Electrochemical Impedance Evaluation Of Coating Under Simulated Splash Zone Condition

by

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22781

Dissertation submitted in partial fulfilment of
the requirements for the
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CERTIFICATION OF APPROVAL

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Approved by,

____
(AP Ir Dr Mokhtar Bin Che Ismail)

UNIVERSITI TEKNOLOGI PETRONAS

BANDAR SERI ISKANDAR, PERAK

January 2020

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

FARID AIMAN BIN SHAHROL AZRAI

ABSTRACT

One of the requirement for a high performance coating to be applied to an offshore structure is to conduct and withstand long term accelerated weathering test for 4200 hours. However, in some cases, the offshore structure's coating may be experiencing premature failure, even though it meets the acceptance criteria of the lab test. Hence, the aim of this paper is to study the quantitative test method by introducing electrochemical impedance test into the accelerated weathering test, and characterize the progressive stages of coating physical degradation under simulated splash zone condition. The test cycle consist of 72 hours of UV-condensation, followed by 96 hours of salt fog exposure. Each cycle, bode plot and Nyquist plot was obtained when running electrochemical impedance test, and were used for validation of the coating's performance. Then, the result was be modeled into its equivalent circuit, which the value of coating capacitance was obtained and used to calculate the percentage water uptake of coating using Brasher and Kingsbury's equation. Visually, the result showed no blistering and rusting from cycle 0 until cycle 4. As for electrochemical impedance test, it showed a decrease in its impedance for all samples from cycle 0 to cycle 4. Moreover, the coating showed a significant increase in its percentage coating water uptake. The outcome of this project provides a quantitative assessment of coating, which can reduce the duration of long term accelerated weathering test for an offshore structure's coating system.

ACKNOWLEDGEMENT

Firstly, I would like to express my sincere gratitude towards AP Ir Dr Mokhtar Che Ismail for giving me an opportunity and experience in this area of study. He is a very knowledgeable, especially on corrosion. His supervision have thought me many things, especially on doing research. Not to forget the staff from CCR, especially Mr Haq and Mr Afif who also guided me to run my experiments.

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CHAPTER 1

INTRODUCTION

1.1 Background

It is known that marine environment is very aggressive, especially towards metallic structure such as an oil platform. An oil platform is divided into three basic categories which are subsea, splash zone, and topside. With continuous salt spray, combined with UV radiation exposure including large oxygen supplies, wave effects and lack of cathodic protection, splash zone definitely is an aggressive environment [1]. Hence, research are being done to study the integrity of coating using an accelerated weathering machine.

According to Corrosionpedia [2]:

> Accelerated weathering is a weathering testing to evaluate the integrity of a material under a certain simulated climate conditions to measure its future outcome. The main function of accelerated weathering test is to speed up the weathering process and assess the impact towards the material such as degradation or corrosion.

There are several organization develops a standard test method for accelerated weathering test such as ASTM International, International Organization for Standardization (ISO) and even Petronas (Petronas Technical Standards, PTS). The objective of these standards are similar, but still have differences in some testing variables. However, according to Petronas Technical Standards, the coating for an offshore platform are required to conduct accelerated weathering test (UV and salt spray) for 4200 hours before evaluating the coating, which is a long time. Unfortunately, in some cases, the coating may be experiencing premature failure whereby the coating does not exceed the expected lifespan, even though it meets the acceptance criteria during the lab test [3].

According to Loveday, Peterson and Rodgers (2004), electrochemical impedance measurement is able to detect changes in the coating way before any visible damage occurs [4]. Many research on coating have been done using an electrochemical impedance measurement and the outcome is very credible. It can measure the condition of the coating, without causing any damage. Electrochemical impedance measurement is expected to be able to detect coating damage faster, which, in theory, can reduce the duration of weathering test

1.2 Problem Statement

On an oil platform, the splash zone have the highest corrosion rate due to exposure to both high and low tide of the sea [5]. With the presence of ultraviolet radiation that deteriorates the coating, combine with sea water which acts as an electrolyte, it surely makes the splash zone the most prone to corrosion on the structure.

That being said, to determine if the coating is qualified for field application, it would take 4200 hours of accelerated long term weathering test before evaluating the coating [6]. Moreover, the evaluation is through visual inspection which are degree of blistering and degree of rusting. However, there are many cases where premature failure occurs because the lab test result does not correlate with the field test. In other words, the coating does not meet its expected lifespan as expected. One of the reasons is due to water uptake of the coating, which eventually may blistering to the coating.

The hypothesis of this project is to introduce a quantitative test method, which is electrochemical impedance measurement to the accelerated weathering and to be able to detect coating failure based on the measurement, which are bode plot, Nyquist plot, and also percentage coating water uptake.

1.3 Objective

The objective of this paper is to:

Characterize progressive stages of coating physical degradation under splash zone condition through:

i. Degree of blistering
ii. Degree of rusting

Evaluate damage property of coating in terms of:

i. Bode plot
ii. Nyquist plot
iii. Percentage water uptake of coating

1.4 Scope of Study

The scope of study for this project as per stated below:

