A combinatorial matrix of rare earth chloride mixtures as corrosion inhibitors of AA2024-T3 - Part I: a comparison between potentiodynamic and EIS measurements

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1 Abstract

A combinatorial matrix of four rare earth chlorides (cerium, lanthanum, neodymium and praseodymium) has been evaluated to investigate their corrosion inhibition of aluminium alloy AA2024-T3. Two electrochemical techniques, potentiodynamic polarisation (PP) and electrochemical impedance spectroscopy (EIS), were used to evaluate the reactivity of AA2024-T3 substrates in 0.1M NaCl with the addition of 10⁻³ M of the 21 rare earth chloride mixtures at time periods of 1, 3, 6, 12 and 18 hours.

PP experiments showed rare earth inhibition of up to 98 % within the first hour and thereafter slow increases in corrosion efficiency were observed. EIS experiments revealed that the surface processes occurring on AA2024-T3 within the first 6-hours of immersion could be analysed using a single time constant. On this basis the polarisation resistances after 6-hour immersion were determined from both PP and EIS experiments and the datasets from the two techniques were compared. PP and EIS results were in good agreement for systems exhibiting a low polarisation resistance, whereas polarisation resistances estimated by PP were larger than those estimated using EIS for solutions with increased inhibition.

The open-circuit potential (OCP) of AA2024-T3 was observed to decrease as a function of time for all solutions, which is indicative of a cathodic inhibition mechanism. However, differing trends in the OCP were observed during PP and EIS experiments. The trends observed for the combinatorial matrix have been discussed in terms of likely mechanisms of corrosion inhibition with time.
Whilst $10^{-3}$ M cerium chloride with no other rare earth addition was found to be the best inhibitor for AA2024-T3 in 0.1 M NaCl, this study developed four polarisation resistance datasets for the further analysis for synergistic effects in part II of this series.

**Keywords:** rare earth, corrosion inhibitors, combinatorial, EIS, potentiodynamic polarisation

## 2 Introduction

Many studies have shown that the presence of lanthanide ions can inhibit corrosion on aluminium alloys. Aluminium alloys investigated include AA2014, AA2024, AA3003, AA5083, AA6060, AA6061, AA6063, AA7075, AA8090 as well as pure aluminium. In most studies cerium (Ce) ions have been reported to inhibit corrosion more effectively than the other lanthanides, however exceptions have been noted. For instance, Bethencourt and co-workers have reported samarium salts to be more efficient than Ce, and Yasakau et al. reported that Lanthanum (La) was more efficient than Ce for AA5083 during two-week immersion studies monitored using electrochemical impedance spectroscopy. Furthermore, several studies have found that combinations of rare earths can produce synergistic effects. For example, Aballe et al. found that 1:1 Ce-La mixtures improved inhibitor activity. Markley et al. also found that a mixture of rare earths as “mischmetal” gave results at least as good as the individual materials, and that rare earth mixtures containing Cerium:Praseodymium (Pr) in the ratio of 8:1 showed superior inhibition when prepared as diphosphophosphate salts. It follows that while individual rare earths have been examined in a large number of studies, there has been relatively few reports, and no detailed studies, of the effect of mixtures of rare earths on corrosion.

This paper explores two electrochemical methods, those being potentiodynamic polarization and electrochemical impedance spectroscopy (EIS), for the evaluation of the corrosion inhibition of four rare earth chlorides (alone and in combination) on the high-strength Cu-rich alloy, AA2024. The experiments performed in this study were designed to provide the input data for a combinatorial assessment of the synergies that may exist between rare earth chloride mixtures. Consequently, this article attempts to relate the data generated from the two electrochemical methods to provide a sound basis for further analysis of the compositional matrix using principal components analysis in part 2 of this series.

## 3 Experimental

### 3.1 Materials

Four rare earth chlorides ($\text{CeCl}_3\cdot 7\text{H}_2\text{O}$, $\text{LaCl}_3\cdot 7\text{H}_2\text{O}$, $\text{PrCl}_3\cdot 7\text{H}_2\text{O}$, $\text{NdCl}_3\cdot 6\text{H}_2\text{O}$ [Nd = neodymium]) and sodium chloride were purchased from Aldrich and were of analytical grade. A 0.1 M aqueous solution of each salt, including sodium chloride, was prepared in deionised water (> 10 MΩ.cm resistivity). A stock solution of each rare earth combination was then prepared (using the proportions shown in Table 1), 3 ml of which was added to the experimental cell, following which a further 300 ml volume of 0.10 M NaCl was added to achieve a total rare earth concentration of $1.0 \times 10^{-3}$ M. The solution mixtures were composed according to an experimental design obtained by using *The Unscrambler 9.7 software* (Camo, Oslo, Norway). The experiments were performed in a randomised sequence according to the sample number listed in Table 1.

