Finite Element Analysis of the Galvanic Couple Current and Potential Distribution between Mg and 2024-T351 in a Mg Rich Primer Configuration

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The distance over which a Mg-Rich Primer (MgRP) coating galvanically protected exposed AA2024-T351 by sacrificial anode based cathodic protection (termed galvanic throwing power) was studied via finite element analysis (FEA) modeling. FEA enabled prediction of the spatial distribution of the galvanic current density over the surface of a simulated bare AA2024-T351 scratch. The galvanic current density in various full immersion and thin layer electrolyte geometries relevant to field service was investigated. Current and potential distributions extended across the simulated bare AA2024-T351 scratch when the electrolyte layer was thick, continuous and more conductive (higher salt concentration) and in the absence of a resistive coating separating the Mg from the electrolyte. Current and potential distributions did not extend across simulated defects when the electrolyte became discontinuous or the ionic path became tortuous due to drying or the addition of a resistive coating over the Mg. Additionally, galvanic protection intensified during a short period of time associated with drying and re-wetting cycles due to changing electrolyte conductivity and E-t behavior. These results qualitatively predict and agree with the experimental behavior of previously reported microelectrode investigations of a similar Mg(AA2024-T351) couple configuration, to a first order approximation.

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Commercial Mg-Rich Primer(s) (MgRP(s)) have been developed for the corrosion protection of aluminum alloys, such as precipitation age hardened AA2024-T351, and have performed well in field studies.1–13 The MgRP is designed to be applied to an aluminum alloy substrate as a primer layer, above any pretreatments, but below any topcoats which may be used (shown schematically in Figure 1). The MgRP is designed to provide sacrificial anode based cathodic protection to the aluminum alloy through galvanic coupling with the less noble Mg pigment in the primer. Results in the literature support the notion of mixed potential theory describing the galvanic coupling behavior between the primer and substrate.1,3–7,15–17 The galvanic couple potential sensed at a given location on an anode (Mg pigment) or cathode (AA2024-T351) depended on the geometric arrangement of the anode and cathode, the surface area ratio between the two electrodes exposed to immersion, the E-i electrochemical kinetics, as well as other factors such as any electrical and ionic resistances that may exist between the anode and cathode.8,18

A critical issue in determining MgRP protection capabilities in the field is developing a means for predicting the throwing power or spatial current/potential distribution of the physical MgRP-AA2024-T351 system. The distance over which the MgRP can protect a scratch or defect exposing bare AA2024-T351 by sacrificial anode based cathodic protection, is hereafter termed the “galvanic throwing power” and is depicted with green shading in Figure 1. Conversely, the term hereafter called the “inverse galvanic throwing power” is the distance into the MgRP in which the Mg pigment is anodically polarized while galvanically coupled to the AA2024-T351 scribe, scratch, or defect (depicted with red shading in Figure 1). A question remains in the literature as to whether a discernable region of increased Mg pigment depletion exists along the edges of an existing defect due to such an inverse throwing power.

The deliquescence point and subsequent thermodynamic equilibrium concentrations with respect to ambient relative humidity (RH) of various salts relevant to sea water are shown in Figure 2 as calculated by Stream Analyzer (OLI Systems, Cedar Knolls, NJ). As a given deposited salt deliquesces on a surface it will, over time, equilibrate to the ambient RH to form an electrolyte layer or droplet of equilibrium concentration. For simplicity, the model developed in this manuscript assumes pure NaCl as the electrolyte. However, the similarity in deliquescence behavior between the primary constituents of sea water, shown in Figure 2, justifies such a simplification. Figure 3 presents the resulting equilibrium electrolyte layer thickness with respect to initial deposition density and ambient RH for NaCl assuming a uniform, infinitely long, continuous electrolyte layer at 25°C. As the RH in an exposure environment changes with time, so does the equilibrium salt concentration and thus ionic conductivity, as well as geometry of the electrolyte layer (depicted assuming continuous thin-layer electrolyte during a hypothetical RH cycle in Figure 4). These factors all play an important part in dictating the galvanic throwing power and subsequent cathodic protection vs. scratch distance afforded by the MgRP.

Finite element analysis (FEA), or similar spatially resolved computational methods, of potential and current distributions in galvanic systems has long been studied in the literature.18–25 Such studies are often carried out to investigate fundamental effects of electrolyte geometry,24,26 electrode kinetics,23,27,28 unique part geometries,19 crevice corrosion,22,29 and other sacrificial anode based, cathodic protection schemes.30 Previous studies addressed a tunable metallic coating system as a function of coating parameters, phys-chemical conditions) to develop a fully functional, physically representative model, to accurately predict the galvanic throwing power of the MgRP coating system as a function of coating parameters, physical conditions, as well as environment. Results will be compared with previously published experiments using a microelectrode array to simulate a scratch.18

Experimental

Materials.—99.9% pure magnesium rod (8.0 mm diam.) and 1.6 mm thick AA2024-T351 sheet were studied in these investigations. Table I and Table II show the chemical analysis of both the AA2024-T351 and the Mg used in this work. Chemical analysis showed the Mg

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rod had a measured purity of over 99.9% and is substantially similar to the powder used in commercial Mg-Rich Primer (MgRP) products.8 The Mg rod was mounted in EpoThin epoxy resin manufactured by Buehler in order to make clamping the sample to an electrochemical flat cell easier. The bare electrodes were prepared by alternating polishing with silicon-carbide paper and rinsing with 18.2 MΩ deionized water to a final abrading grit of 1200. The samples were then dried with lab tissue before use.

**Full immersion electrochemical analysis to establish boundary conditions.**—Potential control during electrochemical experiments was maintained using a potentiostat with computer interface software. Solartron 1287A/1255B and Gamry Reference 600 potentiostats were selected because they enable electrochemical impedance spectroscopy (EIS) measurements along with traditional electrochemical measurements. Saturated Calomel reference electrodes (SCE) were used in full immersion testing.

