Galvanic Corrosion Modelling for Aircraft Environments

Andres PERATTA\textsuperscript{1}, Theo HACK\textsuperscript{2}, Robert ADEY\textsuperscript{3}, John BAYNHAM\textsuperscript{4}, Hubertus LOHNER\textsuperscript{5}

\textsuperscript{1}CM BEASY, UK, aperatta@beasy.com
\textsuperscript{2}EADS, Germany, theo.hack@eads.net
\textsuperscript{3}CM BEASY, UK, r.adey@beasy.com
\textsuperscript{4}CM BEASY, UK, j.baynham@beasy.com
\textsuperscript{5}AIRBUS, Germany, hubertus.lohner@airbus.com

Abstract: The aim of this work is to develop and validate a computational model for simulating galvanic corrosion in macroscopic samples for further application in typical case scenarios appearing in an aircraft environment. The case study involved in this paper consists of a co-planar bimetallic pair composed of Aluminium AA 2024 and carbon fibre reinforced polymer (CFRP) immersed in saline solution. The computational approach, based on the Boundary Element Method (BEM), aims at solving current density and electric potential in the electrolyte and active electrode surfaces. The obtained BEM based numerical simulation tool is validated with experimental measurements in a controlled environment. The modelling approach as well as the experimental methodology for characterising the material properties used as input in the simulation and for validating the results is described throughout this paper.

The experimental measurements of potential at different points in the electrolyte and total current are in good agreement with the simulation results. Furthermore a sensitivity analysis is presented showing the effect of corrosion rate and total current change with varying physical properties of the electrolyte.

Keywords: Galvanic corrosion, AA2024, CFRP, Boundary Element Method, Aircraft

Acknowledgement: This work is supported by the Six Framework Programme for Research and Development of the European Commission in the Specific Targeted Project “SICOM”, Priority 4, Aeronautic and Space ; Project No.: AST5-CT-2006-030804 SICOM.

1. Introduction

Until the end of the 60’s no significant attention was given to corrosion in the aircraft industry. Thereafter manufacturers and engineers became increasingly aware of the impact of different types of corrosion on the lifetime of the structures; while at present, in the United States alone costs estimated in the order of 2.2 billion dollars per year are reported as coming from the aircraft industry [1]. Nowadays, different forms of corrosion (i.e. galvanic, pitting, crevice, inter-granular, etc) are generally recognised as key factors in limiting the operational life time of the aircraft uneconomical high maintenance.

The currently applied “find it – fix it” maintenance concept is a common approach against corrosion where corrosion findings have to be maintained independent of their impact. However, it is widely recognised that scheduled measures are more efficient in the mid and long terms. In this aspect the benefit of modelling for prediction and optimal design becomes clear. The “find and fix” approach must be complemented by an approach based on understanding of the corrosion process and the ability to predict its behaviours. Corrosion prediction models must be developed to enable the development of a cost-efficient predictive corrosion integrity and maintenance programme.
Galvanic corrosion (GC) occurs when different materials are in contact with a common electrolyte. GC on its own can cause severe damage in an aircraft due to highly accelerated corrosion rates compared to other mechanisms. Usually GC can be avoided by proper material selection and appropriate corrosion protection measures. However, combinations of dissimilar materials are often applied due to structural requirements that need to be fulfilled in the design. In this case, costly corrosion prevention systems have to be applied to avoid the access of electrolyte. Often, GC alone may not be directly the main cause of structural failures, but its occurrence may favour proper conditions for initiation of other types of corrosion such as pitting.

The fundamental principles of GC are quite well established and generally understood, but the general understanding gained has so far not yet been exploited enough to narrow the gap between scientific research and engineering applications. On the other hand, the progressive advance of computational resources in the last few decades has today made possible to model a variety of complex corroding systems, thus representing a leading edge technology not only for research in the subject, but also for direct application in engineering design. At present, a computational modelling approach is one of the most effective tools for design and optimization purposes, as well as for failure detection, monitoring, and quality performance assessment. In addition, recent advances in numerical methods have allowed the solution of increasingly larger and more complicated structures [2].

One of the general objectives of modelling GC is to tailor the corrosion protection measure in order to avoid GC for hybrid structures without performing a huge amount of laboratory testing. A crucial aspect of computational modelling for GC is its connection with reality, and its reliability as a predictive tool, and for this reason the validation step of any model is as important as any other aspect of the model. Hence, the aim of this work is to show the validation procedure used to support existing computational modelling capabilities for GC in the case of aircraft environments.