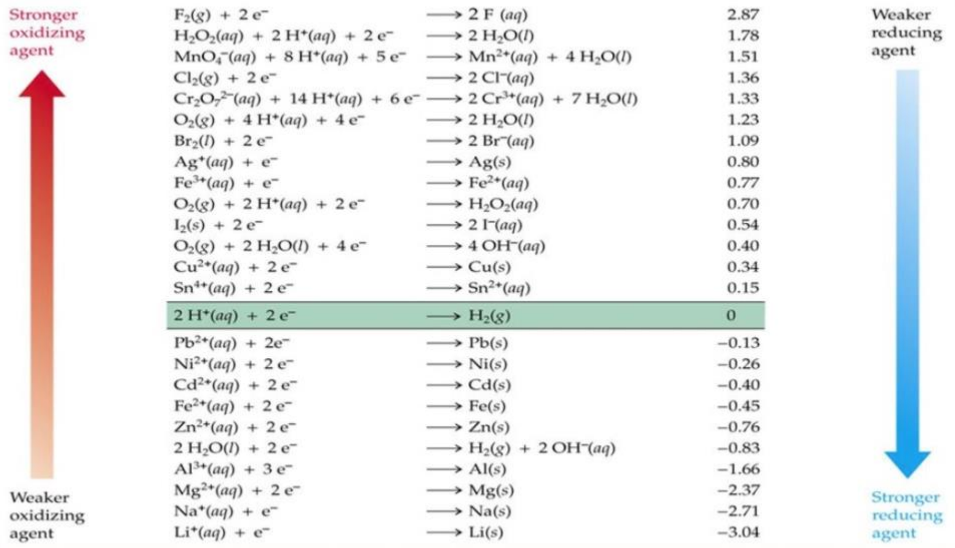
i. Study the coating system of an oil platform.
ii. Study the standard used for evaluating the coating performance using ASTM and ISO.
iii. Develop method to shorten the duration of long term accelerated weathering test using electrochemical impedance measurement tool.

CHAPTER 2
LITERATURE REVIEW

2.1 Concept of Corrosion

Corrosion is the electrochemical reaction, or irreversible interfacial reaction of a metal with the environment. It is a naturally occurring phenomenon commonly defined as deterioration of material. Electrochemical reaction is when there are movement of electron from one place, to another [7]. Corrosion occurs with the presence of cathode, anode, an electrolyte and a complete electrical circuit. The cathode will be receiving electron, that is released from the anode. In order to control corrosion, at least one of the four element must me remove. On an offshore structure, the element that usually being removed is the electrolyte, by introducing coating to the metal structure [8]. The coating prevents the metal structure to be exposed to sea water, which acts as an electrolyte [9].

In determining which is anode or cathode, electrochemical series is referred. Electrochemical series is a series of chemical elements arranged based on the standard electrode potentials. Below is an example of electrochemical series:



$F_2(g) + 2\,e^-$	$\longrightarrow 2\,F\,(aq)$	2.87
$H_2O_2(aq) + 2\,H^+(aq) + 2\,e^-$	$\longrightarrow 2\,H_2O(l)$	1.78
$MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^-$	$\longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$	1.51
$Cl_2(g) + 2\,e^-$	$\longrightarrow 2\,Cl^-(aq)$	1.36
$Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,e^-$	$\longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$	1.33
$O_2(g) + 4\,H^+(aq) + 4\,e^-$	$\longrightarrow 2\,H_2O(l)$	1.23
$Br_2(l) + 2\,e^-$	$\longrightarrow 2\,Br^-(aq)$	1.09
$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80
$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77
$O_2(g) + 2\,H^+(aq) + 2\,e^-$	$\longrightarrow H_2O_2(aq)$	0.70
$I_2(s) + 2\,e^-$	$\longrightarrow 2\,I^-(aq)$	0.54
$O_2(g) + 2\,H_2O(l) + 4\,e^-$	$\longrightarrow 4\,OH^-(aq)$	0.40
$Cu^{2+}(aq) + 2\,e^-$	$\longrightarrow Cu(s)$	0.34
$Sn^{4+}(aq) + 2\,e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15
$2\,H^+(aq) + 2\,e^-$	$\longrightarrow H_2(g)$	0
$Pb^{2+}(aq) + 2e^-$	$\longrightarrow Pb(s)$	−0.13
$Ni^{2+}(aq) + 2\,e^-$	$\longrightarrow Ni(s)$	−0.26
$Cd^{2+}(aq) + 2\,e^-$	$\longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2\,e^-$	$\longrightarrow Fe(s)$	−0.45
$Zn^{2+}(aq) + 2\,e^-$	$\longrightarrow Zn(s)$	−0.76
$2\,H_2O(l) + 2\,e^-$	$\longrightarrow H_2(g) + 2\,OH^-(aq)$	−0.83
$Al^{3+}(aq) + 3\,e^-$	$\longrightarrow Al(s)$	−1.66
$Mg^{2+}(aq) + 2\,e^-$	$\longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.71
$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.04

Figure 2.1 Electrochemical series.

If an element have a lower potential in the electrochemical series (going down the table), the element is a stronger reducing agent, meaning the element is the cathode, while the other element is the anode (corroding element). In order to prevent electrochemical reaction to occur, coating is added to the structure, creating a long lasting structure, and a safe working environment.

However, the coating selection must be suitable with its environment. Marine environment, particularly splash zone area of an oil platform, poses a highly corrosive environment that makes and additional challenges on the coating system which is used to protect the structure [5]. A high quality coating is required for splash zone application since it is an aggressive environment which prone for corrosion to be initiated. Some of the criteria are:

I. High corrosion resistance.
II. Excellent chemical resistance.
III. Superb adhesion to its substrates.
IV. Excellent electrical insulation property and retention thereof on aging or exposure to extreme environment.
V. High abrasion resistance.

Without a sufficient quality of coating, cracks will starts forming due to ultraviolet radiation and tensile stresses. This type of cracking will result causes pores or pinholes. Though initially the pinholes is small (micro scale), after certain period of time, the pinholes will become larger. The consequences is, sea water will start to flow into the pinholes. Over time, corrosion will slowly occur, resulting changes on the metal properties and creates a dangerous working environment.

Doing maintenance at an oil platform is quite a challenge and can be costly [10]. Therefore, selecting a high quality coating from the start with a careful sample preparation and inspection are a crucial decision to make to prevent a high maintenance cost. For comparison purposes, an offshore coating is more expensive compared to onshore is because it needs to take into account several factors especially logistics of getting equipment and worker to site with limited access to the structure due to its extreme weather conditions.