<table>
<thead>
<tr>
<th>Design points</th>
<th>Sample No.</th>
<th>[Ce]</th>
<th>[La]</th>
<th>[Nd]</th>
<th>[Pr]</th>
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*Table 1. Proportions of rare earth solutions used to prepare the solution mixtures.*
Electrochemical tests were carried out on 1.6 mm thick aluminium alloy 2024-T3 sheet (Kaiser Aluminium) cut into sections of approximately 40 mm × 35 mm. A rotating grinder-polisher (Buehler Metaserv) was used to prepare the AA2024-T3 surfaces prior to testing. Samples were ground flat using 800 grit silicon carbide paper, and a final surface preparation was achieved using 2400 grit silicon carbide paper for at least thirty seconds, followed by a thorough rinse with deionised water. Each sample was prepared within ten minutes of the start of an experimental run.

### 3.2 Electrochemical procedures

A 110 mm long × 75 mm diameter flat cell was employed to contain the electrolyte and to expose a 3.14 cm² area of the prepared AA2024-T3 (working electrode) surface, which was clamped vertically on the edge of the cell. A Luggin capillary connected to a SCE reference electrode (Radiometer Pacific, REF401) and a 4 cm diameter platinum gauze served as the counter electrode. The reference and counter electrodes were positioned 30 mm and 75 mm from the working electrode, respectively. High purity compressed air with a flow rate of 20 ml/min was delivered to the centre-bottom of the flat cell through a 2 mm internal diameter PTFE tubing. Two electrochemical methods, namely potentiodynamic polarisation and electrochemical impedance spectroscopy (EIS), were used to investigate the inhibitive properties of each rare-earth combination.

The corrosion rate of AA2024-T3 is limited by the cathodic current exchange processes\(^3\) and therefore cathodic polarisation measurements performed at regular intervals enabled an estimation of the corrosion current, \(I_{\text{corr}}\), as a function of time. Cathodic polarisation measurements were carried out using a Solartron 1286 electrochemical interface. Each polarisation commenced at open-circuit and decreased the potential at a rate of 0.1667 mV s\(^{-1}\) for 300 mV. The open-circuit potential was measured prior to the first cathodic scan and between subsequent cathodic scans, which were performed after 1, 3, 6, 12 and 18 hours. To avoid the acceleration of damage, anodic polarisation scans were not performed at 1, 3, 6 and 12 hours, however, one anodic polarisation was performed...
after the final cathodic polarisation at 18 hours. Determination of the corrosion current, $I_{corr}$, was made for each scan by performing a least-squares regression on the potential versus $\log_{10} I$ data in the range of -150 mV to -250 mV (Tafel range) versus open-circuit, and extrapolating back to the open-circuit potential.

EIS measurements were carried out using a Solartron 1250 Frequency Response Analyser connected to a Solartron 1287 potentiostat. A sinusoidal AC potential of 10 mV was applied whilst sweeping the frequency from 65 kHz to 10 mHz. In order to match cathodic polarisation measurements, EIS scans were also recorded over an 18-hour period. The generated spectra were evaluated using complex non-linear regression using Zview2 software (Scribner Associates, Inc., USA) according to an appropriate equivalent electrical circuit.

3.3 Scanning electron microscopy (SEM)

SEM was performed on a FEI Quanta 400 field emission, environmental scanning electron microscope (ESEM) under high vacuum conditions. The coated samples were mounted on standard 25 mm SEM stubs using adhesive carbon tape. Secondary electron and backscattered electron imaging were performed using beam energies of 15 kV and probe currents of approximately 140 to 145 pA. Energy dispersive X-ray spectroscopy (EDS) was also performed, using a beam energy of 15 kV and a probe current of approximately 145 pA, resulting in count rates of approximately 1000 - 2500 cps.

4 Results

4.1 Cathodic polarisation

Figure 1 shows cathodic polarisation scans for $10^{-3}$M pure solutions of both cerium and lanthanum chloride inhibited solutions after times varying between 1 and 18 hours. All 21 tested inhibitor combinations resulted in decreased cathodic currents on the AA2024-T3 surface, and these cathodic currents also decreased with immersion time. After short immersion time (i.e. one hour) the application of a cathodic potential to the surface of AA2024-T3 created a rapid increase in current at small cathodic overpotentials, whilst at larger cathodic overpotentials the measured current increased more slowly, leading to high Tafel slopes (>1000 mV/current decade). However, cathodic scans performed after longer time periods often showed a less dramatic increase in current at low overpotentials, as is the case for cerium inhibited solutions presented in Figure 1. The Tafel slopes, which are required to be estimated for the prediction of corrosion current, gradually decreased with immersion time, approaching values of approximately 300 mV/current decade after 18 hours. In general, mixtures not containing cerium showed a less dramatic decrease in Tafel slope.
Figure 1. Cathodic polarisation data for AA2024-T3 immersed in 0.1 M NaCl containing $10^{-3}$ M of cerium and lanthanum chlorides. Data for AA2024-T3 immersed into 0.1 M NaCl containing no inhibitor is also shown after 1 hr and 12 hr immersion.

