Validation of predictive model for galvanic corrosion under thin electrolyte layers: An application to aluminium 2024-CFRP material combination

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Abstract
An experimental setup was developed for the validation of a finite element model (FEM) for simulating galvanic corrosion occurring under very thin electrolyte for bi-material combination composed of aluminium AA2024 and carbon-fibre reinforced polymer (CFRP). The validation approach is explained and the results obtained are presented. The main outcomes of the model are electric current density and potential distribution on the electrode surface. Good agreement has been obtained between measured and modelled data. Further parameter studies are discussed to show the effect of different physical properties of the electrolyte on corrosion rates and total current changes in the materials involved.

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1. Introduction

Corrosion protection plays a very important role in the design and maintenance of aircraft. The mechanical properties of alloys currently used are the compromise of high specific strength and corrosion resistance. The extreme long aircraft design life requires durable protection systems to ensure acceptable operational cost while in-service. Inline with this objective, the corrosion protection should also be adequately optimised in-order to reduce design and manufacturing cost of the aircraft.

The recent demand for better fuel-efficiency in aircraft industry has reflected an increase usage of more lightweight materials such as CFRP 1 and titanium, besides aluminium. The increase application of this “mixed materials” enhances the risk of galvanic corrosion when they are coupled in the presence of a corrosive electrolyte. New aircraft designs contain a high degree of CFRP materials, which are in contact with aluminium 2024 (AA2024-T3) in specific areas. Since the carbon fibres behave electrochemically like a noble metal, corrosion of the aluminium alloy can be induced.

The basic principles of galvanic corrosion are quite established and generally well understood [1–3]. Scully et al. has demonstrated an experimental approach to validate a galvanic corrosion model [4]. The author made quantitative predictions of galvanic corrosion by finite element methods and compared it with long term measurements on heat exchanger tubes in seawater. Also, there have been numerous publications laying some background in the area of galvanic corrosion modelling [5–16]. On the other hand, numerous investigations [17–29] have shown that corrosion under thin electrolyte layer is very different from that in the bulk electrolyte due to oxygen transport and reduction kinetics. The thickness of the film may vary from nanometre to millimetre; however micrometre thicknesses are usually the range of interest when investigating atmospheric corrosion [25]. Specifically, structures consisting of AA2024 and CFRP may experience different forms of corrosive environments, e.g. condensed water and melting of ice which could occur in the upper part of the inner aircraft structure. This can be generalised as thin layer electrolytes with variations in thickness and chemical composition. Quantitative knowledge of galvanic coupling under these various form of thin electrolyte films is useful in understanding corrosion mechanisms and in tailoring surface protection against galvanic corrosion. So far, very limited studies have addressed the galvanic corrosion between AA2024 and CFRP [30–34].

More effort has been focused on general corrosion and particularly on the influence of the ion species in solution and the influence of cathodic impurity elements in the alloy on the general corrosion rate for aluminium alloys [35]. The influence of the electrolyte involves many factors such as pH, temperature,
composition and concentration of the ions and the conductivity of the electrolyte. The influence of electrolyte conductivity on galvanic corrosion has been previously stated by Waber [36] in-terms of “macroscopic” and “microscopic” galvanic cells, or in-terms of the Wagner number [36,37].

The main objective of modelling galvanic corrosion is to tailor the corrosion protection measures for “mixed material” structures without performing a huge amount of laboratory testing. A crucial aspect of computational modelling for galvanic corrosion 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. This paper generally describes the development of a validation technique which was successfully used to validate the Finite Element Method (FEM) based computational predictive model namely Elsyca Galvanic Master. The validation approach consists of comparing the experimental measurements of galvanic coupling current, under very thin electrolytes from 13 μm to 45 μm obtained between untreated “macroscopic” AA2024–CFRP coplanar electrodes with the predictions coming from the equivalent computational model.

2. Galvanic corrosion AA2024–CFRP

When CFRP and AA2024 are galvanically coupled with the presence of electrolyte, ionic current flows through the electrolyte from cathodic to the anodic areas. They are balanced by electron flow through the electrodes.