Anodic potentiodynamic scans were conducted on 99.9% pure, bare Mg electrodes. The Mg was supplied in a “rod” form factor with diameter of 8 mm. The cell window used was of 10 mm diameter and thus exposed the whole polished, cross-sectional face of the epoxy-mounted Mg rod. The tests were conducted in various bulk solutions of quiescent NaCl and ASTM Substitute Ocean Water (ASTM SOW) with ambient aeration as well as pre-saturated with Mg(OH)2. A commercial saturated calomel electrode was used as a reference electrode. The bare Mg electrodes were abraded to 1200 grit silicon carbide paper. The potentiodynamic scans were conducted after 10 minutes at the open circuit potential (OCP). A typical anodic scan started at −0.2 V vs OCP up to +0.7 V vs. OCP at 1.0 mV per second.

Cathodic potentiodynamic scans were conducted on bare AA2024-T351 sheet. The AA2024-T351 was of sheet form factor, and the polished LT face was clamped directly to the window with a knife-edge washer to minimize crevice effects. The tests were run in various bulk solutions of NaCl, MgCl2, CaCl2, Na2SO4, and AlCl3.

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**Figure 1.** Hypothetical schematic of AA2024-T351 coated with (a) MgRP and (b) MgRP + Topcoat, depicting MgRP sacrificial cathodic protection function under an infinitely long, uniform electrolyte layer. Hypothetical galvanic throwing power extending away from the edge of the coating is indicated with green shading. Red shading indicates possible galvanic utilization of Mg or “inverse throwing power”.

**Figure 2.** Thermodynamic equilibrium concentration of various saltwater solutions relative to the relative humidity in equilibrium. Calculated by OLI.

**Figure 3.** Uniform, planar electrolyte layer thickness based on thermodynamic equilibrium concentration of NaCl with respect to ambient RH and initial deposition density at 25°C.
solutions of quiescent NaCl and ASTM SOW with ambient aeration as well as pre-saturated with Mg(OH)₂. A commercial saturated calomel electrode was used as a reference electrode. The bare AA2024-T351 electrodes were abraded to 1200 grit silicon carbide paper and then clamped to an electrochemical flat cell with a 1 cm² window. The potentiodynamic scans were conducted after 10 minutes at the OCP. A typical cathodic scan started at +0.2 V vs OCP and scanned down to -1.0 V vs OCP at 0.1667 mV per second.

Two-dimensional finite element analysis (FEA) computational modeling.—COMSOL Multiphysics FEA, solver and simulation software (v.4.4) was used to develop a physically representative, simplified 2-dimensional model of a AA2024-T351 panel coated with MgRP. The model geometry is shown schematically in Figure 5a. The model geometry consisted of a 20 mm electrode of AA2024-T351 overlaid with a 10 mm wide electrode of 99.9% pure Mg; the Mg was a fixed height 30 μm taller than the AA2024-T351 surface to mimic the geometry of the MgRP coating in the environmental studies. The polymer layer covers both the horizontal and vertical surfaces of the Mg electrode as indicated in Figure 5a.

The galvanic model was constructed within the Corrosion Module of COMSOL using the Secondary Current Distribution framework in stationary mode (i.e., no time dependence). The current distribution was solved using the Laplace governing equation:

\[ \nabla^2 \phi = 0 \]  

where \( \phi \) is the potential in a domain and \( \nabla^2 \) is the Laplacian operator. Dependent variables were defined as electrolyte potential (\( \phi_e \)) [V] and electric potential (\( \phi_s \)) [V]. Electrolyte and electrode regions were defined as domains. Current distributions within these domains were described by variations of Ohm’s Law:

\[ i_i = -\sigma_i \nabla \phi_i \]  

\[ i_i = -\sigma_s \nabla \phi_s \]  

where \( i_i \) and \( i_s \) are the current densities [A/m²] flowing through the liquid electrolyte and solid electrode, respectively. \( \sigma_i \) and \( \sigma_s \) are the electrolyte and electrode conductivities [S/m], respectively, and \( V \phi_i \) and \( \nabla \phi_i \) are the potential gradients [V/m] in the electrolyte and electrode, respectively. To simplify the model, solid electrodes (A2024-T351, Mg) were assumed to be perfect conductors with ohmic resistivity of pure Mg (4.39 \times 10⁻⁸ Ω·m) and pure Al (2.6 \times 10⁻⁸ Ω·m) compared to the least-resistive NaCl solution (5 M, 4.16 \times 10⁻² Ω·m, 24.016 S/m in Table III). Therefore, the electrode domain was removed (eliminating the need for solving \( \phi_s \)) and model geometry was reduced to the electrolyte domain as shown in Figure 5b. Charge conservation was assumed within the electrolyte domain where the divergence of the electrolyte current density is zero (\( \nabla \cdot i = 0 \)). The top, left and right boundaries of the electrolyte domain were designated as insulated:

\[ -\mathbf{n} \cdot i_i = 0 \]  

where \( \mathbf{n} \) is the normal vector of the boundary pointing into the electrolyte domain. The electrolyte-electrode interface reaction rates were described by secondary current distributions (i.e., current density as a function of overpotential (\( \eta \)) [V]). In secondary current distributions, overpotential deviation from the corrosion potential arises from the finite ohmic resistivity of the electrolyte and the charge transfer resistance of the electrode kinetics. A non-zero resistance between the electrolyte and the electrode will also contribute to the overpotential:

\[ \eta = -\phi_i + \phi_s - \Delta \phi_{i,\text{film}} - E_{corr} \]  

where \( \Delta \phi_{i,\text{film}} \) is the potential drop over a surface film, and \( E_{corr} \) is the corrosion potential of the metal/electrolyte system [V]. Since the electrodes themselves were not part of the model solution, \( \phi_s \) was neglected and \( \eta \) was reduced to:

\[ \eta = -\phi_i - \Delta \phi_{i,\text{film}} - E_{corr} \]

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**Table I.** Composition of AA2024-T351 used as a bare electrode in these investigations. Compositions provided by QUANT Quality Analysis and Testing Corporation in wt%.