Figure 1 also shows that the open-circuit potential (OCP) of AA2024-T3 in the inhibited solutions was observed to decrease with increased immersion time. The decrease in OCP is indicative of a cathodic inhibition mechanism, as reported by Hinton and coworkers. Changes in the OCP during cathodic polarisation experiments were explored using principal component analysis (PCA) using The Unscrambler software. Figure 2 shows the correlation of the individual lanthanide species that comprise the 21 solution mixtures with the first principle component (PC1). The high negative correlation of cerium indicates that it is heavily associated with decreasing the OCP, and that the OCP is likely to decrease to a greater extent when cerium is present in higher concentration, irrespective of whether AA2024-T3 has been immersed for 1 to 18 hours. Praseodymium concentration has minimal correlation with PC1 with values about 0, and therefore has minimal influence on the OCP. Lanthanum and Neodymium both have the general characteristic of increasing the OCP (relative to the average OCP of all mixtures) and have a positive correlation with PC1. Whilst Neodymium was associated with higher OCPs at all immersion times, the correlation of lanthanum with PC1 became less positive at longer immersion times, suggesting that it results in less positive OCPs with time.
Figure 2. Determined values of the correlation of each individual lanthanide compound with the first principle component for immersion times of 1, 3, 6, 12 and 18 hours.

The ability of the lanthanide mixtures to inhibit corrosion was assessed by determining their inhibition efficiency, as defined in equation 1.

\[
\text{Inhibition Efficiency (\%) } = \left( \frac{I_{corr}^0 - I_{corr}^i}{I_{corr}^0} \right) \times 100\%
\]

where \( I_{corr}^0 \) = corrosion current in the absence of inhibitor and \( I_{corr}^i \) = corrosion current in the presence of corrosion inhibitor. \( I_{corr} \) values measured for AA2024-T3 in 0.1 M NaCl with no added inhibitors showed little variation with immersion time between 1-18 hours, with values in the range of 3.3 ± 0.7 \( \mu \text{A cm}^{-2} \). Figure 3 presents inhibition efficiency values for all experiments as function of time, where the inhibition efficiency increased rapidly within the first hour and more slowly after subsequent determinations at longer times. All combinations tested showed inhibition efficiencies greater than 55 \% and up to 97.6 \% after 1-hour equilibration. After 18 hours all inhibitors have efficiencies greater than 85 \% and up to 99.7 \%.
Figure 3. Determined values of $I_{corr}$ plotted as a function of time for all rare earth combinations measured at 1, 3, 6, 12 and 18 hours.

Errors associated with the determination of $I_{corr}$ values in this study were estimated to be in the vicinity of 65%. This is based on five repeat measurements of a $10^{-3}$ M lanthanide mixture composed of 1:1:1:1 Ce:La:Nd:Pr after 6 hours immersion. Errors in the inhibition efficiency are in the order of 4%.

4.2 Anodic polarisation

After the final cathodic polarisation at 18 hours, an anodic polarisation was performed. Figure 4 shows anodic polarisation data for each sample. The anodic Tafel slope, $\beta_a$, was obtained using a regression of the linear region of each anodic polarisation curve. Values ranged between 11.7 and 30.7 mV/decade with a mean value of 18.0 mV/decade and standard deviation of 5.6 mV/decade. Several anodic polarisations were also performed on AA2024-T3 in the absence of previous cathodic polarisations at both 300 s and 6 hour immersion times. Anodic polarisation measurements after an equilibration time as low as 300 s exhibited $\beta_a$ values of approximately 18 mV/decade and those performed at 6 hours also led to Tafel slopes within the same range as after 18 hours. $\beta_a$ values of 14.5 mV/decade have been quoted for AA2024-T3 in 0.05 M NaCl without an inhibitor, and these values increased upon the addition of an anodic inhibitor. The low value for the anodic Tafel slope, and the lack of increase in its value upon the addition of rare earth chlorides confirms that inhibition is predominantly cathodic.
For electron-transfer controlled electrochemical processes the polarisation resistance of electrochemical interfaces can be related to the corrosion current, $I_{\text{corr}}$, through the Stern-Geary relationship given in Equation 2. This provides a means to link the experimental datasets of cathodic polarisation and impedance spectroscopy, which is explored in more detail below.

$$I_{\text{corr}} = \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)} \times \frac{1}{R_p} \quad \ldots 2$$

Where $R_p$ is the polarisation resistance, and $\beta_a$ and $\beta_c$ are the anodic and cathodic Tafel constants, respectively. Stern-Geary constants averaged over all solutions had a mean of 7.53 mV with a standard deviation of 2.3 mV. Systems containing low cerium concentrations tended to possess increased Stearn-Geary constants of up to 12.7 mV and the lowest value was 4.94 mV for sample 17, which is a 25% equal mix of all four rare earth ions.