Galvanic corrosion under thin electrolyte features different characteristics in mass transport, conductivity, change of liquid layer chemistry due to the formation of reaction products. Besides it also has different characteristics compared to those of a bulk electrolyte. Under thin electrolyte, the oxygen transport is much higher than in bulk electrolyte, as the film thickness is very low. Under conditions of lowered relative humidity, which permits rapid evaporation, convective mixing in the condensed layer further hastens the arrival of dissolved oxygen at the cathode. Both the characteristics of the moisture film can result in an increase in galvanic corrosion rate.

From Fig. 1 the resistance of the electrodes $R_{CFRP}$ and $R_{AA2024}$ are assumed to be zero, due to the fact that they are almost negligible in value since there is a direct electrical contact in comparison to the other resistances. In the event one of the resistance becomes in value since there is a direct electrical contact in comparison to the other resistances. In the event one of the resistance becomes extremely high e.g. at low conductivity electrolyte or in the presence of a coating system on any one of the electrodes, no significant corrosion rates due to galvanic effect are possible except for self corrosion of AA2024. In-service, there are more complicated interactions among these factors, e.g. $R_d$ depends on the geometrical shape of the electrolyte path between the anode and cathode.

3. Governing equations

The mathematical model is based on the potential model. This section gives a short overview of the equations to be solved by the model and the boundary conditions applied.

3.1. Electrolyte

Considering no ion diffusion effects, Ohm’s law describes the current density proportional to the electric field, $E$:

$$\sigma E = -\sigma \cdot \nabla \varphi$$

where $E$ is the electric field (V m$^{-1}$), $\sigma$ the conductivity (Ω$^{-1}$ m$^{-1}$), $\varphi$ is the potential (V).

With the proportionality factor being the conductivity. Expressing current conservation in local form yields the Laplace-equation, which is a partial differential equation of second order [5]:

$$\nabla \cdot (-\sigma \nabla \varphi) = 0$$

Since the electrolyte in this investigation is treated as a homogeneous ohmic conductor, which may not always be the case, the equation simplifies to:

$$\nabla^2 \varphi = 0$$

The local corrosion rate at any point on the surface of AA2024 coupled with CFRP is related to the local current density and can be predicted if the potential distribution is known [5]. For that purpose, proper boundary conditions are to be imposed. They describe in a quantified way the kinetics of the reactions at the interface between electrodes involved and the electrolyte i.e. the polarisation curve. They are usually non-linear and are acquired in an experimental way. Polarisation curves could also be defined mathematically as:

$$j_E = f(\varphi)$$

$j_E$ is the normal current density on anode/cathode (A m$^{-2}$).

In the case of thin electrolytes the change of electrolyte thickness affects a number of processes as mentioned in the preceding section. Therefore, in this investigation in-order to obtain the most representative input data, DRE (Rotating Disc Electrode) experiments were performed for the acquisition of electrochemical properties of the involved materials. Through this method, a stable mass transport is achieved via convection–diffusion that is well defined.

4. Experiments

4.1. Polarisation data

The galvanic corrosion validation activity is done on various aqueous electrolyte film thicknesses containing sodium chloride.
of milled AA2024 and the cathode of a ground plate of CFRP. The challenge here is to generate a constant thin homogeneous electrolyte film during the whole measurement period with different but known and homogenous thickness on the substrate surface. Previously, various techniques had been successfully used in order to quantify a thin electrolyte layer, which includes the volumetric approach [26,27] where the uniformity of the formed film on the specimen can only be assumed. Besides, there will be some uncontrollable evaporation of electrolyte into the atmosphere, which could not be avoided and in most case the size of specimen is quite limited.

In this work, the Nusselt’s theory of falling film-wise condensation on a vertical flat plate was employed as a basis to generate a homogeneous film. Laminar film condensation has first been successfully treated by Nusselt [41] in 1916, whom had provided an analysis for laminar film condensation on an isothermal vertical plate and also has applied it to horizontal plain tubes [42–45]. It depicts the process of laminar film condensation on a vertical plate from a quiescent vapour. In general, the condensation of the film begins at the top and flows downward under the force of gravity, adding additional new condensate as it flows. According to Nusselt’s analysis, other assumptions which were also considered during this experiment are:

(a) The vapour temperature is uniform and at its saturation temperature;
(b) Gravity is the only external force acting on the film (momentum is neglected so there is a static force balance);
(c) Fluid properties are constant i.e. homogeneous electrolyte condition;
(d) The adjoining vapour is stagnant and does not exert drag on the film;

Fig. 6 shows the schematics of the experimental setup designed and developed to produce the thin electrolyte film in order to perform galvanic experiments for the fulfilment of numerical model validation.

