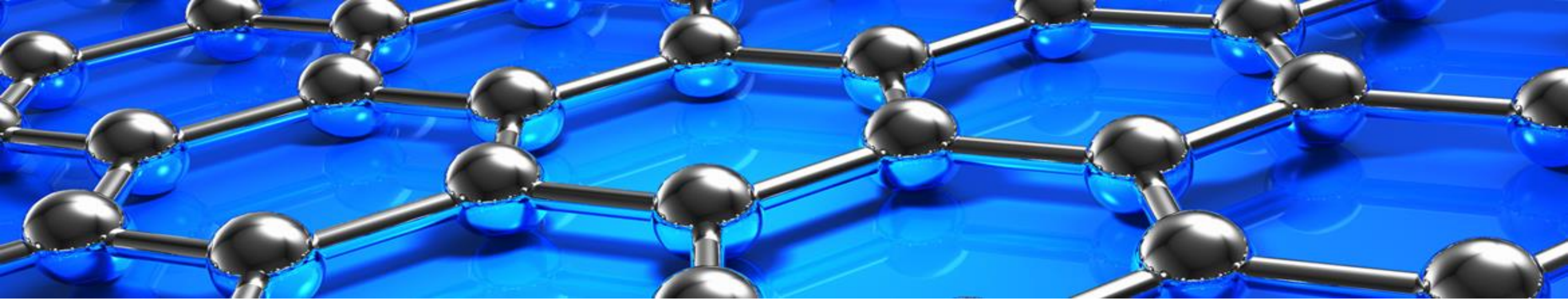
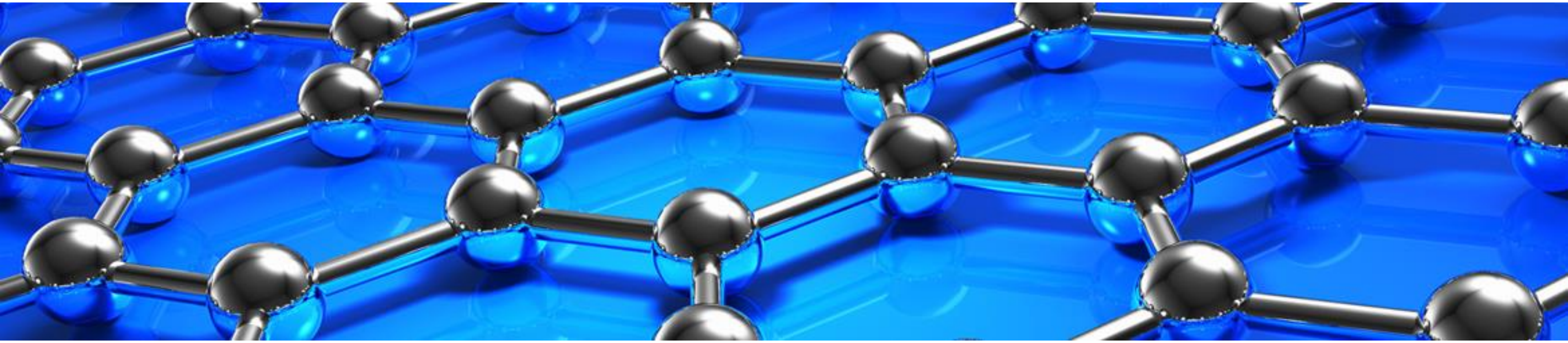


Long Term Corrosion Protection Performance and Activity of Graphene-Based Epoxy Coating Systems for Aluminium and its Alloys

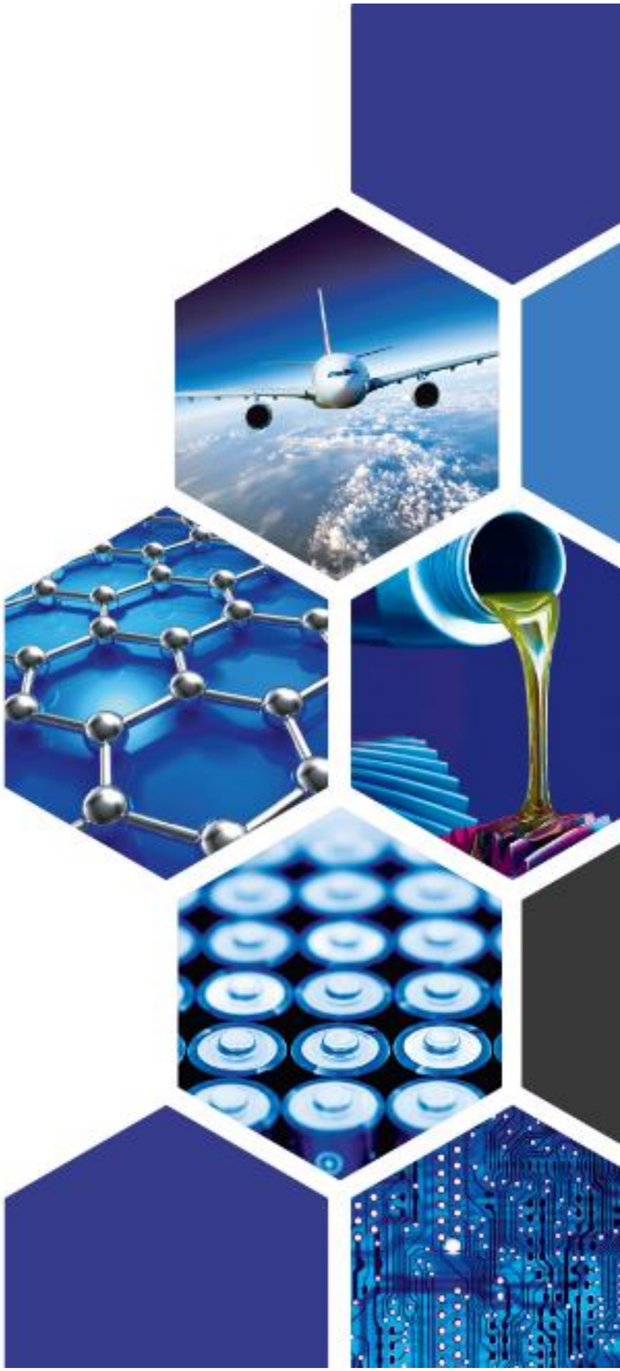
Applied Graphene Materials

Matthew Sharp, Gaven Johnson and William Weaver

April 2019



Introduction



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Introduction

Graphene's two-dimensional structure in the nanoplatelet form results in materials with:

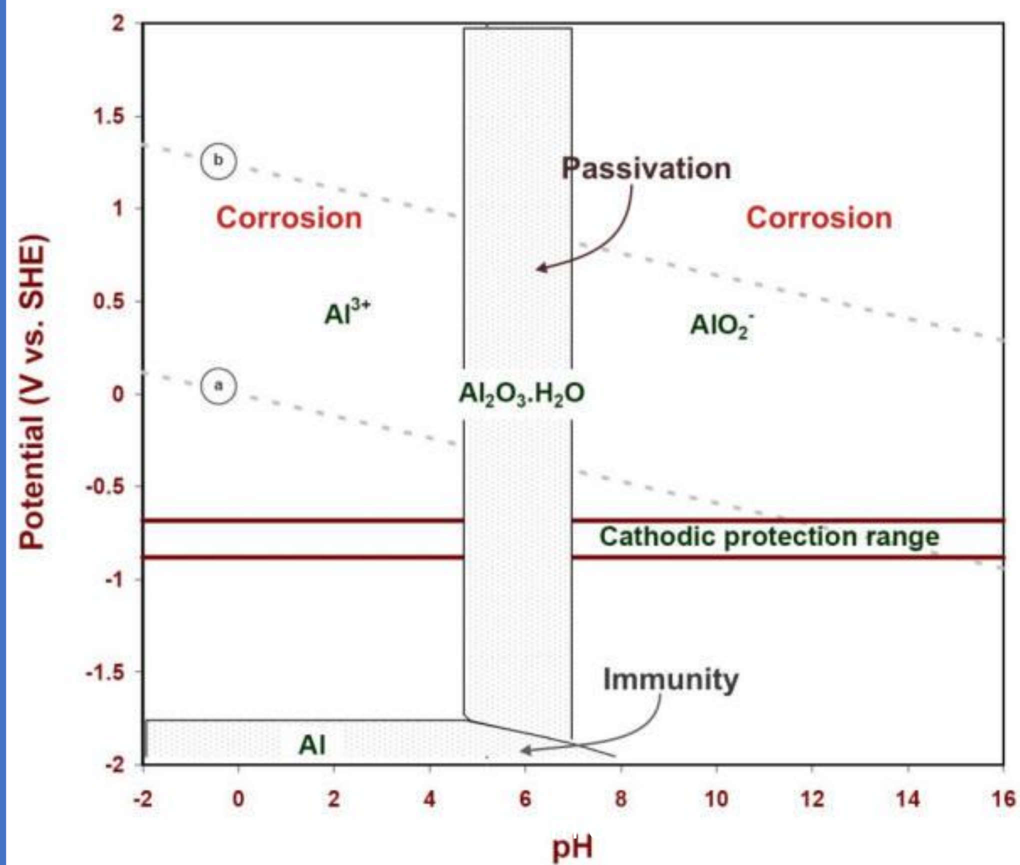
- very high aspect ratio
- high surface area

These materials are particularly suited for use as multi-functional additives in paints and coatings.

The proposed mechanism by which graphene delivers anti-corrosion performance is a combination of physico-chemical process restricting uptake of water (combined with oxygen and salt) and electro-chemical activity.

The Protection of Self-Passivating Metals

- Passivating metals readily form a stable and unreactive surface coating
    - Protection from further corrosion
- Under certain conditions of pH and oxygen concentration, passivation of passivating metals will proceed
- Outside of such conditions passivation will not occur
- The passivation layer may start to break down
- Unprotected aluminium will corrode



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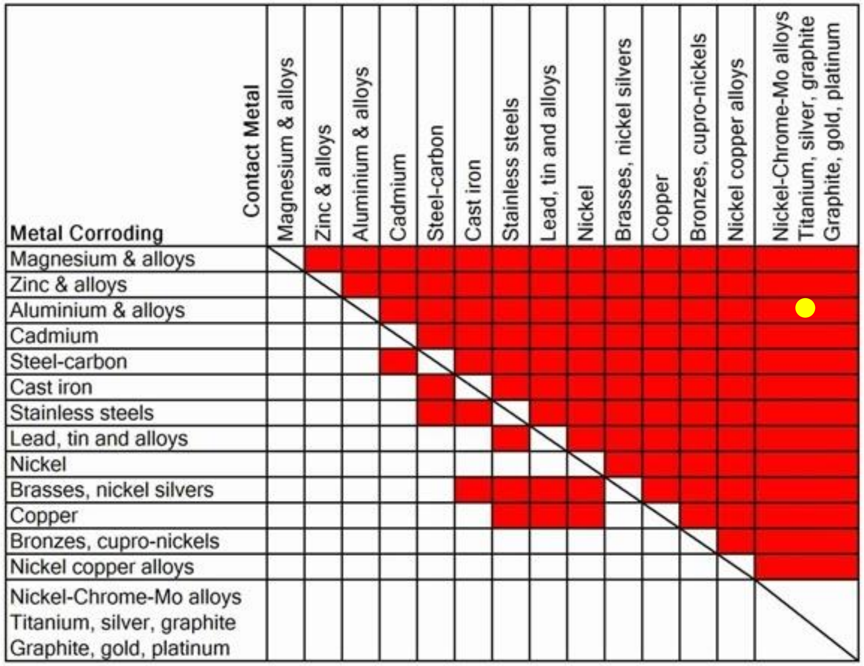
The Protection of Self-Passivating Metals

- Traditionally, self-passivating metals have been protected from corrosion through anodization and alloying
- Anti-corrosive inhibitive coatings may also be applied to aluminium surfaces
- The active constituents of such coatings are typically marginally water soluble and produce active species which inhibit the ongoing corrosion of the metallic substrate
- Active constituents include chromates but other species such as phosphates, molybdates, nitrates, borates and silicates are also used
- The selection of active constituents is increasingly subject to regulatory pressures due to increased concerns for the environment and health and safety

The Protection of Self-Passivating Metals

- Aluminium in contact with carbon materials could exhibit galvanic corrosion
  - Depending on how material is encapsulated
- Graphene has been demonstrated to be electrically conductive
  - Current density is 1,000,000 times greater than copper
- When dispersed into a matrix, graphene nano-platelets offer significantly reduced conductivity
  - Levels below the percolation threshold required to achieving any meaningful conductivity
- Graphene incorporated into a coating may offer the possibility of a dual functionality on aluminium
  - Improved barrier performance
  - Promotion of self-passivation