### 4.3 Scanning electron microscopy

Upon the completion of the final cathodic polarisation at 18 hours and subsequent anodic polarisation, samples numbers 5 and 10 were examined using SEM-EDS. Figure 4(a,b) shows that the surface of the AA2024-T3 exhibits large regions covered by a porous-gelatinous oxide that covers large areas of the general surface. EDS analysis (Figure 4(c)) of this region showed negligible evidence of rare-earth oxide deposition. The lack of rare earth species suggests that large areas of the surface become covered with voluminous aluminium-rich oxides over the 18-hour period. In contrast, Figure 4(c,d) shows that many regions of the surface are not covered with voluminous corrosion product and more specific oxide depositions occur, such as in the case for sample 5 where the deposition of neodymium oxides (see EDS in Fig. 4(f)) occur over more localised and specific regions of the surface.
Figure 4. Scanning electron microscopy images after polarisation experiments. (a) secondary electron image of sample 10 (1:5:1:1 Ce:La:Nd:Pr), (b) backscattered electron image of sample 10 (1:5:1:1 Ce:La:Nd:Pr), (c) secondary electron image of sample 5 (10^{-3} M NdCl₃), (d) secondary electron image of sample 5 (10^{-3} M NdCl₃), (e) EDS of general region of sample 10 (1:5:1:1 Ce:La:Nd:Pr), (f) EDS of general region of sample 5 (10^{-3} M NdCl₃).
4.4 Electrochemical Impedance Spectroscopy (EIS)

As was observed with DC polarization studies, EIS data for each of the samples was observed to vary with time. Figure 5 shows the Nyquist plots for AA2024-T3 immersed into a 1:1:1:1 Ce:La:Nd:Pr mixture of total concentration $10^{-3}$M in 0.1 M NaCl.

![Nyquist plot](image)

**Fig. 5.** Nyquist plot of AA2024-T3 exposed to 0.1 M NaCl containing $10^{-3}$ M total rare earth cations, where Ce:La:Nd:Pr 1:1:1:1. Data fits for 3 and 6 hrs were made using single time constant. Data fits for 12 and 18 hrs were made using double time constant model.

In the present work the impedance data could be modelled using only one time constant for short immersion times, however, after approximately 6 hours a second time constant became evident. Mishra and Balasubramaniam\(^7\), whilst using EIS to study AA2014 in 3.5 wt% NaCl suggested that only one time constant was present when greater than 250 ppm LaCl\(_3\) was added, whereas in the absence of the inhibitor, two time constants were observed. It should be mentioned that Mishra and Balasubramaniam allowed the open-circuit potential to stabilise, however, no specific time was quoted for immersion prior to measurement.

The Nyquist plots shown in Fig 5 demonstrate that for immersion times greater than 6 hours and extending out to 18 hours, a second time constant became evident. This is attributed to a general thickening of oxide across the entire surface, as was observed from SEM analysis. Further detail on the evolution of rare earth inhibition is provided in the Discussion section. The experimental data obtained after 6-hours immersion was deemed to be the most appropriate to enable a comparison between EIS and potentiodynamic polarisation. Recalling that the cathodic polarisation data showed minimal changes in inhibition efficiency after 6 hours, and that EIS analysis is simplified as it required an equivalent circuit with only one time constant.

Several equivalent circuit models were considered for the analysis of impedance spectra. Model 6A, based upon a ‘Randles’ circuit was used for data with one time constant, using a constant phase...
The CPE was used in the place of a capacitor due to the non-linear response of the double layer capacitance across the heterogeneous surface of the AA2024-T3. The impedance of the CPE has the mathematic form of:

\[
Z_{CPE} = \frac{1}{Q(j\omega)^n}
\]

Where \( Q \) describes the frequency-dependent magnitude of a pseudo-capacitance, \( j = \sqrt{-1} \), and \( \omega \) is the angular frequency. For the present system the exponent \( n \), which is constrained to \(-1 \leq n \leq 1\), describes the efficiency of the double layer capacitance. Typical values determined for the elements of the equivalent circuit for 6-hour immersion were \( R_s = 13.5 \pm 1 \Omega \text{ cm}^{-2} \), \( R_p = 10 \pm 4 \text{ k\Omega cm}^{-2} \), \( Q_{dl} = 60 \pm 20 \mu \text{F cm}^{-2} \) and \( n = 0.90 \pm 0.5 \).

Figure 6. Equivalent circuits considered for EIS analysis.

As for potentiodynamic polarisation studies, the OCP was monitored during EIS measurements and good reproducibility was observed between replicate samples. Figure 7 shows OCP data for \( 10^{-3} \) M solutions containing pure Ce, La, Nd and Pr, as well as three replicate runs for a 1:1:1:1 mixture of Ce:La:Nd:Pr. Figure 7a shows that the OCP of AA2024-T3 is initially very similar for all experiments, -0.557 ± 0.031 V SCE (5.5 % absolute error). All lanthanides led to a decrease in the OCP during the first 90 minutes, after which solutions containing Neodymium either showed a stabilisation in the OCP or an increase to more noble potentials for the remainder of the experiment. Praseodymium and cerium initially both showed a more rapid decrease in the OCP than the other lanthanides. Praseodymium maintained the most negative potential until approximately 2 hours, after which the decrease in the OCP slowed until reaching a minimum OCP after approximately 12 hours. The decrease of the OCP in \( 10^{-3} \) M cerium chloride possessed the most negative OCP in the period between 2 and 12 hours, achieving the most negative potential after approximately 7 hours. The OCP in lanthanum chloride showed a slower decrease after short time but eventually reached the more negative values observed in Pr and Ce solutions after approximately 12 hours. Figure 7b presents data for 3 identical samples tested at various times in the experimental matrix. Reproducibility in the OCP provides confidence that errors in the sample and experimental preparation were minimised. The trends observed in the variation of the OCP indicate that the mechanisms of inhibition of rare earths chlorides and their ability to protect against corrosion is somewhat dependent on the individual species (i.e. Ce, La, Nd, Pr).
Figure 7. Open-circuit potential during EIS experiments of AA2024-T3 as a function of time in 0.1 M NaCl containing $10^{-3}$ M of rare earth chlorides composed of either: cerium, lanthanum, neodymium, praseodymium, or a 1:1:1:1 mix of the four rare earth cations.