2.2 Coating Failures

2.2.1 Blistering

Blistering is one of the most common type of coating failure. It occurs when the coating is immersed in a liquid, or even exposed to high humidity environment. Major causes of blistering is the presence of hydrostatic pressure. Air and water is trapped inside the coating. As the pressure inside the coating increases, and external pressure decrease, that causes the blister to expands, resulting in cracking and delamination. This will definitely effect the structure’s integrity and life expectancy.

There are two types of blistering, which are osmotic blistering and non-osmotic blistering [11]. One of the osmotic-blistering factor is due to presence of water soluble salts such as chloride and sulfate, which both are present in the sea water. When the soluble salts becomes trap, moisture will attempt to penetrate through the coating to equalize the concentration of salt on either side of the film.

2.2.2 Polymer Matrix Degradation

Nowadays, coating manufacturers are using polymer coating for harsh environment application. Polymer matrix acts as a barrier, creating a high resistance towards chemical reaction, which includes corrosion. However, harsh weather and chemical attack can slowly and surely effects the polymer matrix. Over time, the polymer matrix will degrade. As the polymer degrades, discoloration, reduction of glossiness, increase of surface roughness is observed.

2.2.3 Elevated temperature

Short term exposure to elevated temperature can lead to irreversible chemical and physical changes towards a coating. As temperature increases, the stiffness and strength decreases. The primary degradation process at an elevated temperature is oxidation. As oxidation occurs, it loses electron, the metal is rusting. When exposed to the environment, high oxygen content will increase the rate of degradation.

2.3 Polyurea Coating.

Polyurea is an elastomer that is obtained from the reaction product of an isocyanate component and synthetic resin blend component through step-growth polymerization. According to Prabhu [12], the advantage of using polyurea coating is:

I. Fast curing time.
II. Excellent resistance towards abrasion.
III. High resistance towards weather and environmental conditions.
IV. Can be applied in various temperature, including high humidity.
V. Resistance to heat up to 130 Celsius.
VI. Excellent chemical resistance.
VII. Good resistance towards UV ray.

All of the above advantages are suitable to be used at marine and harsh environment. Comparing polyurea and epoxy coating, polyurea have better resistance towards moisture, UV, abrasion, chemical and temperature. Comparing polyurea and polyurethane coating, polyurea have better durability, chemical and moisture resistance.

2.4 Correlation Between Field test and Accelerated Weathering Test.

Accelerated weathering test are conducted to simulated long term damaging effect to materials, coatings and many more. The experiment are conducted to see how the coating reacted towards the simulated condition. Once the coating have passed the experiment, the material will then be applied to the desired location, hoping it will last as long as it is designed for. However, there are cases where the coating experiencing premature failure even though the coating meet the acceptance criteria of lab test. According to Cavassi and Cornago, coating at splash zone and deck of T-Block Field, which is located in the North Sea would cost $2,430,000 , which will definitely effect the maintenance cost budget if premature failure occurs.

There have not been any accelerated method that are successful in correlating with field test to be considered satisfactory for universal use, that may cause premature failure to occur. Some of the factors might due to the influence by temperature, moisture and pollutants of the environment. According to Aamodt et al , the corrosion creep from a scribe after running accelerated weathering test was not predictive for the performance in the field. The result does not yield a reliable method for estimating and differentiate the performance of coating when exposed to in-service conditions.

2.5 Electrochemical Impedance Measurement

2.5.1 Overview

The commonly used measurement tool to measure electrochemical impedance of coating is Electrochemical Impedance Spectroscopy. EIS is able give a quantitative analysis on coating before any physical damaged that is visibly seen through photographic reference [4]. The result obtained from EIS (bode plot and Nyquist plot), it is then being modelled into it’s equivalent circuit to obtained its coating capacitance which will be used to calculate the percentage water uptake based on Brasher and Kingsbury’s equation.

2.5.2 Concept of EIS

According to britannica.com [13]:

> Dielectric is a poor conductor of electric current whereby electric polarization occurs. When a dielectric is place in an electric field, no current will flow into it due to no free electrons movement between the materials. One of the application of dielectric is on capacitor.

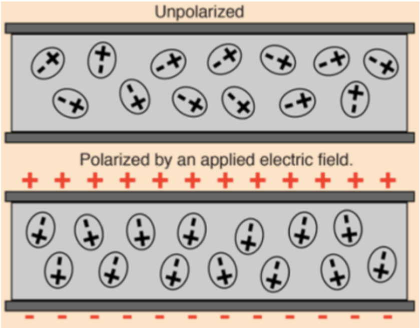


Figure 2.2 Dielectric Concept

A capacitor is formed when a non-conductive medium known as dielectric is in between two conductive elements. The capacitance value relies on the plate size, the distance between the plates and the dielectric properties.

Capacitance formula:

$$Capacitance, C = \frac{\mathcal{E}_0 \mathcal{E}_r A}{d} \tag{2.1}$$

where:

$\mathcal{E}_0 = Electrical\ permitivity$

$\mathcal{E}_r = Relative\ electrical\ permitivity\ (Dielectric)$

$A = Surface\ of\ one\ plate$

$d = Distance\ between\ two\ plates$

Table 2.1 Typical value of dielectric constant.

Material	ε_r
vacuum	1
water	80.1 (20°C)
organic coating	4 - 8

Referring to Table 2.1, organic coating have a low dielectric value. Nevertheless, after exposure to a certain environment, such as harsh marine environment, the coating starts to deteriorate, which makes the dielectric value to increase. EIS can be used to measure that changes. If the dielectric constant of the organic increase, the capacitance will increase, hence, the impedance will decrease [14].

An impedance is an effective resistance of an electric circuit of an alternating current. Impedance is inversely proportional to capacitance, which is why the impedance decrease when capacitance value increase.