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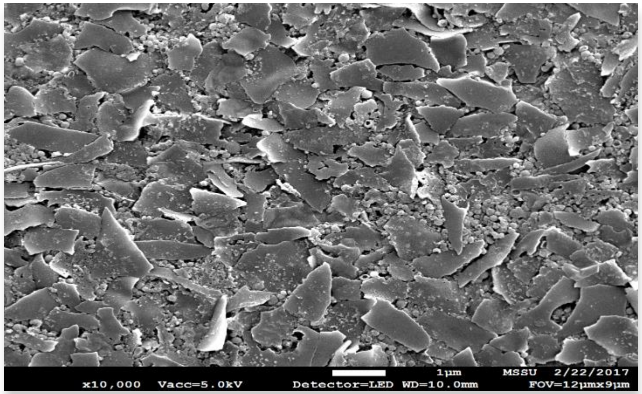
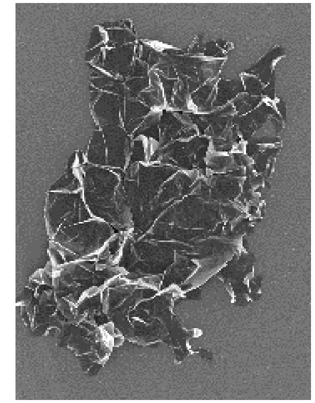
AGM Graphene Nano Platelets



Reduced graphene oxide (RGO)

- Composed of mixture of nanoplatelet type sheets
- Excellent barrier properties
- Moderate density and surface area gives high loading levels in most matrices
- Typically 10% in dispersion for further dilution in final formulation
- Resistivity – 50, 000 Ω.m



Graphene

- Very thin, crumpled sheets. (of 5-15 atomic layers)
- Very low density and high surface area, enabling enhanced corrosion
- Typical loading levels 0.5-1% by weight in dispersion for further dilution in final formulation
- Resistivity – 0.0037 Ω.m

AGM supplies its graphenes in dispersion format

Objectives

Initial work has shown an increase corrosion protection performance using graphene-based coatings with relatively low GNP loadings (down to 0.003 wt.%)

We seek to understand the mechanism behind such improvements in the corrosion protection of aluminium through the use of simple graphene-containing epoxy clears

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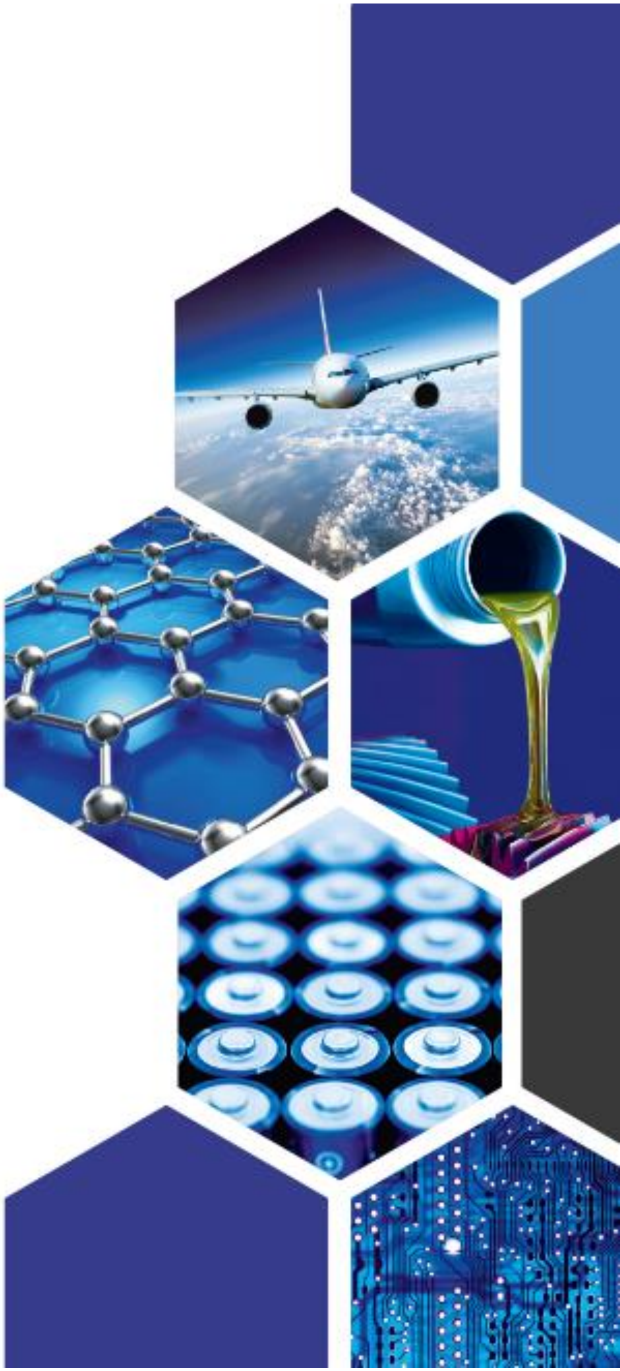
Experimental



Test Program

Prohesion/Salt Spray Testing

- ASTM G85 annex 5 (prohesion) for a period of up to 4000 hours
- Panels were assessed at 500 hour intervals for signs of blistering, corrosion, and corrosion creep in accordance with ISO4628

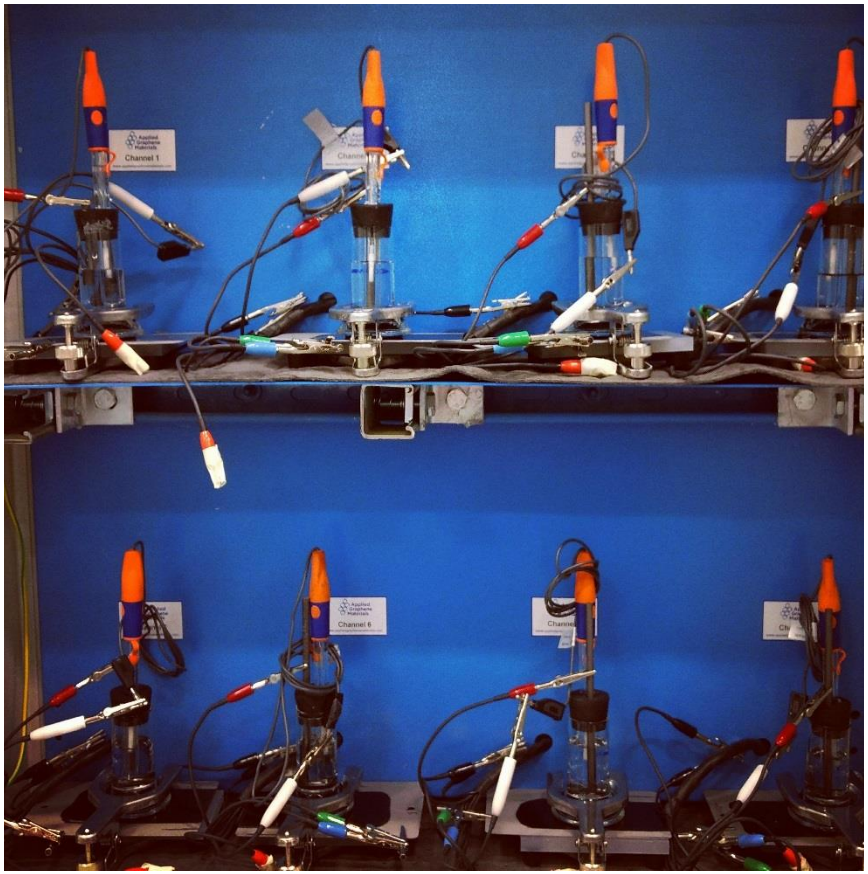
Electro-chemical AC Impedance Spectroscopy (EIS)