5 Discussion

5.1 Correlations between DC polarization and EIS

This section explores the differences between DC polarization and EIS measurements with respect to rare earth corrosion inhibition on AA2024-T3, and attempts to compare the two techniques and derive an understanding of the time-dependent corrosion inhibition of rare earth inhibitors.

Comparison of polarisation resistance
The Stearn-Geary relationship described in equation 1 is valid for electron transfer-controlled corrosion reactions occurring on homogeneous interfaces. Clearly the AA2024-T3 interface is not
homogeneous in aggressive electrolytes due to the activity of S-phase and other intermetallics. However, since the rare earth chloride mixtures in the present system can be described by a single time constant at less than approximately 6 hours, it is possible that the raw data from the two techniques can be related through the Stearn-Geary relationship.

Estimates of the polarisation resistance from PP can be made using Tafel slopes from each polarisation scan, along with the value obtained for I_{corr} from the cathodic polarisation (CP). This value can be directly compare to those obtained using EIS. The open circles in Figure 8 show there is a rather poor correlation (R^2 = 0.30) between R_p values determined using the two techniques when directly compared, sample by sample. This is representative of the large errors associated with the determination of R_p. The average percentage error for individual sample mixtures was 38%, which is a reasonable result considering that errors in the estimation of I_{corr} were in the order of 65%. Where R_p values are low, both PP and EIS appear to have a similar sensitivity to corrosion processes. The slope in the linear fit, 0.15, between the two sets of R_p, and the significant y-intercept, 20.7 kΩ, suggests that as R_p values increase, EIS estimates smaller values than PP.

Figure 8. Comparison of polarisation resistance values for all inhibitor mixtures plotted against R_p estimated from potentiodynamic polarisation experiments. Rp (EIS) is the raw data impedance spectroscopy experiments, and Rp (PP-EIS) is the average of values obtained from PP and EIS.
From the above information it is not clear whether EIS underestimates polarisation resistance or whether cathodic polarisation underestimates corrosion currents where inhibition is good. There are assumptions associated with both techniques. Estimations from cathodic polarisation are complicated by the application of larger overpotentials (up to -300 mV) and the extrapolation to OCP based upon a Tafel slope. The large overpotentials have the ability to drive the inhibition process and may for certain inhibitor solutions decrease $I_{\text{corr}}$ values relative to others. The influence of overpotential is further discussed below through the analysis of open-circuit potential data. The theoretical Tafel slope represents electron-transfer reactions and at room temperature should possess a slope of 59 mV/\text{decade} for single electron transfer. Tafel slopes utilised in this study were significantly greater than would be predicted by theory, suggesting that the presence of protective oxides limit the diffusion of oxygen to the surface. The increased Tafel slope for particular rare earth cations, i.e. cerium, produces lower $I_{\text{corr}}$ values than for inhibitors where the Tafel slope remains low. The determination of $R_p$ from EIS also has complications in the assumptions made in equivalent circuit. This is particularly true considering the heterogeneous microstructure of AA2024-T3. It is also likely that the influence of diffusion limiting processes are unaccounted for in EIS modelling, and that measurement at frequencies less than 10 mHz would be required to detect these oxide layers experimentally.

Further modelling of the datasets is carried out in the second paper in this series\(^\text{28}\) in order to fully characterise the combinatorial systems for synergistic effects. However, both potentiodynamic polarization analysis and EIS suggest that in comparison to the other rare earth species tested, the corrosion inhibition is improved when cerium is present. This supports many previous observations that cerium is a better corrosion inhibitor than other rare earth ions.