Impedance formula:

$$Z = \frac{1}{j\omega C} \tag{2.2}$$

Z = Impedance, Ohm

j = Complex number

C = Capacitance, Farad F

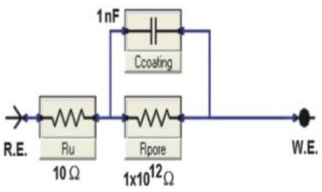
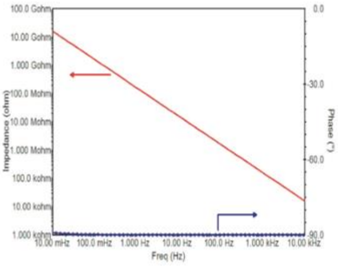
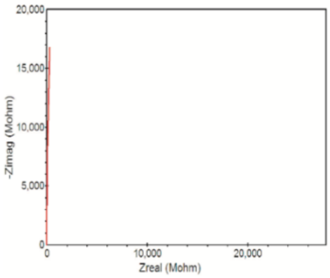
ω = Radial frequency = 2(pi)(frequency)

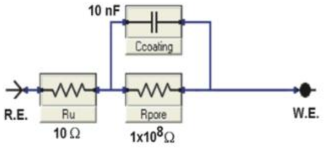
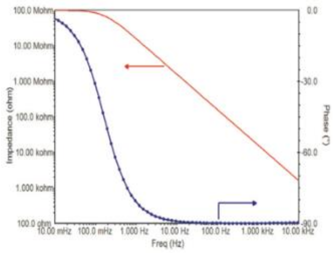
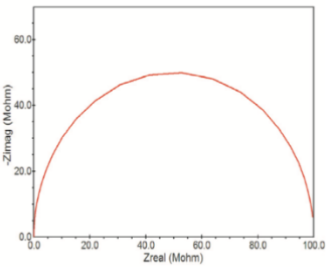
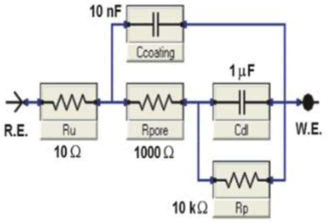
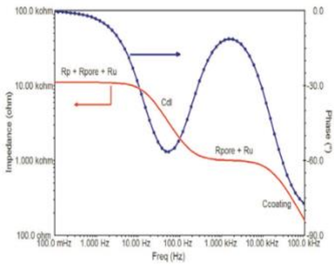
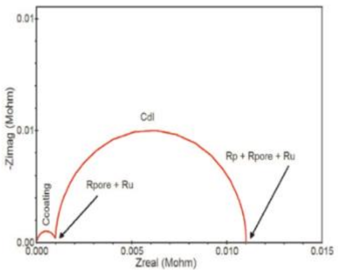
Hence, higher capacitance value will give a low impedance value.

2.5.3 Coating water uptake

Once EIS result is obtained (bode plot and Nyquist plot), the result is then modelled into its equivalent circuit. Below is an example of equivalent circuit modelling:

Table 2.2 Equivalent circuit model. Retrieved from Gamry Instruments

Equivalent Circuit	Bode Plot	Nyquist Plot
Perfect Coating. 		

<table>
<tr>
<td>Coating starts developing pore resistance and coating starts to absorb water.

</td>
<td>
</td>
<td>
</td>
</tr>
<tr>
<td>Damaged coating.

</td>
<td>
</td>
<td>
</td>
</tr>
</table>

In summary, high impedance indicates high resistance towards corrosion. Moreover, the Nyquist plot will show a distinctive patterns and shapes, which shows the state of the coating. With ‘semi-circled’ Nyquist plot, the coating is experiencing water absorption, meaning there is a potential for the metal to experience corrosion. With two ‘semi-circle’ shape at the Nyquist plot means the coating have been damaged.

From the equivalent circuit modelling, coating capacitance is able to be obtained, which will then be used to calculate the percentage coating water uptake using Brasher and Kingsbury equation.

Brasher and Kingsbury equation:

$$\%\ Water\ Uptake = \frac{log\frac{C_{C,t}}{C_{C,0}}}{\log 80} \times 100 \qquad (2.3)$$

Combining all the 3 equations, if the dielectric of coating increase, the capacitance will increase (Equation 2.1), making the impedance to decrease (Equation 2.2) and the percentage coating uptake increase (Equation 2.3). High percentage coating water uptake makes the metal substrate to be more prone towards corrosion.

2.6 Summary of Literature

Corrosion at splash zone have the highest corrosion rate, compared to other parts of an offshore structure. Polyurea coating is known to be better in terms of quality compared to epoxy coating and polyurethane coating. EIS have potential to evaluate long term accelerated weathering test, which, in theory, is more reliable and can detect failure of coating faster, through bode plot, Nyquist plot, and percentage water uptake.