The validation approach consists of comparing experimental measurements of electrolyte potential and corrosion rates obtained from a corroding sample with the predictions coming from the equivalent computational model. The materials involved in the experiment are Aluminium AA2024 and Carbon Fibre Reinforced Polymers (CFRP) acting as anode and cathode, respectively.

2. Conceptual model
The validation tests are based on a basic bi-metallic galvanic corrosion model. This model consists of two co-planar electrodes immersed in an electrolyte as shown in Figure 1.

The anode consists of aluminium alloy AA2024 (clad or unclad) while the cathode consists of carbon fibres reinforced plastic (CFRP). The CFRP panel has been ground to reveal carbon fibres on the surface, thereby exposing them as a cathodic electrode material to the electrolyte solution. The anode and cathode are separated by a small non conductive gap (~1.5 mm wide) to avoid direct electrical contact between the electrodes. The electrolyte consists of a saline solution (NaCl) with varying chloride concentration. The electrolyte is enclosed in a parallelepiped of dimensions $305 \times 150 \times h_e$ mm, in x, y and z directions, respectively. The model height ($h_e$) of the electrolyte is variable.

To establish the galvanic effect, an electrical return path connection is made between anode and cathode. In the experiment this is achieved using an Ammeter.
3. Problem formulation
The problem formulation for the electrolyte is based on the charge conservation equation in the bulk of the electrolyte under steady state conditions.

The mathematical description of the problem is based on the 3D Poisson equation for the electrolyte potential with non-linear boundary conditions imposed by the prescribed polarisation curves on the active electrodes. The physical and mathematical background for the modelling can be followed from [3,4].

In the steady state case, the governing equation for the electrolyte becomes:

\[ \nabla \cdot \mathbf{j} = 0; \tag{1} \]

where \( \mathbf{j} \) is the current density given by: \( \mathbf{j} = -\sigma \nabla V_e(x) \), \( \sigma \) represents the electrolyte conductivity, and \( V_e(x) \) is the electric potential in the electrolyte at point \( x \in R^3 \). The integration domain \( \Omega \) of this problem is the electrolyte, and the boundaries \( \Gamma = \partial \Omega \) are defined by all the surfaces surrounding it, including the anode, cathode and the insulating walls.

The boundary conditions applied to the active electrodes are of the generic form:

\[ j_n = -\sigma \frac{\partial V_e}{\partial \mathbf{n}} = f(\Delta V) \tag{2} \]

where \( j_n \) is the current density flowing throughout the surface in normal direction (\( \hat{n} \)), and \( \Delta V \) is the polarisation potential across the interface metal/electrolyte given by \( \Delta V = V_e - V_m \), where \( V_m \) is the potential in the metal.

This boundary condition is actually given by the corresponding polarisation curves which result from the representative polarisation curves characterisation of the material. The function \( f \), usually containing exponential factors of \( \Delta V \) as prescribed by Butler-Volmer type equations, is in general non-linear and considered as an assembly of linear functions.

This relationship must be known prior to solving the model. The software BEASY [5] used for the simulation needs to know the representative polarisation data as an input in order to assign this type of non-linear boundary condition to the corresponding electrode.

In this particular model, all other surfaces in contact with electrolyte apart from the interfaces with the AA2024 and CFRP samples are considered as insulating, i.e. \( j_n = 0 \).

4. Methodology
The validation work consists of experimental determination of electrochemical data which can be compared with the results of the computational modelling (Figure 2). These electrochemical data are:

\[ V = \left( \frac{\partial}{\partial x_1}, \frac{\partial}{\partial x_2}, \frac{\partial}{\partial x_3} \right) \text{ represents the 3D gradient operator.} \]
Results of potential field measurements in the electrolyte on anode and cathode areas
Total current flowing between anode and cathode

Once the experimental setup has been designed and established, the experimental part of the validation involves the following two steps:

- Measurement of the potential in the electrolyte against a commercial Calomel reference electrode at different distances from the electrode.
- Monitoring of the total current flowing between anode and cathode in the external circuit at the external electric short cut.

In this investigation two case scenarios with different Chloride content (electrolyte conductivity) have been selected as shown in Table 1.

<table>
<thead>
<tr>
<th>Conductivity</th>
<th>Chloride concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>9600 µS/cm</td>
<td>0.10 mol/l</td>
</tr>
<tr>
<td>49500 µS/cm</td>
<td>0.60 mol/l</td>
</tr>
</tbody>
</table>

Table 1. Conductivity values of the electrolyte

5. Modelling approach
The numerical approach for solving eq. (1) is based on the Direct Boundary Element Method (BEM) combined with the collocation technique [6,7,8].