### 5.2 Time-dependent inhibition by rare earth inhibitors

#### Trends in open circuit potentials

The rare earth cations are cathodic inhibitors, and in decreasing the rate of cathodic current exchange, also decrease the OCP or corrosion potential of the metal. Several pieces of evidence have been presented in this work indicating that the inhibition of the corrosion of AA2024-T3 by rare earth chlorides has a strong time-dependence. Figure 7 demonstrated OCP changes over time were reproducible for the various mixtures of rare earth cations during EIS testing. Praseodymium chloride was shown to shift the OCP to the most negative values within the first two hours of an 18-hour immersion. In the time period between 2 and 12 hours cerium chloride created the most negative AA2024-T3 electrode potential, and after 12 hours cerium, lanthanum and possibly praseodymium showed very similar electrode potentials. Therefore, particular lanthanides may be more or less useful depending upon the conditions required for inhibition. Praseodymium may offer a more rapid ability to passivate, whereas lanthanum may be suitable for mild and slow active corrosive environments. Neodymium appears to exhibit poorer performance than the other lanthanides. Cerium shows promise as a good all-round solution. It is however difficult to be confident that these observations are transferable to other systems. Some literature reports are in agreement with these time-dependent observations. For instance, Markley et al.\(^\text{12}\) previously reported that praseodymium diphenylphosphates had similar activity to cerium diphenylphosphates during potentiodynamic polarisation analysis performed after 70 minutes, and Yasakau et al.\(^\text{27}\) reported that lanthanum nitrates were able to inhibit as good or if not better than cerium nitrates over a two week period for AA5083. In contrast a study by Chambers et al.\(^\text{26}\) showed that rare earth inhibition of AA2024-T3 after one week decreased as: Ce > Eu/Nd > Y/La/Gd. It follows that the trends in performance of individual
inhibitors appear to be dependent upon both alloy and solution chemistry conditions (inhibitor concentration, temperature, salt concentration, pH etc.).

From EIS studies it was evident that changes can be detected electrochemically in the period of 6-18 hours, whereby the corrosion processes starts to exhibit a second time-constant. The onset of this second time constant means that current exchange is no longer electron transfer controlled and diffusion processes also begin to limit corrosion. These diffusion processes are attributed to the formation voluminous oxide films on the surface, and it appears that there may be a correlation between the onset of the 2nd time constant and the observed increases in the OCP in the period of 7-18 hours, shown in Figure 7. The deposition of voluminous oxides has the effect of limiting oxygen diffusion to the surface and therefore shifting OCPs to more positive values, as depicted in the schematic in Figure 9.

![Figure 9. Schematic showing the progression of corrosion inhibition and oxide growth for AA2024-T3 immersed into 0.1 M NaCl containing 10^{-3} M rare earth chloride. The dotted line indicates changes in the open-circuit potential (E_{OCP}).](image)

The OCP trends observed during EIS studies (Fig. 7) were found to vary from those during potentiodynamic polarisation studies. Whilst the principal components analysis of OCPs in PP studies shown in Figure 2 suggested that cerium led to the most negative potentials, there was no clear distinction between the behaviours of individual solutions of Pr, La and Nd. It was also much more apparent during cathodic polarisation measurements that OCP variations showed minimal change unless cerium ions were present in solution, as can be observed from Figure 10. Figure 10 also shows that the OCP for AA2024-T3 in Pr solutions can take significant time to return to equilibrium after the application of cathodic potentials, suggesting it too, may have some increased activity during potentiodynamic testing.
Figure 10. Open-circuit potentials of AA2024-T3 in 0.1 M NaCl containing $10^{-3}$ M of rare earth chlorides of cerium, lanthanum, neodymium and praseodymium, measured before and after cathodic polarisation experiments. Time = 0 here denotes start of OCP measurement period.

It is clear from Figure 10 that cerium ions appear to behave rather differently to other rare earth ions, particularly during cathodic polarisation determinations, where cathodic reactions are driven at increased overpotential. The key differences of cerium when compared to other rare earths is its ability to exist in the 4+ oxidation state, as described by Yasakau et al.\textsuperscript{6} may be present in increased amounts due to the formation of peroxide species upon application of cathodic potentials:

$$2H_2O + O_2 + 2e^- \rightarrow H_2O_2 + 2OH^-$$  \hspace{1cm} ...4

Cathodic potentials create two conditions by which accelerated rare earth deposition may occur. Firstly, a negative charge is created and hence rare earth cations are drawn to the metal interface. Secondly, increased oxygen reduction leads to the development of high pH conditions. An estimate of the pH conditions generated under cathodic polarisation can be gained by combining Faraday’s Law with Fick’s First Law of Diffusion, which allows an estimation of the concentration of hydroxide species, assuming that all cathodic current, $i_c$, leads to the generation of hydroxide species:

$$i_c = \frac{nF.D\Delta C_{OH^-}}{\delta}$$  \hspace{1cm} ...5

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$$  \hspace{1cm} ...6

where $n$ is the number of electrons involved in the half-reaction (i.e. = 4 for oxygen reduction reaction in equation 6), $F$ is Faraday’s constant ($9.6485 \times 10^4$ C mol$^{-1}$), $D$ is the diffusion coefficient of hydroxide species ($6.65 \times 10^{-5}$ cm$^2$ s$^{-1}$)\textsuperscript{31}, $\delta$ is the diffusion layer thickness which was permitted to vary...
from 0.01 to 0.1 cm. Using a typical current density from this work of $i = 6 \times 10^{-7}$ A cm$^{-2}$, $\Delta C$ (mol/cm$^3$) = $6 \times 10^{-7}$ (A cm$^{-2}$) x 0.1 cm / $(4 \times 9.6485 \times 10^8$ (A.s mol$^{-1}$) x $6.65 \times 10^{-5}$ cm$^2$ s$^{-1}$) = $2.34 \times 10^{-3}$ mol/L. Therefore, in a neutral solution the pH is likely to approach 11.4 (assuming oxygen reduction is predominantly due to equation 6) and under these conditions all rare earth oxides are likely to form.