As much as Nusselt’s analysis is valid for vertical plates, it is also applicable to an inclined plate as long as the angle of inclination is sufficient for drainage of the condensate or electrolyte. The local film thickness formed can be calculated analytically from the rearranged expression:

$$
\delta = \frac{4\mu L k_{\text{sat}} (T_{\text{sat}} - T)}{\rho L (\rho C_{\text{sat}} - \rho C g h_{\text{sat}})}^{1/4}
$$

(6)

where $\delta$ is the local film thickness (m), $T$ the temperature (saturated; wall) (°C), $\rho$ the mass density (liquid; gas) (kg m$^{-3}$), $\mu$ the viscosity (liquid) (kg m$^{-1}$s$^{-1}$), $g$; gravity acceleration (m s$^{-2}$), $k$ the thermal conductivity (liquid) (W m$^{-1}$), $z$: the z-coordinate point from top of the plate (m), $h$ is the latent heat (kJ kg$^{-1}$).

For an inclined plate, the force of gravity, $g$ on the film in the above expression is replaced with $g \sin \alpha$, where $\alpha$ is the angle of the plate relative to horizontal. Analytical solutions for determining the film thicknesses are not covered within this investigation since the thicknesses were measured in situ during the experiment. The details of the first Nusselt’s analysis for condensation on a plate before arriving to Eq. (6) can be followed at Thome [45]. Fig. 7 depicts the process of laminar film condensation on a vertical plate from a quiescent vapour. Thus, the temperature profile across the film is linear and heat transfer is by one-dimensional heat conduction across the film to the wall.

The temperature of the film being formed is measured and monitored using thermocouples individually at multiple points on the electrode from the start to the end of the fog flow (top to bottom) as shown in Fig. 6 throughout each experiment. The

<table>
<thead>
<tr>
<th>Cl content (mol/L)</th>
<th>Case</th>
<th>Electrolyte thickness, $\delta$ (mm)</th>
<th>Rotation speed, $\omega$ (rpm)</th>
<th>Diffusion coefficient, $D$ (m$^2$/s)</th>
<th>Kinematic viscosity, $\nu$ (Pa s)</th>
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<tr>
<td>0.05</td>
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<td>$2.27 \times 10^{-9}$</td>
<td>$8.85 \times 10^{-4}$</td>
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<td></td>
<td>12</td>
<td>40</td>
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</tr>
</tbody>
</table>

$4.2. Validation of thin film model$
Fig. 2. Cathodic polarisation curves of the CFRP obtained through RDE in 0.05 M NaCl electrolyte at various rotation speeds with 0.5 mV/s scan rate in (a) linear scale and (b) logarithmic scale: |j|.

Fig. 3. Cathodic polarisation curves of the CFRP obtained through RDE in 0.1 M NaCl electrolyte at various rotation speeds with 0.5 mV/s scan rate in (a) linear scale and (b) logarithmic scale: |j|.

Fig. 4. Cathodic polarisation curves of the CFRP obtained through RDE in 0.6 M NaCl electrolyte at various rotation speeds with 0.5 mV/s scan rate in (a) linear scale and (b) logarithmic scale: |j|.
details on the thermodynamic properties of the condensate being formed in this experimental setup i.e. the temperature profile across the film, the temperature profile from top to bottom of the flow and temperature gradient within the tested sample or plate will not be discussed in detail here. Nevertheless, during this investigation it was found that:

(a) The temperature gradient for the points mentioned above are found to be minimal relative to the working temperature i.e. room temperature.

(b) Minimal changes in temperature (± 2 °C) are not expected to influence the final result within the measured domain.

4.2.2. Material and cell configuration

The anode consists of a milled aluminium AA2024-T351 unclad sheet with a thickness of 1.6 mm. The cathode consists of CFRP prepreg laminate plate, which is composed of quasi-isotropic layers of carbon fibres and resin. The CFRP plate was cut to the same size as the anode to achieve a 1:1 cathode to anode surface area ratio. Next, the CFRP surface to be tested is ground down to roughly 100 μm to reach the first carbon ply. The idea is to achieve an almost pure carbon fibre surface, which is then abraded with #4000 grade silicon carbide paper. The cut edges of the CFRP plate are covered by silver glue to connect as much fibres as possible.
Finally, the electrodes are separated by a gap of 2 mm filled with polymer based silicon. Such gap distance i.e. in millimetre range is of relevance in aircraft where CFRP and aluminium structures are connected together. Fig. 8 shows a completed electrode arrangement [34].