Basically, following Green’s identity, eq (1) for homogeneous conductivity is transformed into its integral formulation eq. (3) which describes the potential at any point \( x \) in terms of sources distributed on the boundary \( \Gamma \) of the integration domain:

\[
c V_s(x) + \int_{\Gamma} \frac{\partial G(x,y)}{\partial n} V_s(y) d\Gamma(y) - \int_{\Gamma} G(x,y) \frac{\partial V_s(y)}{\partial n} d\Gamma(y) = 0
\]

where \( G(x,y) \) is the Green’s function of Laplace equation, \( x,y \in R^3 \) are vectors in 3D space, \( n \) is the outward unitary normal of the boundary of the integration domain, and \( c \) is a constant whose value is 0 if \( x \) is outside the integration domain, 1 if interior, and a value \( 0< c < 1 \) which depends on the local curvature of the boundary if \( x \in \Gamma \) [7,8].
Then, boundary discretisation is applied (i.e. $\Gamma$ is represented as an assembly of $N$ boundary elements $\Gamma_j$), and a collocation technique is used to represent potentials and normal current densities on each boundary element in terms of $M$ interpolating functions $W(\eta_1, \eta_2)$. In this way, eq. (3) yields:

$$cV_i(x) + \sum_{j=1}^{N} \sum_{k=1}^{M} H_{jk} V_{ij} - \sum_{j=1}^{N} \sum_{k=1}^{M} G_{jk} \frac{\partial V_j}{\partial n} = 0,$$

where

$$G_{jk} = \int_{\Gamma_j} G(x,\eta) W_k(\eta) d\Gamma_j , \quad \text{and} \quad H_{jk} = \int_{\Gamma_j} \frac{\partial G(x,\eta)}{\partial n} W_k(\eta) d\Gamma_j$$

represent the integrals of the single and double layer potentials, respectively [6]; $\eta = (\eta_1, \eta_2)$ represent the local coordinates of the element; and $d\Gamma_j$ is the differential surface area, (including the Jacobian) of the integration. Potentials and normal current densities on the j-th boundary element are represented in terms of the interpolating functions and their nodal values (index $k$ denotes a collocation node) as:

$$W_i(\eta_1, \eta_2) = \sum_{k=1}^{M} W_k(\eta_1, \eta_2) V_{ij} , \quad \text{and} \quad \sigma \frac{\partial V_i}{\partial n} = \sigma \sum_{k=1}^{M} W_k(\eta_1, \eta_2) \frac{\partial V_j}{\partial n} ;$$

respectively.

Eq (4) leads to an algebraic linear system of equations, in which the unknowns are potentials and current densities normal to the boundary evaluated on the boundaries of the electrolyte. Note that the integrals in both eq.(3) and (4) involve only the boundary of the integration domain.

The Boundary Element Method has important advantages [7,8] over the more widely used Finite Element Method (FEM) approach for galvanic corrosion modelling in industrial applications.

Firstly, the BEM formulation is based on the solution of the leading partial differential operator, thus improving the numerical accuracy in comparison to artificial polynomial approximations. Secondly, the mesh discretisation of the BEM model is required on surfaces only, thus avoiding volume mesh discretisation. This feature helps to decrease the computational burden, especially in complicated geometries. In addition, complex mesh generators for volumes are avoided. Thirdly, in the standard BEM potential field and potential gradient are treated as independent degrees of freedom and are both involved in the formulation, hence the outcome of the calculation is both potential fields and current densities. In contrast, the outcome of calculations based on standard FEM is the potential field so that gradients have to be calculated by differentiation of the potentials – an inherently inaccurate process.

Finally, the degrees of freedom are associated with potentials and current densities on the surfaces surrounding the electrolyte, rather than in the bulk of the electrolyte. This is quite appealing for electrochemical corrosion modelling where the electrolyte problem is driven by surface effects in the thin layers developed on the active electrodes while the bulk of the electrolyte satisfies the potential equation.

The corresponding boundary element mesh of the model is shown in Figure 3. In order to obtain good accuracy for the steep potential gradient near the gap between anode and cathode a finer mesh discretisation was locally assigned to that area.
6. Experimental method
In this investigation unclad (milled) Aluminium alloy AA2024 and ground CFRP were used. The CFRP consisted of a CFRP plate where the outer resin layer was removed by grinding down into the first carbon ply (~100 µm) to achieve an almost pure carbon surface. The experimental work consists of two main stages. The first one involves obtaining the electrochemical properties of the AA2024 and CFRP, by means of an electrochemical cell (see Figure 4). The outcomes of this process are the polarisation curves which are used as input by the modelling tool. The electrochemical properties for the CFRP have been found to be comparable to the behaviour of pure carbon plates, which indicates that the share of carbon on the surface is comparable to a cutting edge situation.