Further investigation of the OCP relaxation after cathodic polarisation was carried out by running a single cathodic polarisation, followed by measurement of the OCP. Figure 11 shows that changes to the surface of AA2024-T3 through the application of a cathodic current vary for each of the rare earth cations. From this data it is concluded that cathodic polarisation encourages the deposition of rare earth ions in the following order: Nd < La < Pr < Ce.

Figure 11. Relaxation of open-circuit potentials of AA2024-T3 in 0.1 M NaCl containing $10^{-3}$ M of rare earth chlorides of cerium, lanthanum, neodymium and praseodymium measured after a single cathodic polarisation experiment.

Trends in electrochemical impedance spectroscopy

Several equivalent circuit models have previously been used to describe the inhibition of aluminium alloys. Mishra and Subramanian proposed a model, presented in Figure 6C, to describe the rare earth inhibition of AA2014. In this model the surface was presented as being composed of both passive and porous regions, where the porous regions represent active intermetallics that have inferior oxide coverage. Upon the exposure to rare earth solution the so-called porous regions are passivated by the deposition of rare earth oxides. Zheludkevich and co-workers proposed a more elaborate model, presented in Figure 6E, in the case of triazole and thiazole inhibition of AA2024 where the electron transfer at the metal interface is described by the polarisation resistance, $R_p$ and constant phase element of the electrical double layer, CPE$_{dl}$. The native passive oxide is described by a resistance, $R_{ox}$ and constant phase element, CPE$_{ox}$. Furthermore, an inhibitive layer was proposed to develop over the
entire surface and was described by a resistance, $R_{inh}$ and constant phase element, $QPE_{inh}$. Figure 6D presents a model that is a variation on the above models where the first time constant is attributed to $R_p/CPE_{dl}$ of the native oxide and a second time constant due to the deposition of an inhibitive oxide film over the entire surface which is described by $R_\alpha$ and $CPE_{\alpha}$. For systems with increased oxide formation, such as those where corrosion products become clearly visible across the surface, corrosion processes become increasingly limited by diffusion and therefore the use of Warburg elements commonly assist in describing the physicochemical processes. For instance, Treacy et al.\textsuperscript{33} utilised the circuit in Figure 6B where white corrosion products could be seen upon the surface of AA2014A-T6.

Considering that AA2024-T3 has a heterogeneous microstructure due to the presence of numerous intermetallic phases, it is interesting to consider the reasons for only one time constant being observed for immersion times less than 6 hours. Other works have shown that the current exchange densities on intermetallic particles are far in excess of the matrix.\textsuperscript{34,35} For this reason, as described by Mishra and Balasubramanian\textsuperscript{7}, the surface may be viewed as possessing both “active” intermetallic sites and somewhat passive regions of the matrix. The equivalent circuit may therefore be represented as in Figure 12a where there are two RC-circuits, $R_{ct1}/C_1$ to describe the active intermetallics and $R_{ct2}/C_2$ for the matrix. Assuming that in the absence of inhibitor, $R_{ct2} >> R_{ct1}$, and therefore two time constants would be observed as reported for uninhibited aluminium alloys.\textsuperscript{7,27} However, cathodic inhibition mechanism of rare earths leads to the passivation of cathodic intermetallic particles through the deposition of rare earth oxides. There are a large number of cathodic particles in AA2024, such as those typically described as $\text{Al}_6(\text{Cu,Fe,Mn, Si})$ phases, that exhibit high cathodic current density.\textsuperscript{36} In addition, the common S-phase intermetallic is typically an active anode at early times.\textsuperscript{37} However, work by Yasakau et al.\textsuperscript{6} has shown rare earth oxides to deposit onto S-phase intermetallics, suggesting that the previously reported dealloying of magnesium and aluminium leads to copper enrichment of the S-phase, such that they too become cathodic in nature. The model in Figure 12b represents the surface of AA2024-T3 at short exposure times in the presence of rare earth corrosion inhibitors, where a passive layer develops preferentially over intermetallic sites. In this case the values of $R_{ct1}$ and $R_{ct2}$ are thought to approach similar values. The equivalent circuit may then be reduced to that of Figure 6A, which was used for comparative purposes in this study. The individual resistances, $R_{ct1}$ and $R_{ct2}$ are combined as:\textsuperscript{38}

$$\frac{1}{R_p} = \frac{\theta}{R_{ct1}} + \frac{(1-\theta)}{R_{ct2}} \quad ...7$$