|     | AA2024 | Al  | Cu  | Mg  | Mn  | Fe  | Zn  | Si  | Ti  | Cr  | V   |
|-----|--------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| T351 Sheet | Balance | 4.56 | 1.26 | 0.59 | 0.22 | 0.12 | 0.08 | 0.02 | 0.01 | 0.01 |

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**Table II.** Compositions of Mg Rod (99.9%) purchased from Alfa Aesar. All compositions reported in wt%. (Mg: Balance). Compositions provided by QUANT Quality Analysis and Testing Corporation. NR: Not Reported.

| Element | Si | Al | Fe | Cu | Zn | Mn | Ni | Zr | Pb | Sn | C | S | O |
|---------|----|----|----|----|----|----|----|----|----|----|---|---|---|
| rod/wire| NR | 0.02 | 0.008 | 0.003 | 0.03 | <0.01 | <0.001 | <0.01 | NR | NR | <0.001 | <0.001 | 0.001 |

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Figure 4. Hypothetical RH cycle and resulting electrolyte layer thickness for various NaCl surface deposition densities based on Figures 2 and 3.
The electrochemical boundary conditions utilized for the AA2024-T351 and Mg materials were based on best fit approximations of experimentally obtained, full immersion polarization data shown in Figure 6a. The electrochemical boundary conditions were input into the COMSOL software as E-i pairs. The specific electrochemical boundary conditions used in the model for various concentrations of NaCl are plotted in Figure 6b which depicts the group of boundary conditions used for FEA as fitted from Figure 6a. Intermediate E-i positions that are not listed in the boundary condition data set were interpolated as needed via a piecewise fitting algorithm built into COMSOL. For each NaCl concentration, cathodic overpotentials on AA2024-T351 ($\eta_{\text{AA2024}}$) were determined from the inputted E-i pairs where the measured potential ($E_{\text{AA2024\_surface}}$) [V vs. SCE] was described as:

$$E_{\text{AA2024\_surface}} = \phi_l - \Delta \phi_{s,\text{film}}$$

Since the AA2024-T351 electrode in contact with the electrolyte was bare (no resistive film) $\Delta \phi_{s,\text{film}}$ was zero. Substitution of Eq. 7 into Eq. 6 resulted in:

$$\eta_{\text{AA2024}} = E_{\text{AA2024\_surface}} - E_{\text{AA2024\_corr}}$$

Where $E_{\text{AA2024\_corr}}$ is the corrosion potential of AA2024-T351 exposed in a particular NaCl. For the Mg anode, current density ($i_{Mg}$) [A/m²] was related to anodic overpotential ($\eta_{Mg}$) through a Tafel expression:

$$i_{Mg} = i_{Mg\_corr} \cdot 10^{(\eta_{Mg} / B_{Mg})}$$

Where $i_{Mg\_corr}$ is the Mg electrode corrosion current density [A/m²] and $B_{Mg}$ is the apparent Mg Tafel slope [V] derived from experimental data. The finite polymer resistance over the Mg ($R_{\text{(polymer)}}$) [Ω·m²] was treated as a zero dimensional source of potential drop across the film $\Delta \phi_{s,\text{film}}$ and defined as $\Delta E_{\text{polymer}}$ (Figure 5a):

$$\Delta \phi_{s,\text{film}} = \Delta E_{\text{polymer}} = \eta_{Mg} \cdot R_{\text{polymer}}$$

Repetition of the derivation of Eq. 8 for the Mg electrode generated the expression:

$$\eta_{Mg} = E_{\text{Mg\_surface}} - \Delta E_{\text{polymer}} - E_{\text{Mg\_corr}}$$

| [NaCl] (mol/L) | $\sigma_{\text{NaCl}}$ (S/m) | $E_{\text{corr, 2024}}$ (V SCE) | $E_{\text{corr, Mg}}$ (V SCE) | $i_{\text{corr, Mg}}$ (A/m²) | $B_{Mg}$ (V/decade) |
|----------------|-----------------------------|------------------------------|-----------------------------|-----------------------------|------------------|
| 0.001          | 0.0123                      | −0.435                       | −1.512                      | 0.003                       | 0.0184           |
| 0.010          | 0.1175                      | −0.508                       | −1.528                      | 0.005                       | 0.0184           |
| 0.100          | 1.061                       | −0.582                       | −1.568                      | 0.020                       | 0.0184           |
| 1.000          | 8.459                       | −0.670                       | −1.600                      | 0.400                       | 0.0184           |
| 5.000          | 24.016                      | −0.875                       | −1.635                      | 3.000                       | 0.0184           |
Boundary conditions were set with \( i = 0 \) for \( E > E_{\text{AA2024}} \) and \( E < E_{\text{Mg}} \), which served to bound the upper and lower potentials possible in the system. For example, in the case of 1 M NaCl, the model was confined to potentials between \(-0.670\) and \(-1.600 \text{ V}_{\text{SCE}}\). Table III lists \( E_{\text{corr}}, b_{\text{Mg}}, B_{\text{Mg}} \) and \( \sigma_{\text{Mg}} \) values as functions of [NaCl]. \( \sigma_{\text{Mg}} \) values were calculated with OLI Analyzer v9.0.

Model geometry was meshed by mapping quad (rectangular) elements over the electrolyte domain. The domain space contained 2000 elements (along the x-axis) with mesh density 1000 times greater at the couple point (\( x = 10 \text{ mm} \)) compared to either end of the model geometry (\( x = 0 \text{ mm}, x = 20 \text{ mm} \)). In the y-direction, elements varied between 1 and 100 \( \mu \text{m} \) in height, depending on the electrolyte thickness.

Typical outputs of the model included potential and current profiles mapped along the surface of the galvanic couple. Potential profiles were provided from just above the polymer film surface (where potential drop due to solution resistance was zero) and termed \( E_{\text{surface}} \) and depicted schematically as the red line in Figure 5 and the potential labeled \( E_{\text{Mg}} \) in Figure 7. The model also directly output the discrete potential along the surface of each metal in the galvanic couple, underneath the polymer film (termed “\( E_{\text{couple}} \)” and depicted schematically as the blue line in Figure 5a and the potential labeled \( E_{\text{couple}} \) in Figure 7). For the Mg electrode, \( E_{\text{Mg}} \) took into account the potential drop through the polymer layer \( \Delta E_{\text{polymer}} \), above the Mg while \( E_{\text{couple}} \) did not. For the AA2024-T351, the lack of a resistive polymer layer resulted in \( E_{\text{AA2024}} = E_{\text{AA2024, surface}} \). The model also produced the net current along the surface of each metal in the galvanic couple as a function of \( E_{\text{couple}} \).