The area of the cell is confined by the border of the polyethylene containing AA2024 and CFRP electrodes. The galvanic coupling current between the electrodes is measured using an ammeter i.e. potentiostat placed in the circuit as shown in Fig. 9.

4.2.3. Procedures

The electrolytes used are 0.3 wt.% (0.05 M), 0.6 wt.% (0.1 M) and 3.5 wt.% (0.6 M) NaCl solutions. The electrolyte is filled into a container mixed with a non-ionic surfactant Triton® X-114 (Sigma–Aldrich) to reduce the interfacial tension between liquid and the surface. This is to further support the wettability and formation of a homogeneous film without affecting the conductivity of the electrolyte. There was also no effect of surfactant detected on the polarisation behaviour of the materials in the investigated domain.

Next, an ultrasonic nebulizer is used to generate a fog of the electrolyte. The fog flows from top to bottom on the surface in-parallel to the interface. It is important to ensure that the fog flow direction does not influence transport of electrolyte species, corrosion products or ions in the film. Further, to assure an undisturbed laminar flow of the fog out of the container onto the surface of the specimen, the whole setup is enclosed by a transparent PVC compartment with lid. The film properties are defined by the electrolyte composition of the bath, inclination of the electrodes and the flow rate of the fog out of the container. The flow-rate of the fog can be controlled though a variable opening size of the container (Fig. 6). The continuous flow of fog creates a thin electrolyte film of interest where the thickness of the film is stabilized through time. The electrolyte film will be in equilibrium state with the continuously flowing water saturated fog. Since it is not directly exposed to the ambient low humidity atmosphere, evaporation of the film can be neglected. In addition, the film deposition is found to be almost independent of the thermal conductivity of the substrates under investigation.

Different thickness of the electrolyte film is achieved by altering the angle of the inclination, $\alpha$ of the electrode plane. The film thickness is measured online by optical spectroscopy technique. The thickness achieved at certain inclination angle can be measured at different locations on the specimen during the experiment. In this investigation, the thickness of the film is varied between 13 and 45 μm. At the same time the corresponding or correlating total current (coupling current) required for the validation of the computational results is measured using ZRA (Zero Resistance Ammetry) via potentiostat and recorded.

4.2.4. Numerical setup

The FEM discretization of the model solved in this paper is shown in Fig. 13. In-order to obtain good accuracy for the steep gradient of electric potential and current density close to the interface between anode and cathode a finer mesh discretization was locally assigned.

Eq. (3) is solved for the electrolyte domain as shown schematically in Fig. 13, subject to boundary conditions at CFRP and AA2024 surfaces i.e. Eq. (4) that are vital to accurately predict the corrosion rate. The boundaries of the geometry are considered as perfect insulators. It has also been found that when the electrolyte film gets very thin, the electric potential in the electrolyte is almost constant along the thickness of the film i.e. $z$-coordinate compared to other dimensions [10,46]. Therefore, it gives the possibility for the model to treat the problem as a two-dimensional problem in space for solving Eq. (4). In this case the model becomes:

$$\nabla_{2D} \cdot (-\sigma \nabla_{2D} \varphi) = - f(\varphi)$$  \hspace{1cm} (7)

where $\nabla_{2D}$ is 2D gradient operator solving for $x, y$-coordinates and $f(\varphi)$ is the imposed boundary condition divided by the thickness of the film. By solving Eq. (7), we obtain the current density and potential values at all the nodes on both the electrodes.

5. Results

5.1. Total current measurement from experimental validation setup

The experimental measurement of galvanic corrosion current by means of the established validation setup is conducted. The present work is related to the study of 12 different case scenarios as listed in Table 2. The case number matches the notation adopted for the experimental part. The surface area ratio between cathode and anode is fixed as 1:1 throughout the investigation.

Figs. 10–12 shows the total current measurement from the developed experimental setup as a function of time for cases 1–12 at variable electrolyte film thicknesses, $\delta$ and chloride concentration. Result shows that an increase in the electrolyte film thickness and chloride concentration translates into an increase of the total current.