Where $\theta$ is the area fraction of the surface covered by intermetallics. Studies have shown that AA2024-T3 contains an intermetallic area fraction of approximately 3%.\textsuperscript{39,40} Therefore the polarisation resistance, $R_p$ becomes controlled by the properties of the native oxide covering the matrix, $R_{ct2}$, where inhibition is effective on intermetallic particles. Similarly, the capacitance of the two surface regions may be added as $C_{dl}(\text{total}) = \theta C_{dl1} + (1-\theta)C_{dl2}$. The addition of these two capacitances creates the effect of a non-linear capacitor, which could be modelled as a CPE.
After longer periods of immersion there was a thickening of the oxides over the general surface, creating a 2\textsuperscript{nd} time constant, as schematically represented in Figure 7c. Markley et al. attributed the time-dependent decrease in the corrosion current of AA2024-T3 in mischmetal rare earth diphenylphosphates to result from a gradual thickening of the rare earth containing oxide, particularly over intermetallic particles. SEM analysis also indicated that there will be an increase in the thickness of porous oxides that deposit over the general surface of AA2024-T3 (Figure 4) and increases in the measured OCPs also indicates oxide thickening. Therefore, an equivalent circuit similar to that proposed by Mishra and Subramanian (Figure 6C) appears appropriate for modelling the corrosion behaviour during time periods of 6-18 hours. Although it should be mentioned that to get a good fit the \( n \) value for the thickening oxide layer often exceeded 1 and therefore a capacitor could be used to replace \( \text{QPE}_{\text{ox}} \). An example of the data fitting for this model is presented in Figure 5. The properties of the porous oxide film develop over time and initially the values of the capacitance are large (i.e. > 100 \( \mu\text{F cm}^{-2} \)) as thicknesses are minimal, and resistance values modest (i.e. 6000 \( \Omega \text{ cm}^{-2} \)). Typically, capacitance values decreased from 5 \( \text{mF cm}^{-2} \) after 9 hours to 4.5 \( \text{mF cm}^{-2} \) after 18 hours. The capacitance of oxide films on AA2024-T3 have previously been reported in the range of 1-20 \( \mu\text{F cm}^{-2} \).\(^{29}\) The accurate prediction of \( R_{\text{ox}} \) values was problematic in the present study due to the need to
analyse at lower frequency. Typical values were in the range of 6 - 20 kΩ cm². In utilising this model (Figure 6C) it was assumed that the entire surface was covered by a voluminous oxide and as SEM analysis revealed, this assumption may not be hold for all samples. However, as the coverage of the voluminous oxide is widespread enough to alter the OCP properties for 6-18 hour immersion periods, this equivalent circuit model seems practical but requires further validation.

6 Conclusions

The corrosion inhibition of AA2024-T3 by mixtures of four rare earth chlorides (cerium, lanthanum, neodymium and praseodymium) in 0.1 M NaCl has been evaluated using PP and EIS electrochemical techniques. Both approaches showed all rare earth chlorides to be good inhibitors.

PP experiments showed rare earth inhibition of up to 98% within the first hour and thereafter slow increases in corrosion efficiency were observed. EIS experiments revealed that the surface processes occurring on AA2024-T3 within the first 6-hours of immersion could be analysed using a single time constant, whereas longer exposure times required more elaborate equivalent circuits.

Polarisation resistances after 6-hour immersion were determined from both PP and EIS experiments and the datasets from the two techniques were compared. The polarisation resistances measured for the 21 solutions showed an average variation of 38%. PP and EIS determinations were in good agreement for systems exhibiting a low polarisation resistance, whereas polarisation resistances estimated by PP were greater than those estimated using EIS for solutions with increased inhibition.

The open-circuit potential (OCP) of AA2024-T3 was observed to decrease as a function of time for all solutions, which is indicative of a cathodic inhibition mechanism. However, differing trends in the OCP were observed during PP and EIS experiments. PP experiments showed that the potential of AA2024-T3 in cerium containing solutions had a significantly lower OCP for all immersion times (1-18 hours). However, OCP recorded as a function of time during EIS showed praseodymium solutions to display the most rapid decrease in OCP at times up to 2 hours, with cerium solutions eventually resulting in the most negative OCPs after approximately 6 hours. Lanthanum solutions appeared to decrease the OCP at a slower rate and Neodymium solutions had negligible effect on the OCP.

Measurement of OCP following cathodic polarisation of AA2024-T3 showed variation in the restoration of the OCP to a steady state. Assuming that the rate at which the steady state is restored is inversely proportion to the cathodically-enhanced deposition of rare earth oxides, cathodic polarisation was found to encourage the deposition of rare earth ions in the following order: Nd < La < Pr < Ce. This data combined with the trends in OCP observed during EIS testing indicate that each of the rare earth species are likely to provide varied corrosion inhibition over time. For this reason alone there is the possibility that mixtures of rare earth cations may provide synergistic effects for corrosion inhibition. The raw data, however, suggests that 10⁻³ M cerium chloride with no other rare earth addition was found to be the best inhibitor. This does not rule out the possibility of synergistic interactions between rare earth species and part 2 of this series explores trends in the combinatorial dataset in further detail.

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8 References