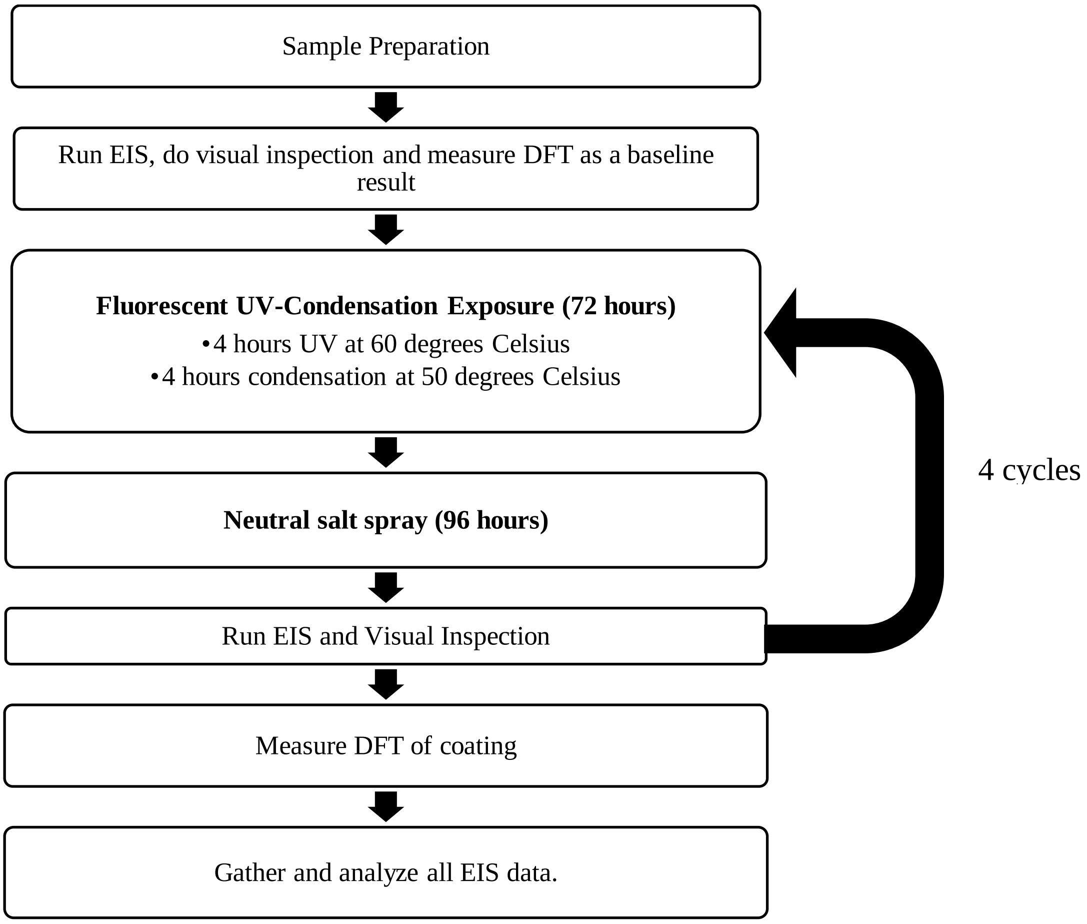
CHAPTER 3

METHODOLOGY

3.1 Overview

The objective of this project is to characterize progressive stages of coating physical degradation under simulated splash zone condition through degree of blistering and rusting, and evaluate damage property of coating in terms of impedance and percentage water uptake. To achieve the objective, the samples are exposed to ageing test, which are UV and condensation, and salt spray to simulate splash zone condition. After each cycle, the samples are evaluated visually, and through electrochemical impedance test. From the electrochemical impedance test, the result obtained is bode plot and Nyquist plot. The result is then being modelled to its equivalent circuit to calculate the percentage coating water uptake.

Below is the flow chart of the experiment:



3.2 Project Gant Chart and Milestone

Below is the gant chart and milestone for FYP I and FYP II:

Table 3.1 Gant chart and milestone

FYP 1

Activity (FYP 1)	Week													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Title confirmation with supervisor	🟩													
Research														
Background study		🟩	🟩											
Identification of problem statement		🟩	🟩											
Literature review related to project			🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩		
Submission of progress report								🟩	🟩 ▯					
Proposal defence													🟩 ▯	
Project Planning														
Collecting relevant test procedure											🟩	🟩	🟩 ▯	
Design of experiment												🟩	🟩	🟩
Develop test matrix												🟩	🟩	🟩
Sample preparation														🟩

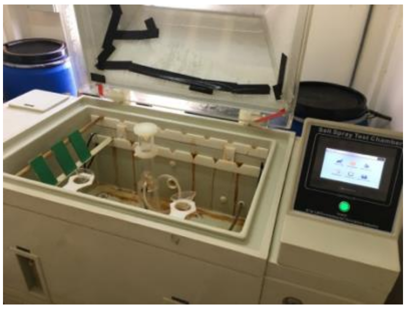
FYP 2

Activity (FYP 2)	Week													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Experimental Period														
Develop test matrix	🟩	🟩												
Preparation of job safety analysis		🟩	🟩	🟩	🟩 ▯									
Measure dry film thickness					🟩					🟩				
Run sample inside UV chamber						🟩	🟩	🟩	🟩					
Run sample inside salt spray chamber						🟩	🟩	🟩	🟩					
Run EIS						🟩	🟩	🟩	🟩	🟩 ▯				
Compile and evaluation of result											🟩	🟩		
Pre sedex preparation											🟩	🟩	🟩 ▯	
Viva and submission of dissertation														🟩 ▯

3.3 Tools and Equipment

The tools and equipment that are required to carry out the experiment are as follows:

Table 3.2 Tools and Equipment

Number	Equipment	Uses
1	Coating thickness gauge 	Measure the dry-film thickness of coating.
2	Salt spray chamber 	Simulate sea condition
3	UV and condensation chamber 	Produce damage caused by UV and humidity.

4	Electrochemical Impedance Spectroscopy (EIS) machine 	Characterize the coating through measurement of impedance.
5	EIS Cell 	A place to pour electrolyte solution to ensure complete circuit for EIS

3.4 Sample Preparation

3.4.1 Coating on mild steel plate

The size of samples are 150mm x 75mm x 3mm. The coating was coated by the manufacturer, which is MCU Coatings. 3 samples were used in order to obtain a reliable result as per stated in ISO 16773. Moreover, to make the sample to be a working electrode, an intentional holiday was created for every sample with minimum size of $1cm_2$, to ensure connectivity of electric flow for electrochemical impedance test.