5.2. Modelling results

5.2.1. Potential and current density distribution

From all the cases investigated, both experiment and modelling showed that case 1 and case 12 (Table 2) gives the highest and the lowest galvanic current respectively. Figs. 14 and 15 describe the current density and potential distribution as a function of distance
in x-direction predicted by the model exemplarily for case 1 and 12. The values in the graphs of Figs. 14a and 15a are series of points on the surface extracted along the centre of the electrodes in the model as indicated by dotted lines on the model picture (inset in Fig. 14a). The curves in Figs. 14b and 15b show the experimental polarisation curves (dashed lines) and polarisation status (bold solid lines) i.e. the region of the polarisation curve of AA2024 and CFRP electrodes used by the model as boundary conditions for solving case 1 and 12 respectively. It can be seen from the polarisation status of the CFRP electrode marked as “Model” for both these cases, only low overpotential areas are utilised for solving the problem compared to AA2024 polarisation. From the result, the anodic current density distribution on AA2024 is concentrated close to the interface of the CFRP electrode with very steep gradients. In contrast, the CFRP surface shows more uniform distribution. In general, the modelling outcome from all the cases indicates that the anodic current density increases with increasing electrolyte thickness and chloride concentrations. Additionally, the potential distribution at the observation line shows that the AA2024 area very close to CFRP is polarised towards the pitting current density of around 1 A m\(^2\)/C\(_0\) or even higher i.e. to more positive potentials. However, the areas away from CFRP are almost unaffected. It was found that the areas away from CFRP will be gradually polarised with increasing chloride concentration and electrolyte thickness. Fig. 16a depicts the 2-dimensional current density distribution prediction for case 1, where the highest anodic current density distribution is seen very much localised at the brim of the AA2024 electrode. This is due to the change of galvanic

<table>
<thead>
<tr>
<th>Electrolyte aggressiveness</th>
<th>Case</th>
<th>Cl(^-) content (mol/L)</th>
<th>Electrolyte temperature (°C)</th>
<th>pH</th>
<th>Conductivity, (\sigma) ((\mu)S/cm)</th>
<th>Electrolyte thickness, (\delta) ((\mu)m)</th>
<th>C/A ratio</th>
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<tr>
<td>Low Cl(^-) concentration</td>
<td>1</td>
<td>0.05</td>
<td>23</td>
<td>7.1</td>
<td>4990</td>
<td>13</td>
<td>1</td>
</tr>
<tr>
<td></td>
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<td>0.05</td>
<td>23</td>
<td>7.1</td>
<td>4990</td>
<td>25</td>
<td>1</td>
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<td>1</td>
</tr>
<tr>
<td>Medium Cl(^-) concentration</td>
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<td>0.1</td>
<td>24</td>
<td>6.9</td>
<td>9600</td>
<td>13</td>
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</tr>
<tr>
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<td>8</td>
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<td>24</td>
<td>6.9</td>
<td>9600</td>
<td>44</td>
<td>1</td>
</tr>
<tr>
<td>High Cl(^-) concentration</td>
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<td>0.6</td>
<td>24</td>
<td>6.75</td>
<td>49,600</td>
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<tr>
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<td>24</td>
<td>6.75</td>
<td>49,600</td>
<td>25</td>
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<td>24</td>
<td>6.75</td>
<td>49,600</td>
<td>40</td>
<td>1</td>
</tr>
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</table>
Fig. 13. Mesh discretisation of the bi-metallic galvanic corrosion model, viewed from below the electrodes.

Fig. 14. Plot of (a) current density and potential profile prediction by the model on the surface along the centre and across the model and (b) polarisation state of electrodes during simulation for Case 1.

Fig. 15. Plot of (a) current density and potential profile prediction by the model on the surface along the centre and across the model and (b) polarisation state of electrodes during simulation for Case 12.
reaction pattern from 1-dimensional at the central areas of the cell, to more 2-dimensional pattern at the top and bottom edges of AA2024 close to CFRP.

5.3. Comparison of experiment with simulation

The modeling results were validated against the galvanic coupling current acquired from the validation experiment in NaCl electrolytes of three different concentrations and varying electrolyte thickness. Fig. 17 shows that in general the modelling results are in good agreement with the experimental results and it is important to note, that overall, the model predicts a similar trend as the experiment.