- Demonstrate the improvement of the barrier properties through the addition of graphene to organic coatings
- Assess the impact of graphene within organic coatings on the rate of passivation of aluminium

Potentiodynamic Polarisation Technique

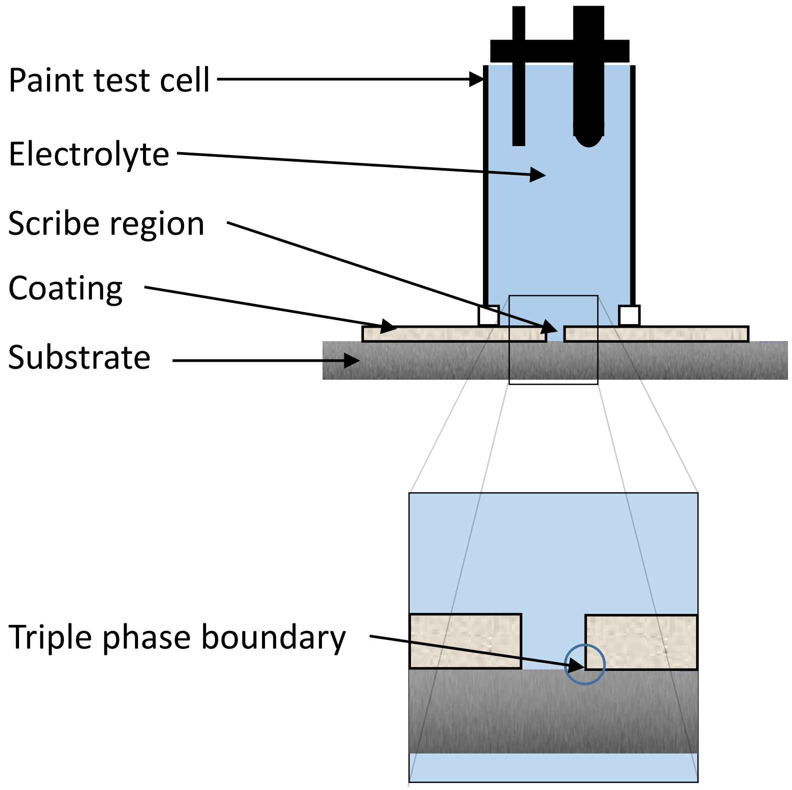
- Assess the impact of graphene within organic coatings on the rate of passivation of aluminium

Electro-chemical Testing



- Measurements recorded using a Gamry 1000E potentiostat in conjunction with a Gamry ECM8 multiplexer
- The test area of the working electrode was 14.6 cm^2 and run using a 3.5 wt% NaCl electrolyte
- For EIS, an AC voltage of 10 mV was applied across the samples, with a zero volt DC bias, over a frequency range of 1 MHz to 0.05 Hz
- For potentiodynamic tests, a potential of ±250 mV from the open circuit potential (500 mV sweep) was applied at a scan rate of 0.5 mV/second

Testing of Scribed Coatings



- Scribed samples were studied in addition to unscribed samples
- Scribing offers an immediate study of the bare metal substrate in contact with electrolyte and functional coating (triple phase boundary)
- To identify any electrochemical influence imparted by the graphene
- Provides the opportunity to observe changes prior to the lengthy breakdown/degradation of the functional coating

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Coating Formulation

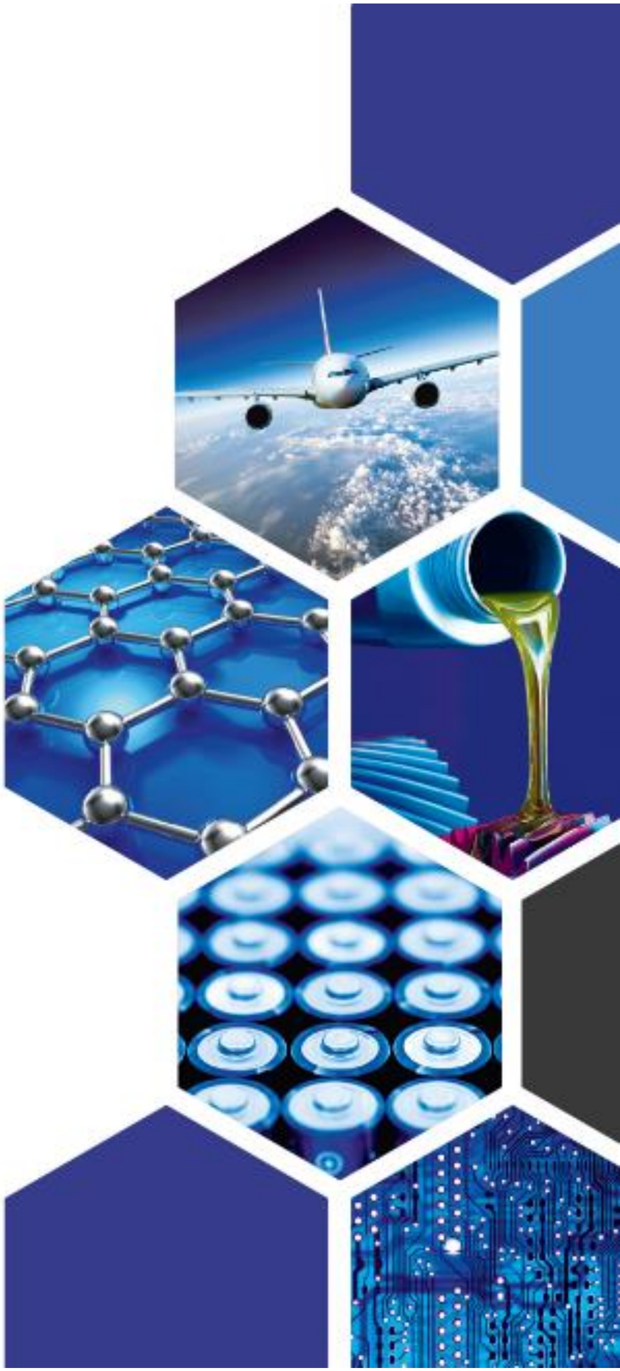
- Various loadings of GNPs were incorporated into an epoxy resin system
- Resin only clears and not fully formulated products
- Typical GNP Loadings for enhanced barrier properties are 0.1 – 0.5 wt.%

		Graphene Type	
Sample	**Epoxy System (wt.%)**	**RGO (wt.%)**	**Graphene (wt.%)**
1 (Epoxy Blank)	100	0	0
2	99.5	0.5	0
3	99.97	0.03	0
4	99.997	0.003	0
5	99.9	0	0.1
6	99.97	0	0.03
7	99.997	0	0.003

Panel Preparation

- Aluminium 5005 panels of dimensions 150 x 100 x 2mm
- Panels were degreased using acetone prior to coating application
- Coatings were applied using a conventional gravity-fed spray gun
    - DFTs 40-60 µm
- All panels were allowed to cure for a period of 7 days at 23°C (+/-2°C).