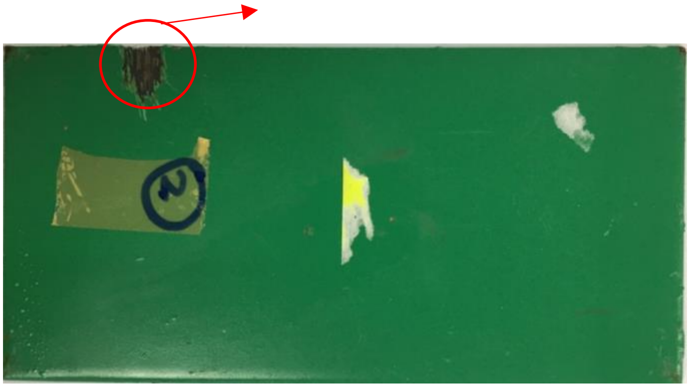


Figure 3.1 Example of exposed area on coating (Red Circle)

3.4.2 Thickness of coating

The thickness of coating were measured using dry-film thickness (DFT) machine. The function of measuring DFT is to see the effect in terms of thickness of the coating, before and after the weathering test, and also to determine the location of coating with 300 micron, which are to be used during EIS for consistency purposes.

3.4.3 EIS Cell

EIS cell is a place where electrolyte solution is poured to ensure connectivity of the EIS test. There are certain criteria must be met when constructing the EIS's cell as per stated in ISO 16773: Electrochemical Impedance Spectroscopy on coated and uncoated metallic specimens [15], which are:

I. The EIS cell's material must not react to the electrolyte to prevent error.
II. The EIS cell must be leak-proof to ensure the exposed area is constant because capacitance depends on the exposed area. Hence, the use of O-ring is recommended.
III. The compression of O-ring must be adequate, until no leakage is seen.

Figure 3.2 EIS Cell

3.5 Test Matrix for Salt Fog and UV Exposure.

Below are the test matrix for this project:

Table 3.3 Test matrix of this project

Sample	
Dimension (Length*Width*Thickness), mm	150 x 75 x 3

Material	Carbon steel
Number of Specimen	3
Coating	
Coating System	MCU Coating
Test Method	
Test Flow	1) UV-Condensation Exposure (72 hours) 2)Neutral salt spray (96 hours)
Duration (hours)	0 168 336 504
Characterization	1) Visual - Rusting and Blistering 2) Impedance measurement - EIS 3) Coating water uptake 4) Nyquist Plot
Machines Required	• Accelerated weathering chamber (UV - condensation) • Accelerated weathering chamber (neutral salt spray, using sea water) • Electrochemical Impedance Spectroscopy (EIS)
Standards referred	• ISO 12944-6 (Corrosion Protection of Steel Structures by Protective Paint Systems) • ISO 16773 (Electrochemical Impedance Spectroscopy EIS on Coated and Uncoated metallic Specimens) • ASTM D714 (Evaluating Degree of Blistering) • ASTM D610 (Evaluating Degree of Rusting on Painted Steel Surface) • Petronas Technical Standards: Protective Coatings and Linings

3.6 Visual Inspection

3.6.1 Degree of Blistering

To evaluate the degree of blistering, ASTM D714: Standard Test Method for Evaluating Degree of Blistering of Paints is referred. According to the standard, there are 3 reference standards:

I. Photographic reference

It illustrate two characteristics of blistering which are size and frequency.

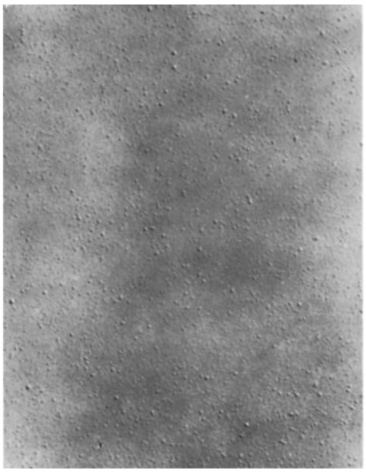
II. Size

The size of blistering are categorized numerically from 10 to 0. Blistering standard number 10 represents no blistering. Blistering standard number 8 represents the smallest size blister easily seen by the unaided eye.

III. Frequency

Frequency is categorized into four which are dense (D), medium dense (MD), medium (M), and few (F).

Table 3.4 Degree of blistering rating 8. Retrieved from ASTM D714

Few	Medium
	
Medium Dense	Dense
	

3.6.2 Degree of rusting

To evaluate degree of rusting, ASTM D610: Standard Practice for Evaluating Degree of Rusting on Painted Steel Surfaces [16]. Similar to ASTM D714, the degree of rusting is evaluated using a scale of 0 to 10 based on the percentage of visibility of surface rust. The distribution of rusting are classified into 3 which are spot rust, general rust and pinpoint rust.

Table 3.5 Scale and Description of Rusting Rating. Retrieved from ASTM D610

Rust grade	Percent of surface rusted	Visual Examples		
		Spot (S)	General (G)	Pinpoint (P)
10	Less than or equal to 0.01%	None	None	None
9	Greater than 0.01% Less than or equal to 0.03%	9-S	9-G	9-P
8	Greater than 0.03% Less than or equal to 0.1%	8-S	8-G	8-P
7	Greater than 0.1% Less than or equal to 0.3%	7-S	7-G	7-P
6	Greater than 0.3% Less than or equal to 1.0%	6-S	6-G	6-P
5	Greater than 1.0% Less than or equal to 3.0%	5-S	5-G	5-P
4	Greater than 3.0% Less than or equal to 10.0%	4-S	4-G	4-P
3	Greater than 10.0% Less than or equal to 16.0%	3-S	3-G	3-P
2	Greater than 16.0% Less than or equal to 33.0%	2-S	2-G	2-P
1	Greater than 33.0%. Less than or equal to 50.0%	1-S	1-G	1-P
0	More than 50%	None	None	None