Besides, almost all the modelling prediction of total current is more conservative than the experimental results and most of them fall within the measured experimental scatter for all three chloride concentrations. However, the differences in total current between experiment and model are increasing with thickness. This is likely caused by the concentration build-up e.g. metal ion concentration in the electrolyte layer and change in precipitation rate of corrosion products on the AA2024. At higher film thickness, \( \alpha \) is smaller which as consequence reduces the gravitational force on the film. This would reduce the film flow out velocity and increase the probability for the built up of corrosion products on the surface. In contrast, during the acquisition of the input data for the AA2024, the electrolyte is well stirred and this would have reduced the deposition of corrosion products on the electrode.

6. Discussion

6.1. Thin film validation setup

A general explanation was given on how the thin film validation setup works in Section 5.2. Fig. 18 shows some detail on formation of the film being formed on the electrodes during the experiments.

As mentioned before, the electrolyte film thickness formed on the surface is defined by the electrolyte fog deposition/condensation rate and electrode inclination angle. The evaporation of the film particles is avoided by constant flow of the fog particles above and parallel to the electrode throughout the duration of each experiment. The figure also shows that the rate of evaporation of the film is lower than the rate of condensation/deposition since the air adjacent to the film surface is the flowing fog, which is of high percentage of relative humidity (>90% R.H). It consists of very fine electrolyte droplets which promotes deposition/condensation and suppresses evaporation. At the very start of the experiment, the film is most likely to be formed by means of both condensation and deposition due to initial temperature difference between the electrode surface, \( T_w \) and the fog, \( T_s \) itself. As a function of time, the condensation will be reduced and only deposition will take place as there will be almost no temperature difference between them. However, the increased rate of condensation/deposition compared to evaporation does not affect the thickness stability of the formed film due to the dynamics of the film itself, which is constantly flowing down slowly out of the electrodes at a rate depending on the inclination angle. This can be realised in Fig. 19 which shows exemplarily a single point film thickness measurement as a function of time on CFRP electrode inclined at \( \alpha = 30^{\circ} \). Here the measurement starts on a pre-wetted electrode in which due to its inclination angle, the film thickness is seen to reduce drastically from initial thickness of around 70 \( \mu \)m, as the film flows down and evaporates. The fog system is turned on after 30 s, which causes an initial increase in the formed film thickness. Nevertheless, the thickness of the film reaches an equilibrium point relatively fast around 17 \( \mu \)m.

On the other hand, the way this film is made is such that the dissolving oxygen concentration is high and renewed in the film by the fog particles condensing/depositing on the film since they are very small and saturated with oxygen content. Due to this reason, the concentration of oxygen can be almost maintained throughout the period of each experiment. The oxygen concentration profile in the film is assumed to be as illustrated in Fig. 18. In
any case, in the thin films like the one considered here, the refreshment of the electrolyte due to the flow conditions in this setup is not expected to further increase the oxygen concentration at the electrode surface. Here, the oxygen access is expected to be larger which would favour the oxygen reduction reactions. Moreover, the film flow velocity is very low and expected to be ideally zero at the electrode surface. As for the modelling, the oxygen concentration parameter is dictated by the polarisation curve created using RDE, in which there is also a constant vertical flow of electrolyte high in oxygen from the bulk towards the electrode surface during the measurement.

6.2. Potential and current density distribution

From Figs. 14 and 15 is to be interpreted that the current density distribution on AA2024 is highly non-uniform especially for a very low electrolyte thickness compared to CFRP. For case 1, the potential on AA2024 also varies only at areas close to CFRP i.e. up to 4 mm away from interface. The closest area shows the most positive potential of \(-470\) mV. The rest of the area away from the interface shows almost constant and uniformly distributed potential (Fig. 16b). In case 12 there were almost no potential variations for areas of AA2024 around 10 mm away from the interface to CFRP. On the contrary, the potential of the CFRP varied most negative closest to AA2024 and the most positive furthest from the interface for both the cases due to the galvanic coupling. The shift in the potential profile to more negative values in case 12 compared to case 1 is caused by the decrease in the pitting potential of AA2024 with higher chloride content of the electrolyte.