Results



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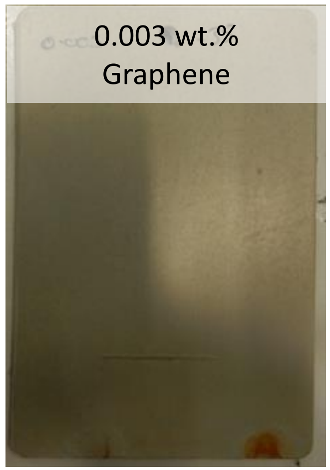
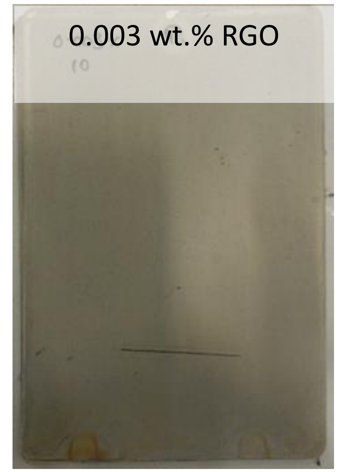
Prohesion/Salt Spray Testing

- 4000 hours prohesion testing
- No obvious signs of corrosion were noted in any of the graphene-incorporated epoxy samples
- Graphene loadings as low as 0.003 wt.% (barrier type effect from the graphene nanoplatelets expected to be relatively low)


Epoxy Blank


0.003 wt.% Graphene

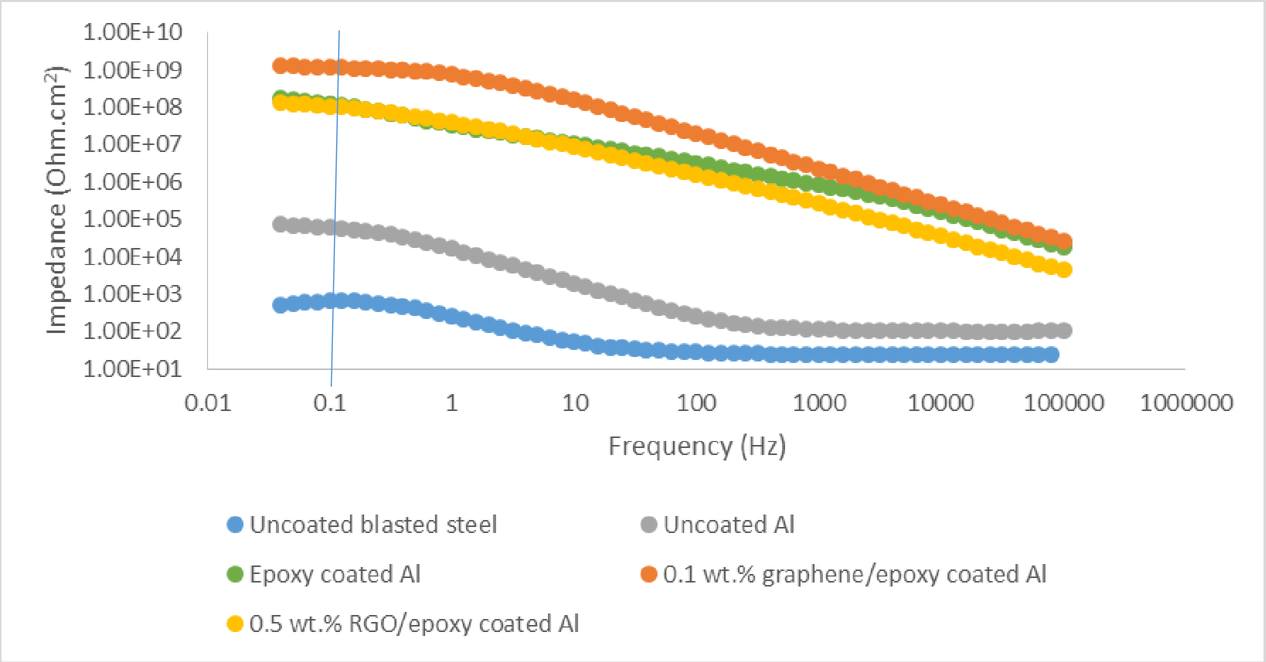

0.03 wt.% Graphene


0.003 wt.% RGO


0.03 wt.% RGO

Sample	Degee of Corrosion	Area (%)	Blistering	Adhesion to substrate
Epoxy Blank	Ri 5	40-50	-	Delamination
0.003 wt.% Graphene	Ri 0	0	-	Good
0.03 wt.% Graphene	Ri 0	0	-	Good
0.003 wt.% RGO	Ri 0	0	-	Good
0.03 wt.% RGO	Ri 0	0	-	Good

EIS results



Bode plots post 60 hours immersion

- Difference in impedance between steel and aluminium due to presence of passivation layer
- Increased barrier performance seen with all coated samples
- An order of magnitude improvement in barrier performance over the blank coating is seen for the graphene sample