Below is an example of area percentage of rusting with rating 9, 8 and 7:

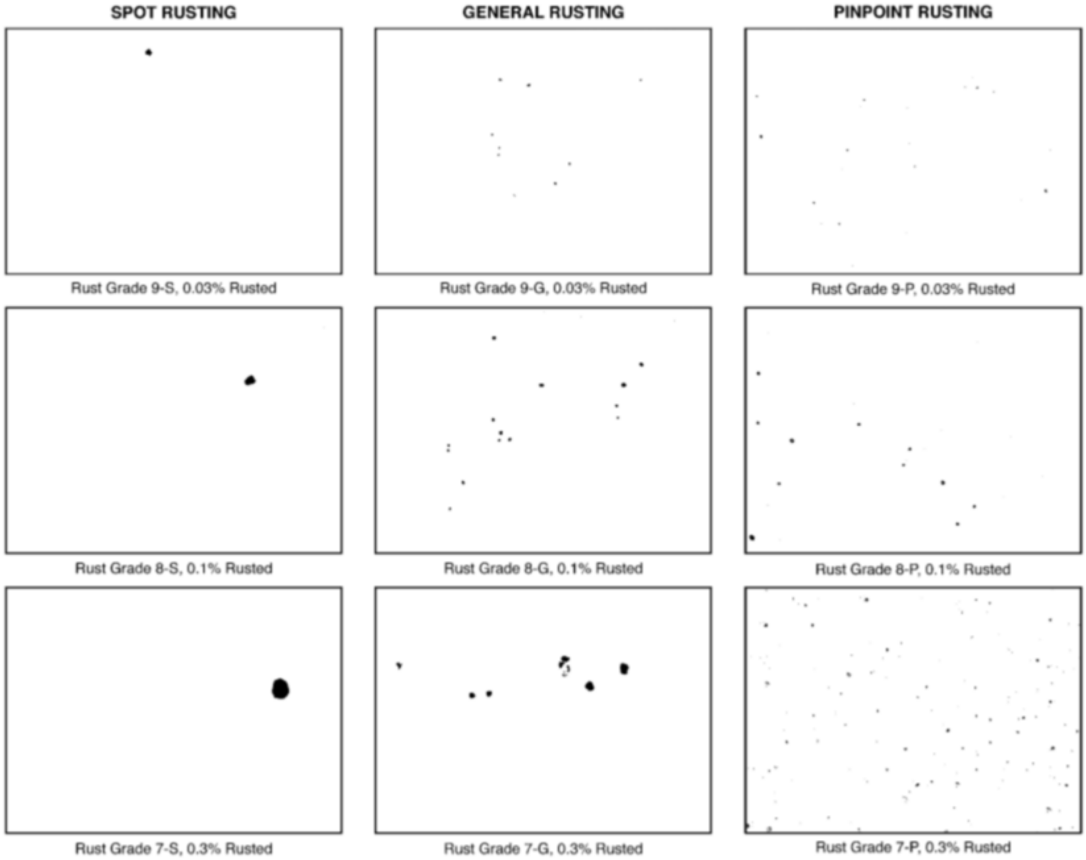


Figure 3.3 Examples of area percentage of rusting (rating of 9, 8 and 7).

3.7 Electrochemical Impedance Spectroscopy (EIS).

The standard used to run Electrochemical Impedance Spectroscopy is ISO 16733: Electrochemical Impedance Spectroscopy (EIS) On Coated and Uncoated Metallic Specimens.

The procedure for EIS for this project are as follows:

I. Securely place the EIS cell onto the sample. The cell was compressed onto the sample using a sufficient amount of rubber band.
II. 3% NaCl of electrolyte was poured into the EIS cell. Wait for 5 minutes and ensure there were no leakage.
III. All required cell cable wire are onto its respective places (Reference electrode, working electrode and counter electrode).
IV. Run Open Circuit Potential and make sure the potential is stable (±5 mV of difference).
V. Once the Open Circuit Potential is stable, run EIS with 10mV of AC voltage (rms), from 0.1 to 100,000 of frequency.
VI. Once the EIS test is done, run UV and salt spray exposure as stated before.

VII. Step I to VI were repeated until 504 hours is reached. To prevent error, the location of the EIS cell are recorded to ensure the cell are ran at the same place every cycle during EIS test.

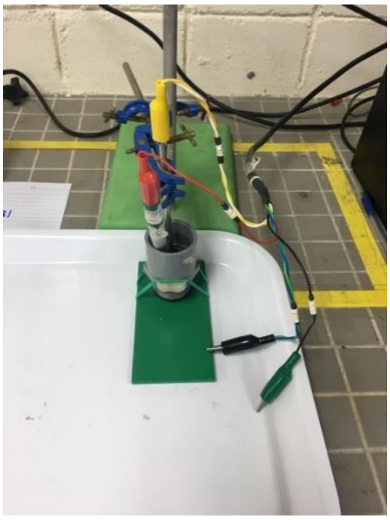


Figure 3.4 EIS Setup

Representation of EIS:

I. Bode plot
   a. Observe large impedance change due to its log-scaled graph.
II. Nyquist plot
   a. Observe small impedance change
   b. Characterize coating's state as in Table 2.2.

Once all EIS data are available, the result will be used to model it's equivalent circuit (referring to Table 2.2). The circuit model estimates the value for the model's parameter such as coating capacitance [14].

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Result

4.1.1 Thickness of Coating

The thickness of the coatings are measured before and after completing the experiments.