### Results

**Model justification and validation.—** Justification for use of this simplified treatment of the MgRP coating is illustrated in Figure 8. It is acknowledged that the simplified geometry involving a plate of Mg (Figure 8c) covered with resistive film does not represent the full complexity of an actual MgRP coating with discrete Mg pigment particles (Figure 8a). In the current version, the significant factor that was examined was the composite resistive nature (\( R_{\text{polymer}} \)) of the polymer matrix that surrounds the Mg particles and its effect on throwing power (Figure 8). While some Mg particles may be directly exposed to electrolyte, they will undergo self-corrosion (Figure 8b) and not be involved in the throwing power of the coating; rather, the cavities formed as a result of self-corrosion were incorporated into the reduced

![Figure 6](image6.png)

**Figure 6.** E-log(i) boundary condition data for bare high purity Mg and bare AA2024-T351 sheet in various concentrations of ambiently aerated NaCl solution utilized as inputs in FEA. The E-log(i) data has been IR corrected. (a) Experimentally obtained, full immersion polarization data in ambiently aerated NaCl solution and (b) corresponding boundary conditions used for FEA.

![Figure 7](image7.png)

**Figure 7.** Mixed potential model depicting \( E_{\text{surface}} \) and \( E_{\text{couple}} \) as they pertain to a galvanic couple between AA2024-T351 and polymer coated Mg.

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For instance a film resistance of \( 10^7 \text{ ohm-cm}^2 \) is common for a polymer resin of tens of micrometer thickness or \( 10^3 \text{ ohm-m} \).
value of $R_{\text{polymer}}$ examined parametrically by FEA. These assumptions were justified because the surviving Mg primer is covered with a resistive coating that in the case of deeply buried particles experiences a slightly larger film resistance compared to particles located at a shallow depth. However, on average all particles experience $R_{f/m}$.

To validate that charge was conserved in the FEA in accordance with mixed potential theory, the total net cathodic and total anodic currents in selected scenarios (under 100 μm of 1.0 M NaCl with no polymer covering the Mg, under 100 μm of 0.01 M NaCl with no polymer covering the Mg, and under 100 μm of 1.0 M NaCl with 10 Ω·m² polymer covering the Mg) were compared (Figure 9). The residual current integrated over the entire geometry remained at a level near 0 ± 10 nA, confirming that the FEA of the galvanic interaction between the bare AA2024-T351 and the bare or polymer coated Mg was also in accordance with mixed potential theory and conservation of charge principles.

Additionally, to validate that the results of the FEA were consistent with the E-i boundary conditions, the resulting potential and current values for various positions on the surface of the galvanic couple between bare AA2024-T351 and polymer coated Mg, as predicted by FEA, were plotted on a mixed potential model (points labeled A, B, C₁, C₂, D, and E in Figure 10). The predictions made by the finite element computational model were found to be consistent with values from the E-i boundary conditions shown in Figure 6b. In Figure 10, the cathodic current on the cathode (AA2024-T351, positions A – C₁) is negative and the anodic current on the anode (Mg, positions C₂ – E) is positive, however all currents are plotted as absolute value due to logarithmic scale. In Figure 10 at the interface between the anode and cathode (points C₁ and C₂, but not C₂'), the potential is equal and is the interfacial potential sensed at both the surface of the bare cathode (C₁) and surface of the polymer coating (C₂). Points C₂', D', and E' depict the potential and current sensed by the anode (Mg) under the polymer coating. In Figure 10c the various points depicted spatially in Figures 10a and 10b are plotted on the E-i diagram of AA2024-T351 and Mg boundary conditions. Figure 10c shows, conceptually, how the spatial distribution of current and potential is manifested in the boundary conditions.

**Effects of electrolyte layer thickness.**—Figure 11 presents the modeled potential ($E_{\text{Surface}}$ and $E_{\text{Couple}}$) and current over a galvanic couple between AA2024-T351 and polymer coated 99.9% Mg as predicted by FEA under 1.0 M NaCl electrolyte layers of various thickness with polymer layer resistances of 0 Ω·m² (left column) and 10 Ω·m² (right column). Given the same electrolyte chemistry (1.0 M NaCl) and in the absence of a polymer layer (Figure 11a), the galvanic couple potential, for all electrolyte layer thicknesses studied, that is sensed by the AA2024-T351 and the Mg at the interface between the AA2024-T351 and Mg was equal ($−1.52$ V$_{\text{SCE}}$) and agreed with estimates from Figure 6b. However, a thicker electrolyte layer resulted in less ohmic drop through the electrolyte and enabled the Mg to cathodically polarize the AA2024-T351 to a lower $E_{\text{Couple}}$ (2024) at the far geometrical limit of the AA2024-T351 model scratch geometry (10 mm from the couple interface). For instance, $E_{\text{Couple}}$ 2024 was

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**Figure 8.** (a) Schematic representations of MgRP-coated AA2024-T351 and scratch exposing bare aluminum to the electrolyte. (b) Mg particles exposed directly to electrolyte undergo self-corrosion with the remaining particles buried in a resistive polymer. (c) Simplified geometry used in FEA modeling with solid Mg (in polymer covering the Mg, under 100 μm of 1.0 M NaCl with no polymer covering the Mg) and under 100 μm of 1.0 M NaCl with 10 Ω·m² polymer covering the Mg. (d) Resistive circuit representation of schematics (b) and (c) with corresponding parametric variables ($R_{\text{polymer}}$; $R_s$) and potential outputs ($E_{\text{couple}}$; $E_{\text{surface}}$) shown in Figure 5a and Figure 7.