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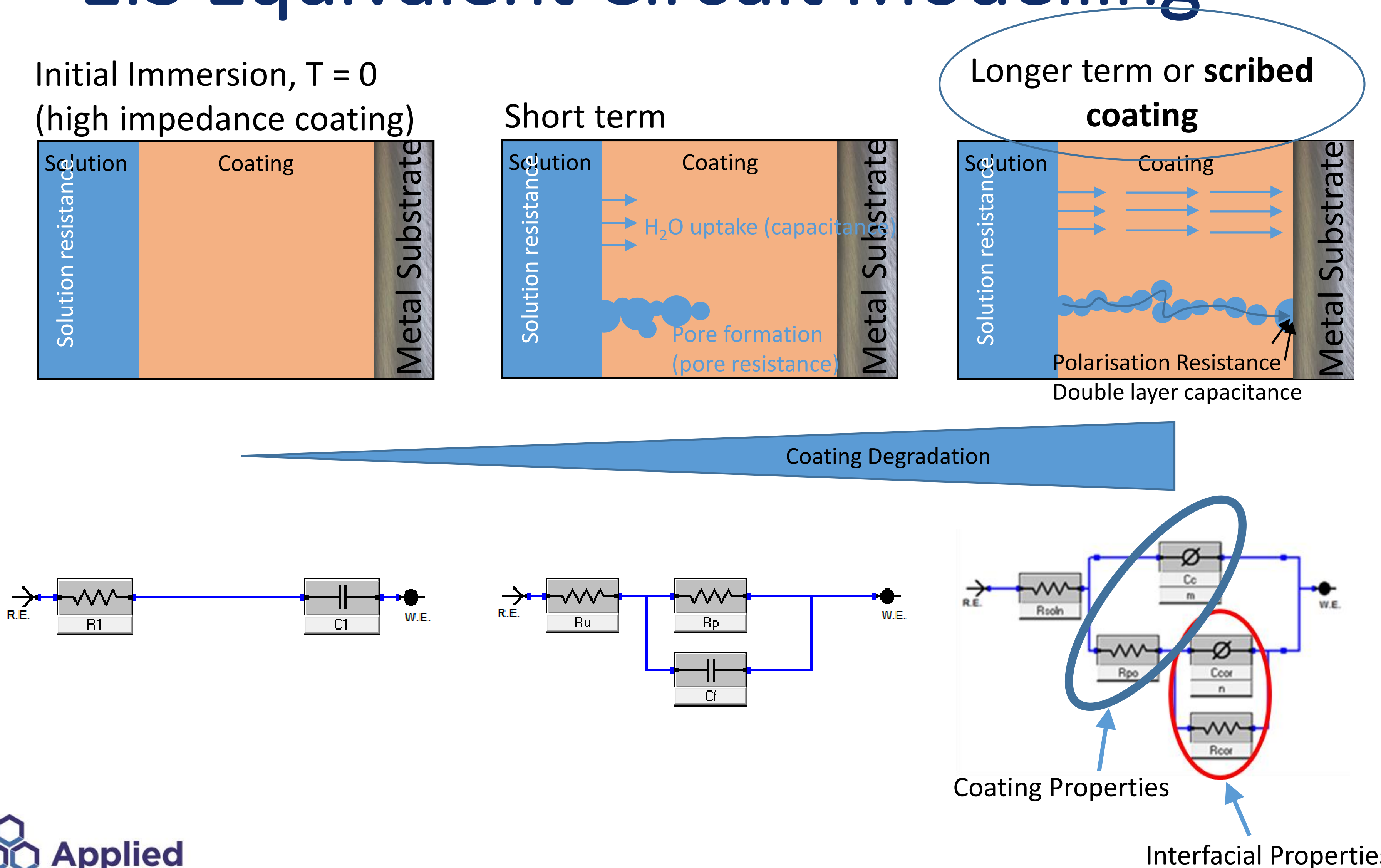
EIS Equivalent Circuit Modelling



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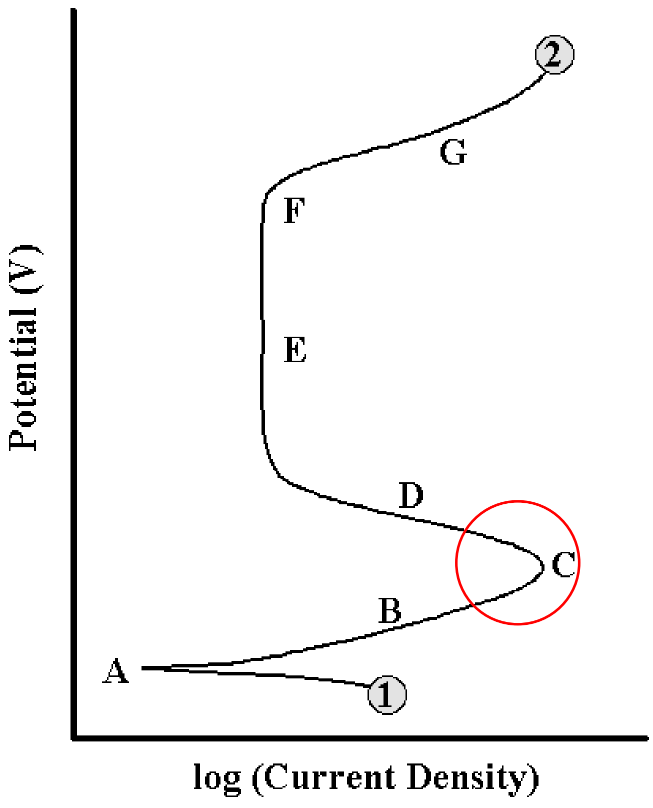
EIS Equivalent Circuit Modelling

Circuit element	Epoxy blank	0.003 wt.% Graphene	0.03 wt.% Graphene	0.1 wt.% A Graphene	0.003 wt.% RGO	0.03 wt.% RGO
Solution resistance, R_{soln} (Ω)	22.97	23.62	17.27	21.35	21.13	32.10
Double layer capacitance, C_{cor} (F/cm^2)	8.97×10^{-9}	7.23×10^{-11}	5.48×10^{-11}	3.26×10^{-12}	1.70×10^{-8}	3.34×10^{-9}
Corrosion resistance, R_{cor} ($\Omega.cm^2$)	6.29×10^5	4.38×10^6	7.37×10^6	3.34×10^7	7.45×10^5	4.20×10^5

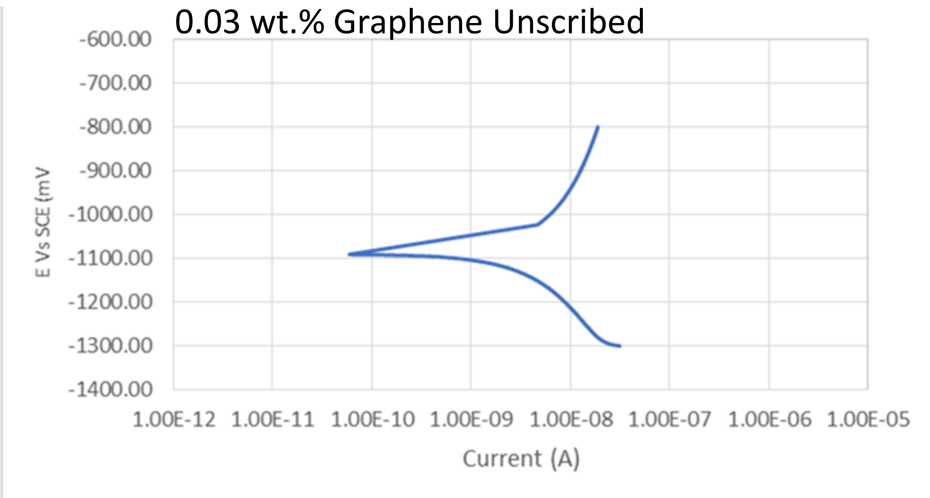
- Similar values for solution resistance indicative of good data fit
- The epoxy blank sample shows a relatively high double layer capacitance and low corrosion resistance (normal passivation of aluminium)
- The double layer capacitance is seen to decrease with the addition of Graphene as low as 0.003 wt.% (likely greater passivation)
- Graphene addition appears to increase corrosion resistance – 2 orders of magnitude for the 0.1 wt.% sample with a smaller increase as low as 0.003 wt.%
- Again suggests Graphene is acting to increase the rate of passivation within the scribed region
- Graphene can act as both a barrier and also increases rate of passivation
- RGO appears to make no difference to corrosion resistance and double layer capacitance
    - No real impact on the rate of passivation of aluminium
    - Appears to act mostly as a barrier material