Figure 4. Electrochemical cell for obtaining polarisation curves
The resulting polarisation curves are shown in Figure 5.
Figure 5. Polarisation curves of the CFRP and AA2024 samples used for the validation test. The potential is referred to the standard hydrogen electrode (SHE).

The second stage consists of measuring the potential at different points in the electrolyte and the total current flowing from anode to cathode.

A schematic drawing of the validation device is shown in Figure 6. A scanning reference electrode is used for monitoring of the potential in the electrolyte.

Figure 6. Schematic diagram of the experimental setup

The Al-sample is insulated from the CFRP sample. The short cut is performed via an external electrical connection through the current measurement device. The total current flowing between anode and cathode is determined in the external circuit. The value of the potential of the electrolyte is determined with a movable electrolyte.
The following experimental parameters can be varied:
- Height of the electrolyte ($h_e$)
- Composition of the electrolyte (conductivity, Chloride concentration)

The electrolyte was agitated and air purged comparable to the conditions that were established during measurement of the polarisation curves.

7. Results

Two case scenarios are presented in this paper.

**Case scenario 1**

The modelling and experimental conditions for this case are given in Table 2.

<table>
<thead>
<tr>
<th>Anode:</th>
<th>AA 2024 unclad + milled</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode:</td>
<td>CFRP ground</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>(NaCl solution)</td>
</tr>
<tr>
<td>[Cl-]</td>
<td>0.1 mol/L</td>
</tr>
<tr>
<td>Conductivity</td>
<td>9580 µS/cm</td>
</tr>
<tr>
<td>Thickness</td>
<td>2 cm and 5 cm</td>
</tr>
<tr>
<td>Temperature</td>
<td>25,8°C</td>
</tr>
<tr>
<td>pH</td>
<td>6.65</td>
</tr>
</tbody>
</table>

**Table 2.** Modelling and experimental conditions for case scenario 1.

Figure 7 and Figure 8 show the comparison between experimental measurements and simulation results for electrolyte potential for an electrolyte thickness of 5 and 2 cm respectively. The figure displays the electrolyte potential measured with respect to the sample. The distance in the x-axis from 0 to 150 mm is corresponding to the cathode area and from 150 to 300 mm relates to the anode. The continuous curves represent modelling results while the symbols connected with dashed lines represent experimental measurements at different times ($t_0 = 30$ min; $t_1 = 60$ min; $t_2 = 90$ min; $t_3 = 120$ min).

The 3 parallel curves obtained with the same symbol are relating the three different scan rows of the experiment. The scatter or potential shift between the different rows is slightly higher on the cathode side. The different bundles correspond to electrolyte thicknesses of 2 cm and 5 cm. The scattering in the different measurements series are due to time dependent variations which are not considered in the simulation.
Figure 7. Comparison between experimental measurements and simulation results for electrolyte potential for an electrolyte thickness of 5 cm

Figure 8. Comparison between experimental measurements and simulation results for electrolyte potential for an electrolyte thickness of 2 cm

The experimental measurements and the simulated results for electrolyte potential are in very good agreement.

Table 3 shows a comparison between simulated and experimental results for two different electrolyte thicknesses. The discrepancy may be due to a dynamic behaviour in the polarisation curve, which in the simulation has been considered as static.

<table>
<thead>
<tr>
<th>Electrolyte thickness</th>
<th>Total Current [mA]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental</td>
</tr>
<tr>
<td>$h_e = 2$ cm</td>
<td>0.48</td>
</tr>
<tr>
<td>$h_e = 5$ cm</td>
<td>0.61</td>
</tr>
</tbody>
</table>
Table 3. Comparison of total current between experimental and simulation results

The driving force of the system is the potential difference established between AA2024 and CFRP. The increase of electrolyte thickness implies a decrease of ohmic resistance, and therefore on the IR drop in the electrolyte. Hence, as observed from the results, an increase of electrolyte thickness translates into an increase of total current between anode and cathode. The relationship is not linear, and in general depends on the Chloride contents of the solution as shown in section 7.3.