**Figure 9.** Comparison of net cathodic and anodic current from various configurations of a galvanic couple between AA2024-T351 and polymer coated 99.9% Mg as predicted by FEA (COMSOL) under a 100 μm thick NaCl electrolyte layer. (a) under 100 μm of 1.0 M NaCl with no polymer 0 Ω·m² covering the Mg (b) under 100 μm of 0.01 M NaCl with no polymer covering the Mg (0 Ω·m²) and (c) under 100 μm of 1.0 M NaCl with 10 Ω·m² polymer covering the Mg.
as low as $-1.37 \text{ V}_{\text{SCE}}$ ($\eta_{\text{AA2024}}$ with respect to $E_{\text{cor} \text{ AA2024}} \approx -680 \text{ mV}$). This is an indication of increased throwing power under thicker electrolyte layers, when all other parameters were fixed. When the polymer resistance was zero (Figures 11a, 11c, and 11e), the model predicts that the Mg anode material is largely non-polarizable in 1.0 M NaCl (a result of fast Mg anodic kinetics, observed in Figures 6a and 6b) and as a consequence experiences a maximum anodic overpotential ($\eta_{\text{Mg}}$ with respect to $E_{\text{cor of Mg}}$), proximate to the couple interface, of $+100 \text{ mV}$ vs. OCP or less. When the electrolyte layer is less than 100 $\mu$m an inverse throwing power (distance away from galvanic couple interface the Mg is anodically polarized above its OCP) of no more than 6 mm. As larger polymer resistances are added to the model over the Mg anode (Figures 11b and 11d), the maximum anodic overpotential on the Mg ($\eta_{\text{Mg}}$), proximate to the couple interface is less than 5 mV. Additionally, when larger polymer resistances (i.e, 10 to 10,000 $\Omega \cdot \text{m}^2$) are included in the model over the Mg anode (Figures 11b, 11d and 11f), the effect of the ohmic drop through the electrolyte is no longer a dominant factor. The galvanic current is now significantly mediated by the resistance of the polymer layer. In such a case, the effect of electrolyte layer thickness, over the range studied here, is minimal. However, with an electrolyte thickness $>1 \mu$m and with a polymer resistance of 10 $\Omega \cdot \text{m}^2$, $E_{\text{couple}}$ over the AA2024-T351 drops to $-0.9 \text{ V}_{\text{SCE}}$. In all specific scenarios studied by the model where the galvanic couple is operative, a thicker electrolyte layer results in increased cathodic polarization of the AA2024-T351 to a further distance and subsequently increased throwing power of Mg.

**Effect of electrolyte concentration.**—Figure 12 presents potential ($E_{\text{Surface}}$ and $E_{\text{couple}}$) and current profiles over a galvanic couple between AA2024-T351 and polymer coated Mg as predicted by FEA (COMSOL) under a 100 $\mu$m thick NaCl electrolyte layer of varying concentrations with polymer resistance of 0 $\Omega \cdot \text{m}^2$. In the absence of a polymer layer (Figure 12), the galvanic couple potential, in all electrolyte layer thicknesses studied, that is sensed by the AA2024-T351 and Mg at the interface between the AA2024-T351 and Mg became more negative and the galvanic current increases with increasing NaCl concentration. These results agree with the mixed potential
Figure 11. Potential (ESurface and Ecouple) and current profiles over a galvanic couple between AA2024-T351 and polymer coated 99.9% Mg as predicted by FEA (COMSOL) under 1.0 M NaCl electrolyte layers of various thickness with polymer layer resistances of (a, c, e) 0 Ω·m² and (b, d, f) 10 Ω·m².
The characteristics of the ORR and HER cathodic kinetics on the AA2024-T351 are largely unaffected by an increase in NaCl solution concentration, with the largest effect being a negative shift in the free corrosion potential of the AA2024-T351 (Figure 6). Due to the similarity of E-i boundary conditions of both the Mg and AA2024-T351, in all NaCl electrolyte concentrations studied, the maximum anodic overpotential (η\text{AA2024}) proximate to the couple interface sensed by the Mg anode material was a relatively constant value of +100 mV vs. OCP. The model also predicts that increasing the NaCl solution concentration by an order of magnitude resulted in an increase in the galvanic current by roughly one order of magnitude (Figure 12c) which also agrees with the mixed potential model shown in Figure 7. The inverse throwing power is roughly 4 mm except for the condition of 0.1 M NaCl. Interestingly, in the NaCl concentrations studied here, \Delta E\text{couple} (potential difference between freely corroding Mg and AA2024-T351) is at a maximum in 0.1 M NaCl (Figure 6). The moderate solution conductivity, in conjunction with a large \Delta E\text{couple}, results in the maximum η\text{AA2024} on the AA2024-T351 as well as the largest inverse throwing power over the Mg, extending the full distance of the Mg electrode compared to 4 mm for 0.001 M NaCl and 5.0 M NaCl, respectively. In the case of very concentrated solutions, \Delta E\text{couple} is not at a maximum, in fact approaches a minimum (Figure 6b). Even though the ohmic drop through the electrolyte layer is minimized due to high solution conductivity, the electrochemical driving force for sacrificial protection given by \Delta E\text{couple} is lower in 5.0 M NaCl than in moderate electrolyte concentrations such as 0.1 M NaCl (Figure 6) but the current density is still the greatest in magnitude and the local couple potential on the AA2024-T351 is still the most negative. Conversely, under very dilute electrolyte layers (0.001 M NaCl in Figure 12) the decreased solution conductivity becomes significant, and reduces the throwing power over the AA2024-T351 and the inverse throwing power over the Mg, significantly due to the significant ohmic drop through the electrolyte layer.

**Effect of polymer resistance.**—Figure 13 presents the modeled potential (E\text{Surface} and E\text{couple}) and current profiles over a galvanic couple between AA2024-T351 and polymer coated 99.9% Mg as predicted by FEA (COMSOL) under a 100 μm thick NaCl electrolyte layer of varying concentration.