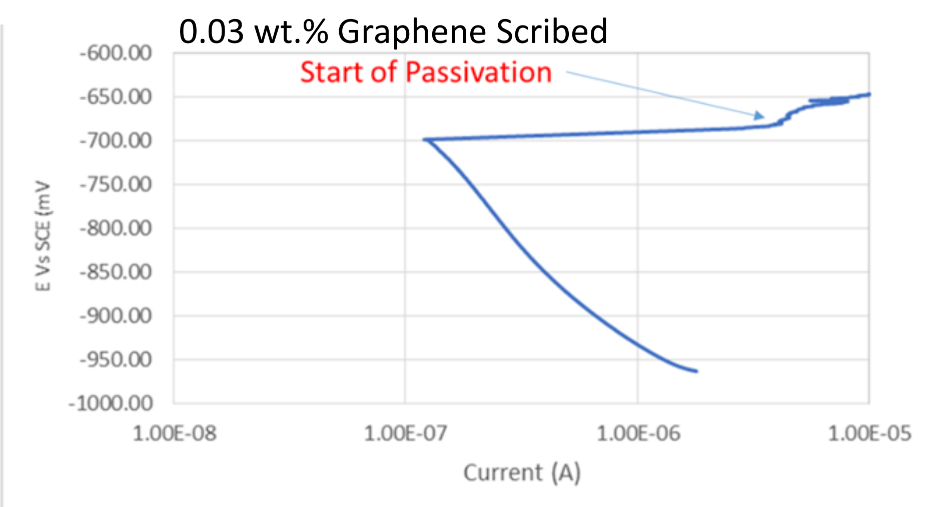
Potentiodynamic Polarisation Scans

- Beyond the Tafel regions, when an extended potential range is applied, additional useful features may be observed in the polarisation data
- One such feature is the passivation potential
  - As the applied potential increases above this value, a decrease in the measured current density is observed until a low, passive current density is achieved
  - The point at which the current density undergoes no change with an increase in applied potential (passive region)
- Beyond this point, if the applied potential permits, and is sufficiently positive, the current rapidly increases: the breakaway potential. For aluminium alloys, this breakaway potential may be due to a localised breakdown in passivity (pitting).



Potentiodynamic Polarisation Scans





0.03 wt.% Graphene (Unscribed)

- No direct access to the metal surface
- No passivation occurring
- Relatively high Tafel constant
- Coating acting as a barrier

0.03 wt.% Graphene (Scribed)

- Direct access to the metal surface
- Onset of passivation observed at ~+18 mV from the corrosion potential
- Relatively low Tafel constant – high anodic reaction

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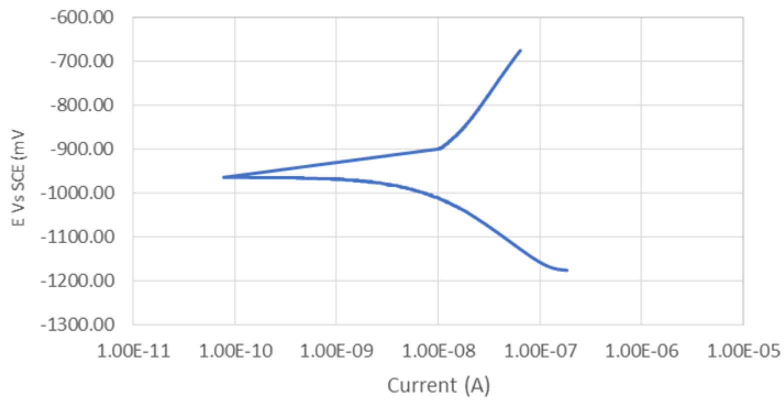
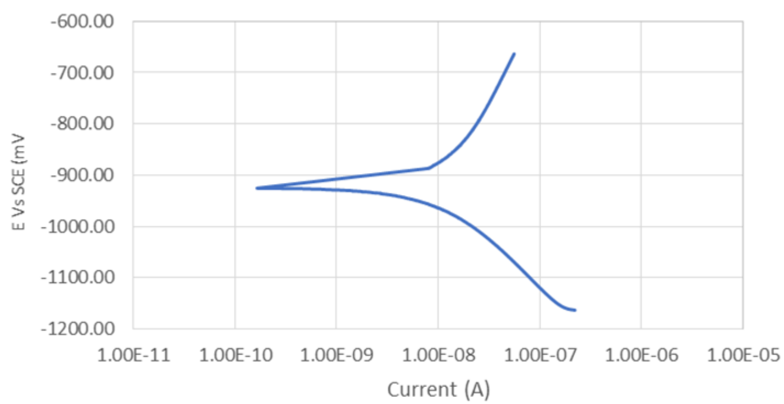
Potentiodynamic Polarisation Scans