Looking at the rest of the cases, one observes a very small cathodic current on CFRP surface distant from AA2024. This is combined with relatively small potential variations especially when the electrolyte film gets thinner. For example in Fig. 14a, the regions of CFRP which are around 40 mm away from the interface show apparently the open circuit potential i.e. 0 mV, meaning these areas are not contributing to the galvanic coupling with AA2024. This is also verified during experimental measurement, where there is no effect on the total current measured when the electrolyte film on areas of CFRP away from the AA2024 is wiped off. This is due to the apparent reason that the galvanic corrosion is under ohmic resistance control as the gap between the two electrodes is relatively big. In this study the gap is 2 mm and the electrode size is macroscopic in scale compared to the electrolyte thickness. Therefore, the ohmic potential drop in the electrolyte composed most of the potential difference between CFRP and AA2024. One could further support this with the polarisation status (see Fig. 14b) of the electrode for case 1 from the model, where an ohmic (IR) drop around 85 mV due to electrolyte resistance and distance can be visualised. In general, the model predicted that the cathodic reaction for all the investigated cases is kinetically limited. However in case 12 (Fig. 15b), the cathodic reaction is found to be at the transition between kinetic limited to mixed diffusion regime, at least at the areas closest to AA2024. One could expect this due to the minimal effect from electrolyte resistance and distance in comparison to other tested cases.

In any case, the model considered here is predicting the integral values of current densities and potentials, and not the pitting of AA2024 as such. But one could say that when the current density exceeds a given value, the probability for pitting is very high. The boundary conditions in Fig. 5 are an integral value of anodic dissolution rate for a defined AA2024 surface area in different solutions. Similarly, the model prediction using these boundary conditions for the coplanar geometry also in principal shows the integral corrosion area on AA2024 in-terms of current density and potential distribution. As shown earlier, this is concentrated close to interface and CFRP. Implicitly it shows that pitting will be very high at these areas which are also inline with experimental findings.
The particular concentration pattern is expected due to the effect of polarisation resistance of AA2024, geometry, electrolyte thickness and conductivity.

6.3. Electrolyte thickness

Generally, preceding literature states that the galvanic coupling current under thin electrolyte conditions is dependent on the electrolyte thickness, as long as the layer is near to or smaller than the diffusion layer thickness. This is also evident from the measured polarisation curves as previously shown. However, this investigation shows that galvanic current is the highest for the thinnest electrolyte i.e. 40 μm in 0.6 M NaCl and lowest for the thinnest electrolyte i.e. 13 μm in 0.05 M NaCl, simply due to the distance between the electrodes which is high in comparison to the electrolyte thickness investigated and the cell size is macroscopic in scale. Consequently, a decrease in the electrolyte thickness will increase the resistance of the galvanic cell and reduce the galvanic current, leading to a larger potential change on the CFRP electrode. In result, increasing CFRP surface area to support oxygen reduction reaction, in-parallel would increase the ohmic resistance contribution eventually changing the potential distribution, rendering two opposite effects. However, through the FEM model prediction, the latter is found to be more dominant in current investigation.

6.4. Electrolyte concentration

Electrolyte or the environmental conditions especially the electrolyte resistance, is a governing factor in galvanic corrosion. Fig. 17 depicts also the effect of NaCl concentration on the galvanic coupling current of AA2024–CFRP for different electrolyte thicknesses. The fluctuation in the galvanic coupling current in various chloride concentrations shows the effect of anions on the reaction kinetics especially for the AA2024. The modelling prediction shows that the potential on the CFRP is very much dependent on the resistance or concentration of the electrolyte. The increase in solution resistance reduces the total current the cathode can provide. The electrolyte resistance in a simple 2D plan parallel cell arrangement could be calculated using equation [1,6]:

\[ R_d = \frac{L}{\sigma \delta w} \]  

(8)

where \( L \) is the length of the cell or distance between AA2024 and CFRP, \( \sigma \) the electrolyte thickness, \( \delta \) the electrode width at the interface and \( \sigma \) the electrolyte conductivity. Electrolyte resistance, \( R_d \) is a determining element to the measured galvanic current and therefore it can be deduced that \( R_d \) is directly influenced by distance between the electrodes, and are inversely proportional to product of electrolyte thickness, electrode width and electrolyte conductivity. Therefore, if the product is kept at constant, the result will remain the same for the same imposed boundary conditions: geometrical configuration and polarisation curve. In effect, shows that the electrolyte concentration and thickness has an equal effect on a given galvanic coupling situation.