The ionic resistance of the added polymer layer over the Mg electrode strongly mediated the galvanic current passing between anodes and cathodes (Figures 13e and 13f) and, when large enough, completely prevents the galvanic coupling of the electrodes altogether (when R\text{polymer} = 1000 Ω·m² in Figure 13). The combination of a very thin electrolyte layer and moderate to high polymer resistance (when R\text{polymer} > 0.1 Ω·m² in Figures 13a, 13c, and 13e) results in further mediation of the galvanic couple potential sensed at the interface between the AA2024-T351 and the Mg can be observed more clearly. The ion resistance of the added polymer layer over the Mg electrode significantly moderates the sacrificial galvanic protection function afforded by the Mg to the AA2024-T351 (Figure 13b). For this reason, in the MgRP system the electrical and ionic resistances of any pretreatment layers, primer formulations, or topcoat systems can be said to be the most important factor governing the galvanic protection function of the MgRP pertaining to throwing power and self-corrosion of the Mg pigment.

**Effect of Mg pigment depletion (Area\text{Mg}/Area\text{AA2024}).**—In service, the MgRP contains a pigment volume concentration of roughly 45% and a pigment geometry of irregularly shaped flake with a mean width increased from 0.001 M to 5.0 M, the boundary E-i conditions of Mg become more active (Figure 6) presumably as a result of increased solution conductivity and chloride. The characteristics of the ORR and HER cathodic kinetics on the AA2024-T351 are largely unaffected by an increase in NaCl solution concentration, with the largest effect being a negative shift in the free corrosion potential of the AA2024-T351 (Figure 6). Due to the similarity of E-i boundary conditions of both the Mg and AA2024-T351, in all NaCl electrolyte concentrations studied, the maximum anodic overpotential (η\text{AA2024}) proximate to the couple interface sensed by the Mg anode material was a relatively constant value of +100 mV vs. OCP. The model also predicts that increasing the NaCl solution concentration by an order of magnitude resulted in an increase in the galvanic current by roughly one order of magnitude (Figure 12c) which also agrees with the mixed potential model shown in Figure 7. The inverse throwing power is roughly 4 mm except for the condition of 0.1 M NaCl. Interestingly, in the NaCl concentrations studied here, \Delta E\text{couple} (potential difference between freely corroding Mg and AA2024-T351) is at a maximum in 0.1 M NaCl (Figure 6). The moderate solution conductivity, in conjunction with a large \Delta E\text{couple}, results in the maximum η\text{AA2024} on the AA2024-T351 as well as the largest inverse throwing power over the Mg, extending the full distance of the Mg electrode compared to 4 mm for 0.001 M NaCl and 5.0 M NaCl, respectively. In the case of very concentrated solutions, \Delta E\text{couple} is not at a maximum, in fact approaches a minimum (Figure 6b). Even though the ohmic drop through the electrolyte layer is minimized due to high solution conductivity, the electrochemical driving force for sacrificial protection given by \Delta E\text{couple} is lower in 5.0 M NaCl than in moderate electrolyte concentrations such as 0.1 M NaCl (Figure 6) but the current density is still the greatest in magnitude and the local couple potential on the AA2024-T351 is still the most negative. Conversely, under very dilute electrolyte layers (0.001 M NaCl in Figure 12) the decreased solution conductivity becomes significant, and reduces the throwing power over the AA2024-T351 and the inverse throwing power over the Mg, significantly due to the significant ohmic drop through the electrolyte layer.

**Effect of polymer resistance.**—Figure 13 presents the modeled potential (E\text{Surface} and E\text{couple}) and current profiles over a galvanic couple between AA2024-T351 and polymer coated 99.9% Mg as predicted by FEA (COMSOL) under a 100 μm thick NaCl electrolyte layer of varying concentration.

The ionic resistance of the added polymer layer over the Mg electrode strongly mediated the galvanic current passing between anodes and cathodes (Figures 13e and 13f) and, when large enough, completely prevents the galvanic coupling of the electrodes altogether (when R\text{polymer} = 1000 Ω·m² in Figure 13). The combination of a very thin electrolyte layer and moderate to high polymer resistance (when R\text{polymer} > 0.1 Ω·m² in Figures 13a, 13c, and 13e) results in further mediation of the galvanic couple potential sensed at the interface between the AA2024-T351 and the Mg can be observed more clearly. The ion resistance of the added polymer layer over the Mg electrode significantly moderates the sacrificial galvanic protection function afforded by the Mg to the AA2024-T351 (Figure 13b). For this reason, in the MgRP system the electrical and ionic resistances of any pretreatment layers, primer formulations, or topcoat systems can be said to be the most important factor governing the galvanic protection function of the MgRP pertaining to throwing power and self-corrosion of the Mg pigment.
Figure 13. Potential ($E_{\text{Surface}}$ and $E_{\text{couple}}$) and current profiles over a galvanic couple between AA2024-T351 and polymer coated 99.9% Mg as predicted by FEA (COMSOL) with various polymer layer resistances under 1.0 M NaCl electrolyte layers of thickness of (a, c, e) 1 $\mu$m (b, d, f) 100 $\mu$m.
of 20 μm and thickness of 10 μm. The primer coating is applied in a 30–60 μm thick layer over the AA2024-T351 substrate. Such a configuration results in a maximum possible area ratio of Mg to AA2024-T351 (assuming all pigment is wetted) of roughly 10:1 (Table IV).

The effective area ratio between the Mg pigment and the AA2024-T351 substrate will evolve with time in service as the primer wets or dries, as the electrolyte layer grows or shrinks in size, as pigment is depleted from the coating, or as new scratches or defects are formed in the coating exposing bare AA2024-T351. As such, it is important to study the effect of a wide range of area ratios between the Mg pigment and the AA2024-T351 substrate. Since the polymer layer in the finite element computational model is dimensionless, and since the depletion of Mg from the MgRP coating would not change the horizontal dimension of the couple scenario it was decided that the appropriate way to accommodate an increase or decrease in PVC_{Mg} was by shifting the anodic Mg kinetics in 1.0 M NaCl by multipliers of 20 μm and thickness of 10 μm in Figure 14 by shifting the anodic Mg kinetics in 1.0 M NaCl by multipliers of 0.001, 0.01, 0.1, 10, 100, and 1000 (plotted in Figure 14) rather than change the length of the Mg anode in the model. It is interesting to note, over the entire range of area ratios studied here, the mixed potential model in Figure 14 predicted a subsequent change in E_{couple} at the Mg/AA2024-T351 of only ±50 mV compared to an Mg/AA2024-

T351 area ratio of 1:1. This is because the Mg is active and non-polarizable in salt solutions (all cases in Figure 6b).