Scribed



Unscribed

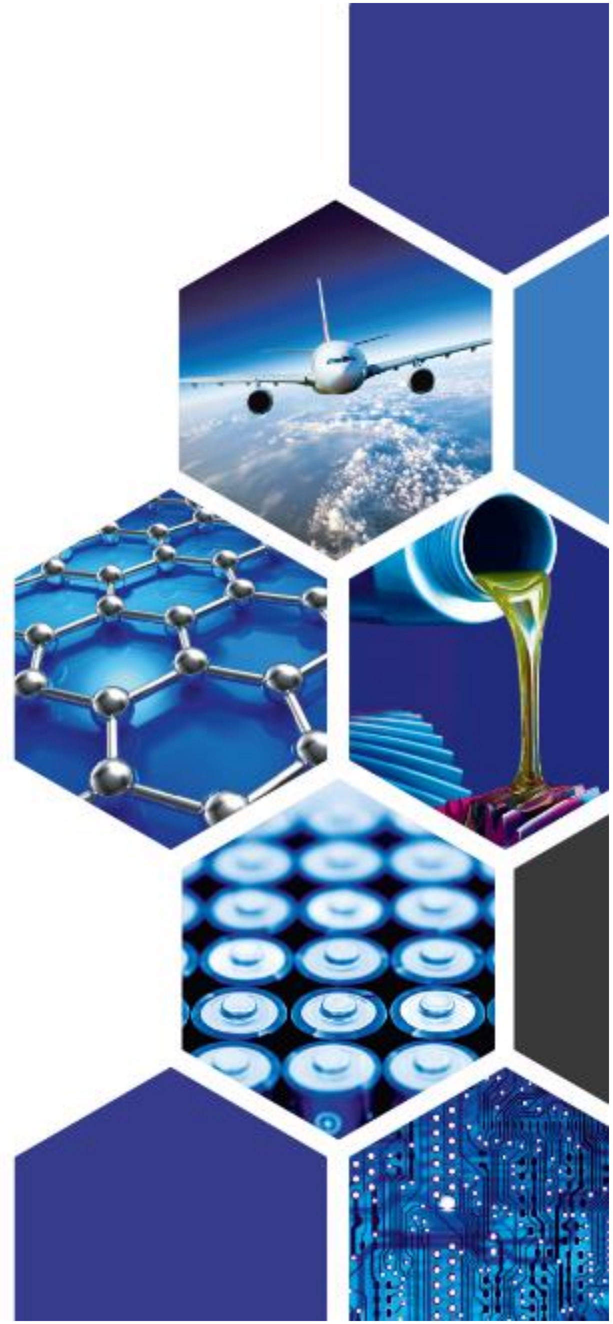


0.03 wt.% RGO (Scribed & Unscribed)

- Almost identical plots for scribed and unscribed samples
- Passivation onset does not appear in the RGO samples
- RGO, of lower conductivity, is performing more as a physical barrier than controlling corrosion by accelerated passivation

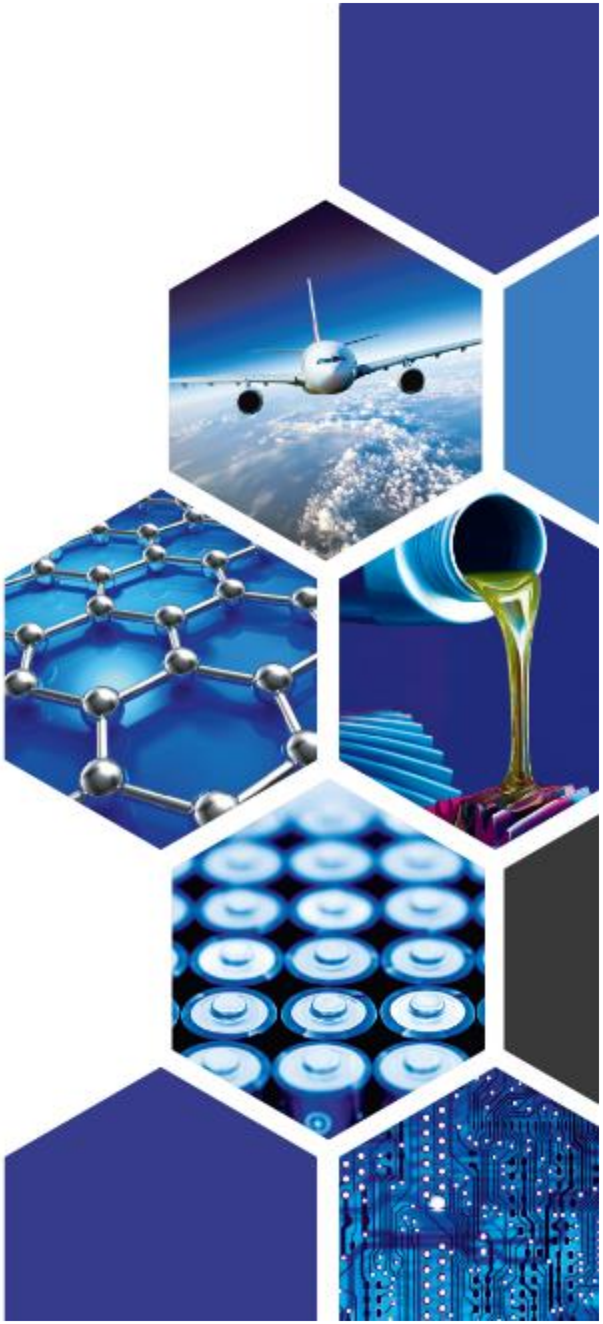
Summary

- During prohesion testing, all graphene incorporated samples significantly outperformed the epoxy blank control
- EIS has shown that graphene incorporated at 0.1 wt.% offers a greater barrier performance than the blank control
- Fitting of equivalent circuits models to the EIS data has shown an increase in corrosion resistance where RGO samples showed no change from the control
- Potentiodynamic testing has shown an onset off passivation in the more conductive graphene samples
- Suggests graphene is acting to increase the rate of passivation of the metal surface, acting in a catalytic manner



Potential Applications

- Low build primers – extension of lifetime
- In combination with anodised metals
- In combination with other forms of conversion coating



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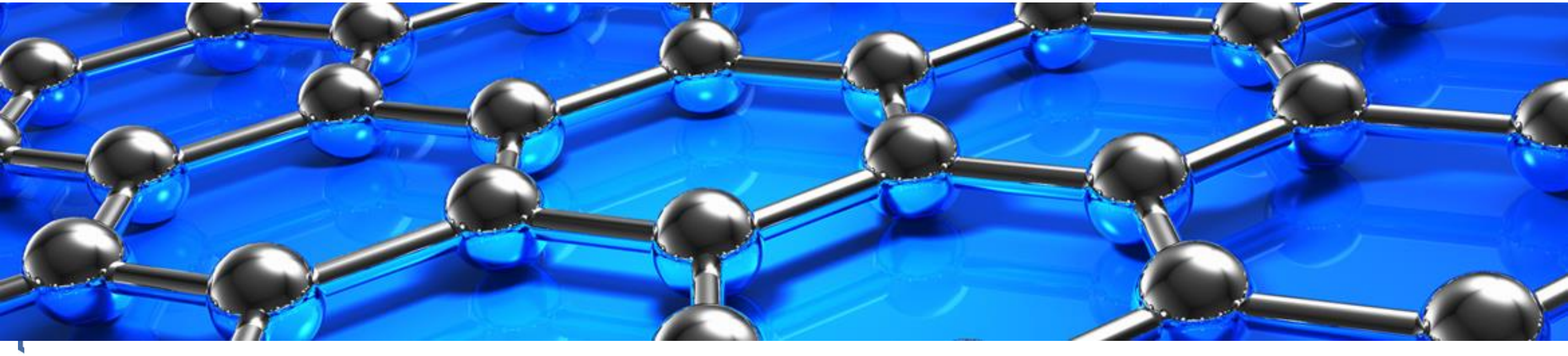

…Graphene in products used by everybody, everyday