-level comparisons in the primary-model refinement sequences; Table S5: Current metrics for the fifteen coating-input/configuration combinations at 3.209 μm ; Table S6: Signed regional currents under the two sidewall reaction assignments at 3.209 μm ; Table S7: Charge conservation for the 36 matched-concentration primary configurations; Table S8: Saved interfacial potential ranges for the 36 matched-concentration primary configurations; Table S9: Successive elliptical-groove comparisons at 3.5 wt.% NaCl; Table S10: Native area-factor implementation for the reference shapes at 3.209 μm ; Table S11: Equal-total-volume controls for the three shapes at the thinnest film; Table S12: Apparent-thickness statistics from one field of one specimen; Table S13: Position-by-position endpoint coordinates and apparent thickness; Table S14: Effective-participation sensitivity: control and oxygen-coupled bottom currents at 3.209 μm ; Table S15: Oxygen reduction reaction (ORR) consumption and minimum oxygen concentration for the effective-participation cases; Table S16: Finite element results compared with the independently calculated limit; Table S17: Conditional partial-reaction coefficients; Table S18: Native one-dimensional analytical and source-recovery checks; Table S19: Complete normal-mesh oxygen matrix; Table S20: All representative oxygen mesh comparisons; Table S21: Configuration inventory; Table S22: Source parameters for the external CS/SS benchmark; Table S23: Errors relative to four published depth observations per geometry; Table S24: Geometry of the prescribed wetting configurations; Table S25: Steel-bottom net response with prescribed net-polarization curves; Table S26: Steel-bottom response with conditional oxygen feedback ($f = 1, M = 1$); Table S27: Final successive-mesh comparisons; Table S28: Partial-current reconstruction for the nine final representative full-groove cases ($f = 1, M = 1$). Supplementary Data: Supplementary_Data_R3.xlsx; Supplementary Code: Supplementary_Code_R3.txt.

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