Figure 15 presents potential (E_{surface} and E_{couple}) profiles over a galvanic couple between AA2024-T351 and polymer coated 99.9% Mg at various area ratios as predicted by FEA under a 100 μm thick, 1.0 M NaCl electrolyte layer with polymer layer resistance of 0.1 Ω · m² and 0.1 Ω · m². The area ratio of Mg to AA2024-T351 ("A_{Mg}/A_{AA2024-T351}") specifically pertaining to the depletion of Mg pigment from the MgRP in service are estimated in Table IV and are estimated to be between 0.1 and 10. Using this range of area ratios in Figure 15, it can be seen that a lower PVC coating containing less Mg will develop a larger anodic overpotential and subsequently exhibit a larger inverse throwing power (anodic polarization and subsequent pigment depletion further from the edge of the coating when R_{polymer} = 0 to 10 Ω · m²). It is important to note that Figure 15 portrays a hypothetical situation in which a continuous electrical and ionic path exists between all pigment particles and the AA2024-T351 substrate such that they are not isolated in polymer. If after moderate pigment depletion, the remaining pigment particles were electrically isolated in the primer polymer or under a topcoat with greater polymer resistance, it is likely that the sacrificial galvanic function would be severely mediated or altogether not operative (similar to when R_{polymer} = 10 or 1000 Ω · m² in Figure 13b, 13d, and 13f). Increasing the polymer resistance still alters the current distribution such that it spreads more uniformly across the Mg but is lower when the polymer resistance is high. Current density is always non-uniform and lower at positions further away on the AA2024 then at the interface but is lower when the polymer resistance is high at all Mg_{PVC}.

### Discussion

**Effect of electrolyte layer on the Galvanic throwing power in the MgRP/AA2024-T351 system.**—Through finite element modeling, the chemistry, thickness, and geometric area of coverage of the electrolyte layer were all shown to play an important role in governing the galvanic throwing power of Mg across a simulated defect or scratch of bare AA2024-T351. FEA predicted that increasing the NaCl solution concentration by an order of magnitude resulted in an increase in the galvanic current density by almost one order of magnitude (Figure 12) which also agrees with the mixed potential model shown in Figure 7 and microelectrode array measurements in prior work in which the electrolyte had been assumed to saturate just before drying. Interestingly, in the NaCl concentrations studied here, the FEA highlighted that the ΔE_{couple} (potential difference between the corrosion potentials of freely corroding Mg and AA2024-T351) is at a maximum in 0.1 M NaCl (Figure 6). The moderate solution conductivity, in conjunction with a large ΔE_{couple}, results in the maximum local cathodic overpotentials sensed by the AA2024-T351 proximate to the couple interface as well as the largest inverse throwing power over the Mg, compared to under 0.001 M NaCl or 5.0 NaCl (Figure 12).

When electrolyte layer thickness was studied it was found that a thicker electrolyte layer results in less ohmic drop through the electrolyte and the Mg cathodically polarized the AA2024-T351 to a more negative E_{couple} at the far geometrical limit of the AA2024-T351 in the model (Figure 11). This was an indication of increased throwing power under thicker electrolyte layers, when all other parameters are fixed. Similar results were observed in prior microelectrode array studies where under continuous, thin electrolyte layers the throwing power extended across the entire array. However, whenever the electrolyte became tortuous which reduced the ionically conductive path length (i.e., due to drying), the throwing power was limited.

**Effect of organic polymers on the Galvanic throwing power in the MgRP/AA2024-T351 system.**—The role of the polymer layers in the MgRP/AA2024-T351 system is extremely important and twofold. The primer and topcoat polymers both act to (1) act as a barrier to protect the Mg pigment from rapid self-corrosion and (2) to mediate the cathodic protection provided to the AA2024-T351 substrate.
Figure 15. Potential (ESurface and ECouple) and current profiles over a galvanic couple between AA2024-T351 and various area ratios of polymer coated 99.9% Mg as predicted by FEA (COMSOL) under a 1.0 M NaCl electrolyte layer with polymer layer resistance of (a, c, e) 0 Ω·m² and (b, d, f) 0.1 Ω·m².
by the Mg pigment to avoid detrimental cathodic corrosion of the AA2024-T351 substrate and subsequent blistering by rapid H₂ evolution at cathodic sites. The mediation is brought about through insertion of a large ohmic resistance in the galvanic couple in accordance with mixed potential theory. It has been shown in the past that AA2024-T351 polarized cathodically to −1.5 V vs. SCE in aerated NaCl solution dissolves at a rate as high as 4 μA/cm². However, the same alloy was shown to avoid significant cathodic corrosion when cathodically polarized above −1.1 V vs. SCE. Recent, independent field and lab studies of commercial MgRP products did not report any observations of cathodic corrosion of the AA2024-T351 substrate after prolonged environmental exposure and in the case of topcoated systems, depletion of Mg pigment from the coating was significantly mediated. Such results highlight the importance of the the primer and topcoat polymers in controlling the coating performance.

The effect of polymer resistance revealed that the ionistic resistance of the added polymer layer over the Mg electrode functioned to significantly mediate the galvanic current passing between anodes and cathodes (Figure 13a and 13b) and, when large enough, completely prevented the galvanic coupling of the electrodes altogether (when R_polymer = 1000 Ω · m² in Figure 13a). In previous experimental work, a quick-drying, acrylic polymer with similar barrier properties to that of a commercial MgRP was applied to the surface of the Mg electrode in the Mg/AA2024-T4 microelectrode array, the added resistance of the polymer mediated the sacrificial galvanic protection afforded by the Mg electrode to the AA2024-T4 electrodes in the microelectrode array as shown by net current densities of zero on the Mg and AA2024-T4 electrodes due to the large ohmic resistance of the intact polymer.