6.5. Polarisation status of CFRP and AA2024

The galvanic coupling current for macroscopic cell is found to be mostly limited by ohmic resistance due to the distance between the electrodes, electrolyte conductivity and thickness. On the CFRP, it is found from simulation (Figs. 14 and 15) that the maximum local cathodic current density \( J_{\text{local,CFRP}} \) for all cases investigated lies below \(-1 \text{ A m}^{-2}\) as shown in Table 3.

<table>
<thead>
<tr>
<th>Electrolyte concentration (M)</th>
<th>Maximum local current density, ( J_{\text{local}} ) (A m(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode</td>
<td>Anode</td>
</tr>
<tr>
<td>0.05</td>
<td>-0.29</td>
</tr>
<tr>
<td>0.1</td>
<td>-0.42</td>
</tr>
<tr>
<td>0.6</td>
<td>-0.71</td>
</tr>
</tbody>
</table>

Therefore in the present case, one could generally state that total current density for CFRP, \( J_{\text{total,CFRP}} \) is equal to only current density due to charge transfer kinetics, \( J_{\text{kinetics,CFRP}} \) and no mass transfer effect i.e. \( J_{\text{total,CFRP}} = J_{\text{kinetics,CFRP}} \). So, the CFRP exhibits only contributions in the kinetics region of the oxygen reduction which is independent of rotation speed during the galvanic coupling. Hence for modelling, it gives us the possibility to employ a single polarisation curve from CFRP for all the 12 cases considered here. However, it may no longer be the case when the geometry is changed, the gap between these electrodes is reduced tremendously and the conductivity of the electrolyte rises. In the event this occurs, the polarisation curve of AA2024 will be shifting to more negative potentials and the ohmic resistance will also be reducing at the same time, which means CFRP will already be in mixed kinetics and mass transfer regime, in which the diffusion rate of oxygen will start dominating the cathodic current density.

7. Conclusion

An experimental set-up has been established for validation of the computational results on macroscopic co-planar bi-metallic galvanic corrosion cell under very thin electrolyte layers. The principle of the experimental setup, homogeneity and reproducibility of electrolyte film with no geometry size limitation achieved through this setup is the enabling factor for the validation activity. Next, a model considering a co-planar unpainted bi-material combination composed exemplarily of aluminium AA2024-T3 and carbon fibre reinforced polymer (CFRP) had been developed. The main assumption made for both experimental and computational model, is the conductivity of the thin electrolyte layer on the bi-material combination is isotropic during each investigation. A FEM based predictive computational model for galvanic corrosion under very thin electrolyte layers was validated for multi-material structures exposed to thin aequous layer of NaCl electrolytes in specific application case scenarios appearing in an aircraft environment. The results predicted by the developed computational model for galvanic corrosion has been compared against experimental measurements. In total, 12 different cases were investigated experimentally, in which the modelling results were validated in-terms of galvanic coupling current. These includes variations in properties of the thin electrolyte film i.e. concentration, thickness and complemented with some discussion on kinetics of oxygen reduction on cathodic current.

Generally, the trends and galvanic coupling current results obtained from the Elsyca Galvanic Master model are in good agreement with the experimental measurements. The galvanic current is found to be under ohmic control, in which is sensitively dependent on concentration and thickness of the electrolyte layer. When concentration and thickness of the electrolyte layer decreases, the current density on AA2024 is concentrated at narrow edge, closest to the CFRP, resulting in a very steep distribution on AA2024. Hence, both model and experiment shows that most of the cathodic current contribution from CFRP electrode is coming from areas up to a critical distance from AA2024, beyond which there is no further increase in galvanic coupling current under thin electrolyte conditions. On the other hand, it is observed from the model electrode polarisation status for all cases that the cathodic current density from CFRP is almost just limited to charge transfer kinetics and...
no mass transfer effects are seen during the galvanic coupling with AA2024.

In any case, the limitations and applicability of polarisation data of the involved materials which acts as an input to the model must be well understood and known prior, to further exploit the modelling results qualitative and quantitatively. The result of this investigation, led to the development of an effective thin electrolyte galvanic cell for the purpose of validation of computational numerical model. In addition, it grants a basis for further investigation on galvanic corrosion protection of multi-material structures supported by good validation achieved for the cases considered. The computational model can now be used for sensitivity studies in order for a better understanding on the galvanic corrosion phenomena occurring under thin electrolytes for design of experiments and also for practical reasons.

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