Case Scenario 2

The modelling and experimental conditions for this case study are given in. This case scenario represents a highly conductive electrolyte.

| Anode: AA2024 unclad + milled | Cathode: CFRP ground |
| Electrolyte | (NaCl) | [Cl⁻] 0.6 mol/L |
| Conductivity | 49500 µS/cm |
| Thickness | 5 cm |
| Temperature | 25.8°C |
| pH | 6.65 |

Table 4. Experimental conditions for case scenario 2

The distribution of normal current density on the cathodic region is more uniform than in the anodic, as observed in the Figure 9 obtained from numerical modelling. The overpotential distribution on the sample is shown in Figure 10 and Figure 11, as contour plot and 2D graphs respectively. Figure 12 compares the profile of potentials obtained at the top and bottom of the electrolyte (at \( z = h_e \)) and close to the sample, respectively.

Figure 9. Contour plot of normal current density on the electrodes obtained by simulation. The left side represents the cathode (CFRP) and the anode (AA2024) is on the right.
Figure 10. Contour plot of overpotential on the electrode surface obtained by simulation. The left side represents the cathode (CFRP) and the anode (AA2024) is on the right.

Figure 11. Variation of overpotential along the sample obtained with the numerical model. Red dots represent simulated results on the sample, while the solid green curve represents simulated results at $h_e = 5\text{cm}$.

Figure 12 compares the electrolyte potential referred to the sample received from the modelling with the values obtained from the experiment. Good agreement has been observed. The scattering in the different measurements series are due to time dependent variations which are not considered in the simulation ($t_0 = 30 \text{ min}; t_1 = 60 \text{ min}$). In comparison to the experiment with the lower conductivity of scenario 1 (Figure 7) the potential drop between anode and cathode is much smaller. The shift in the potential profile to more negative values is caused by the decrease in the pitting potential with higher Chloride content of the electrolyte.
Figure 12. Comparison between electrolyte potential measured at the ...cm relative to the sample (symbols connected with dashed lines) and modelling results (blue, thick continuous curve).

Figure 13 shows the normal current density on the sample obtained with numerical modelling with BEASY. Figure 14 illustrates the polarization status of CFRP and AA2024 in this particular configuration.

Figure 13. Normal current density along the sample obtained with numerical modelling.

A minimum value of 20 µA/cm² is found as a minimum current density at the end of the Aluminium specimen (x = 300mm). A clear galvanic corrosion effect is expected above 2 µA/cm² [4].
This representation of the results allows identification of the portion of the polarisation curve which is involved in the simulated process. As expected, the plot is consistent with the polarisation data shown in Figure 5.

The comparison between modelling and experimental results for the total current flowing between anode and cathode is shown in Table 5. The agreement between observed and simulated results is very good.

<table>
<thead>
<tr>
<th>MODEL</th>
<th>EXPERIMENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.94 mA</td>
<td>7.01 mA</td>
</tr>
</tbody>
</table>

Table 6. Total current flowing between anode and cathode

From the results in both case scenarios it can be observed that decrease of the electrolyte thickness causes increase of potential drop between anode and cathode.

8. Sensitivity Analysis

After validation against experimental results, the modelling tool was used to study the dependence of the total current on the electrolyte thickness and conductivity. The results are represented in Figure 15 and Figure 16. As expected, an increase of electrolyte conductivity translates into an increase of total current. The rate of increase for low conductivity electrolytes is much higher than for highly conductive electrolytes.

In addition, an increase of the electrolyte thickness on top of the corroding cell leads to higher currents. This effect is less pronounced in highly conductive electrolytes.
Figure 15. Total current flowing from anode to cathode for different electrolyte conductivity and thicknesses as a function of electrolyte conductivity.

Figure 16. Total current flowing from anode to cathode for different electrolyte conductivity and thicknesses as a function of logarithm of electrolyte conductivity.

From an experimental point of view it is not necessary to employ electrolyte thickness greater than 5cm, as there is no significant change in total current beyond that point. On the other hand, electrolyte conductivity below 10000µs/cm helps to reduce the influence from incorrect or unstable conductivity condition and to improve the discrimination of total current.
Conclusions

A computational model for galvanic corrosion has been tested against a basic co-planar corrosion experiment. The modelling approach is based on the boundary element method. The advantages of this formulation over other existing approaches have been indicated. The results obtained from the model are in good agreement with the experimental results. The total corrosion current between anode and cathode are not sensitive to small variations in the electrolyte conductivity. The polarisation data of the participating electrodes, obtained usually from the material characterisation, must be provided as accurately as possible in order to obtain results of good quality, i.e. good matching between experimental and modelling results.

After calibration and validation, this type of computational tools can be applied to a variety of R&D projects related to corrosion modelling in real case scenarios.

References