A modest polymer coating resistance of 0.1 Ω · m² between the Mg anode and AA2024-T351 cathode significantly moderated the sacrificial galvanic protection function afforded by the Mg to the AA2024-T351 (Figure 13d). For this reason, the electrical and ionic resistances of any pretreatment layers, primer formulations, or topcoat systems appear to be the most important tunable factors governing the galvanic protection function of the MgRP pertaining to throwing power and self-corrosion of the Mg pigment in the MgRP system, in addition to any geometric limitations brought about by a discontinuous ionic pathway. However, the polymer resistance levels the potential and current distribution across the scratch of exposed AA2024-T351 at the expense of the galvanic current which is lowered. The primer and topcoat polymers are shown to severely mediate the throwing power of the Mg over the AA2024-T351 scribe. In the actual coating scenario this is presumed to be accurate except for locations very proximate to the edge of the coating where, in contrast to the model, there exists a small area of bare Mg exposed to solution next to the cross-section of the scratch where R_polymer is zero or small.

Comparing the throwing power predictions during and episodic wet/dry cycle by microelectrode array and finite element computational modeling.—In order to assess the consistency of the findings from both the microelectrode galvanic array and the current FEA study, their results were compared with each other. Specific current profiles produced by the finite element computational model were selected in order to best represent various times during specific current profiles produced by the finite element computational model were selected in order to best represent various times during the finite element computational study, their results were compared with each other. Specifically at t₁ (under the as-applied electrolyte layer) the current distribution spreads across the AA2024-T4. At t₂ (<40% RH) the current distribution on the AA2024-T4 fell and became non-uniform at distance of 3–4 mm from the interface of the galvanic couple with Mg. The FEA prediction of the current distribution is still finite (after 3–4 mm) but below 10⁻³ A/cm². However, the finite element model assumes an infinitely long, thin electrolyte layer and does not take into account the shrinking and irregular geometric boundaries of the electrolyte layer as it dried. As the electrolyte layer dried over the microelectrode array, the geometric boundaries of the electrolyte layer shrank as the surface tension of the electrolyte drew the edges of the shrinking droplet inwards. H₂ bubbles formed above the cathodically polarized AA2024-T4 microelectrodes. This change in geometric boundaries cut off the ionic pathway between the outermost microelectrodes and the cathodic current was limited to within the geometric boundaries of the droplet. This effect was observed at t₂ and t₃ in Figure 16b. At t₄ (<30% RH) the cathodic current density on AA2024-T4 was below 10⁻⁶ A/cm² which is near its free corrosion potential (Figure 6).

Important limitations of the FEA—future work.—FEA proved to be extremely useful tool in helping to examine the galvanic throwing power of a simulated MgRP / AA2024-T351 system. However, there are significant improvements which could be made that would improve the correlation to real environmental exposure.

The finite element computational model could be made more robust by including the consideration of evolving electrolyte chemistry due to the presence of new species (such as Mg(OH)₂) produced by the corroding Mg anode), electrolyte geometry during wetting and drying, or other unaccounted for sources of IR drop such as the formation of H₂ bubbles on the surface of the cathodes as a function of position and time. For example, in the MgRP/AA2024-T351 system, when Mg pigment corrodes, the electrolyte becomes saturated with Mg(OH)₂. When this occurs the pH rises locally and can reach values as high as 10.5. This will have a dramatic effect on the electrochemical boundary conditions of the AA2024-T351 and Mg electrodes (Figure 17 compared to Figure 6) and would be extremely useful if accounted for in the model. Additionally, electrolyte and coating geometries can control the level of aeration and subsequent diffusion limited cathodic current density on AA2024-T351. This would also be extremely valuable to account for in the model. The galvanic couple current and potential between bare AA2024 and bare Mg occurs well to the HER dominated region of the cathodic current density on AA2024-T351 (Figures 6 and 7). As such significant shifts in iₜₐ are expected to have little impact, however they warrant discussion. When the net electrical and ionic resistance between the AA2024 and Mg become significant, a shift in diffusion limited cathodic current density would ultimately change (and iₜₐ effectively serves as) the minimum galvanic current required to polarize AA2024 below its critical pitting potential (Figure 7 depicts this well) as AA2024’s critical pitting potential is often cited as close to its free corrosion potential. As an example, if iₜₐ were to increase (representative of a thin-layer environment) the minimum required galvanic current to polarize AA2024 below critical pitting potential would be increased, thus the galvanic protection mechanism afforded by Mg would be less robust.

Conclusions

- A finite element computational model was successfully developed to study the effects of electrolyte chemistry, electrolyte layer
Figure 16. Comparison of select cathodic current profiles (over bare AA2024-T4) obtained experimentally from a microelectrode galvanic array and computationally from a finite element computational model of a galvanic couple between bare Mg and bare AA2024-T351 as a function of perpendicular distance from the interface. The Mg electrode is to the left of position zero. (a) RH profile of exposure (b) current density profile vs. position obtained experimentally from a microelectrode galvanic array and (c) current density vs. position obtained computationally from a finite element computational model.

Figure 17. E-log(i) kinetic boundary condition data for bare high purity Mg and bare AA2024-T351 sheet in 1.0 M NaCl and 100% ASTM SOW that have and have not been preconditioned by allowing pure Mg powder to dissolve in solution for 24 h prior to testing.
added resistance of the polymer significantly mediated the sacrificial galvanic protection afforded by the Mg electrode to the AA2024-T4 electrodes and resulted in a measured throughing power of only 50 μm for an intact coating which had not failed.

- In general, the magnitude and distribution of cathodic and anodic current densities predicted by the finite element computational model throughout a wet/dry cycle matched the trend in current densities measured by the microelectrode galvanic array on the coupled electrodes reported elsewhere. However, the finite element model assumed an infinitely long, thin electrolyte layer and did not take into account the shrinking geometric boundaries of the electrolyte layer or variable electrolyte height upon drying where individual droplets are formed.

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