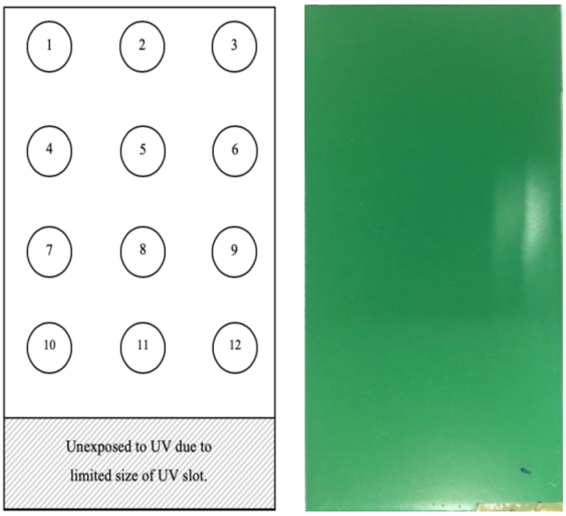


Figure 4.1 DFT location on sample

Below is the dry film thickness of coating (before and after UV and salt fog exposure):

Location	Thickness (micron)								
	Sample 1			Sample 2			Sample 3		
	Before	After	Difference	Before	After	Difference	Before	After	Difference
1	315	314	0.32%	327	323	1.22%	311	308	0.96%
2	297	295	0.67%	322	312	3.11%	322	317	1.55%
3	302	300	0.66%	339	329	2.95%	315	312	0.95%
4	316	306	3.16%	324	317	2.16%	289	288	0.35%
5	305	301	1.31%	280	279	0.36%	298	289	3.02%
6	322	318	1.24%	355	351	1.13%	330	321	2.73%
7	310	309	0.32%	343	338	1.46%	276	274	0.72%
8	321	320	0.31%	351	348	0.85%	287	286	0.35%
9	329	322	2.13%	367	365	0.54%	304	301	0.99%

10	314	311	0.96%	362	354	2.21%	274	271	1.09%
11	328	324	1.22%	354	353	0.28%	270	269	0.37%
12	358	357	0.28%	371	369	0.54%	301	292	2.99%
Avg	318.08	314.75	1.05%	341.25	336.50	1.39%	298.08	294.00	1.37%

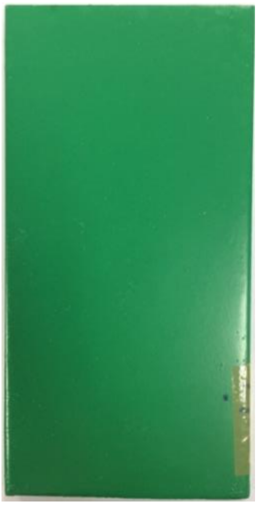
In average, the DFT have decreased by 1.05%, 1.39% and 1.37% for sample 1, 2 and 3 respectively.

4.1.2 Visual

Below are the visual results of all samples, from cycle 0 to cycle 4:

Table 4.1 Photographic result

Cycle	Sample 1	Sample 2	Sample 3
0			
1			

2			
3			
4			

Degree of Blistering

To determine the degree of blistering, ASTM D714: Standard Test Method for Evaluation of Blistering of Paints is referred [17]. From the result obtained (Table 4.1), the are no blistering or rusting seen on all samples. Hence, all samples have a rating of 10.

Degree of Rusting

Rust is a yellowish-brown flaking coating of iron oxide that is formed on iron or steel by oxidation. To determine the degree of rusting, ASTM D610: Standard Practice for Evaluating Degree of Rusting on Painted Steel Surfaces is referred [16]. From the result obtained (Table 4.1), there are no rusting seen on all samples. Hence, all samples have a rust grade of rating 10.

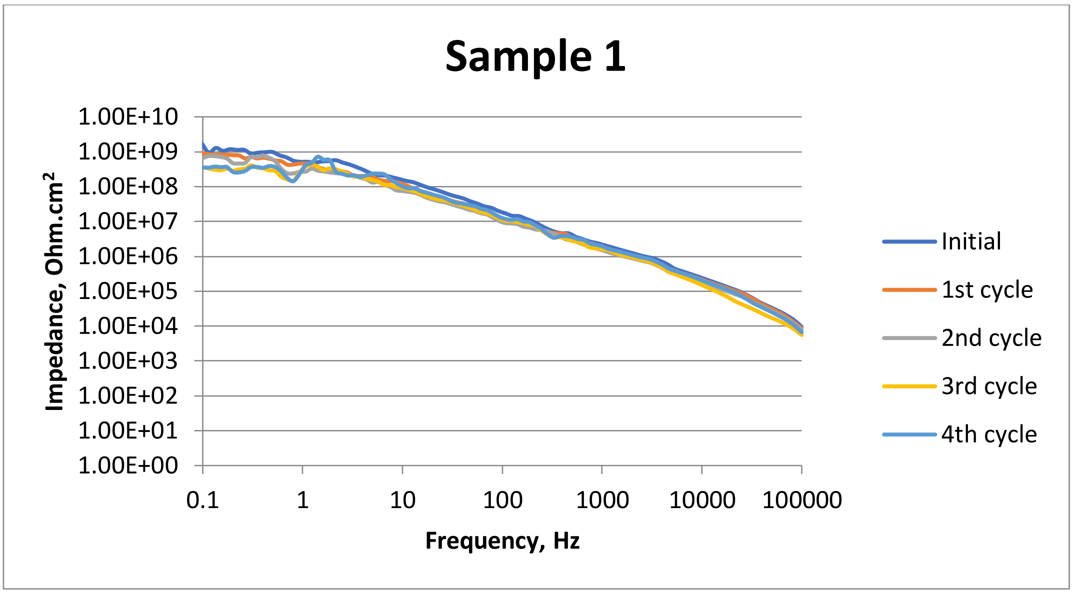
4.1.3 Electrochemical Impedance Test

EIS are conducted before running the experiment, and also after every cycle of the ageing test. From the electrochemical impedance test, 3 types of results are obtained which are bode plot, Nyquist plot, and percentage water uptake.

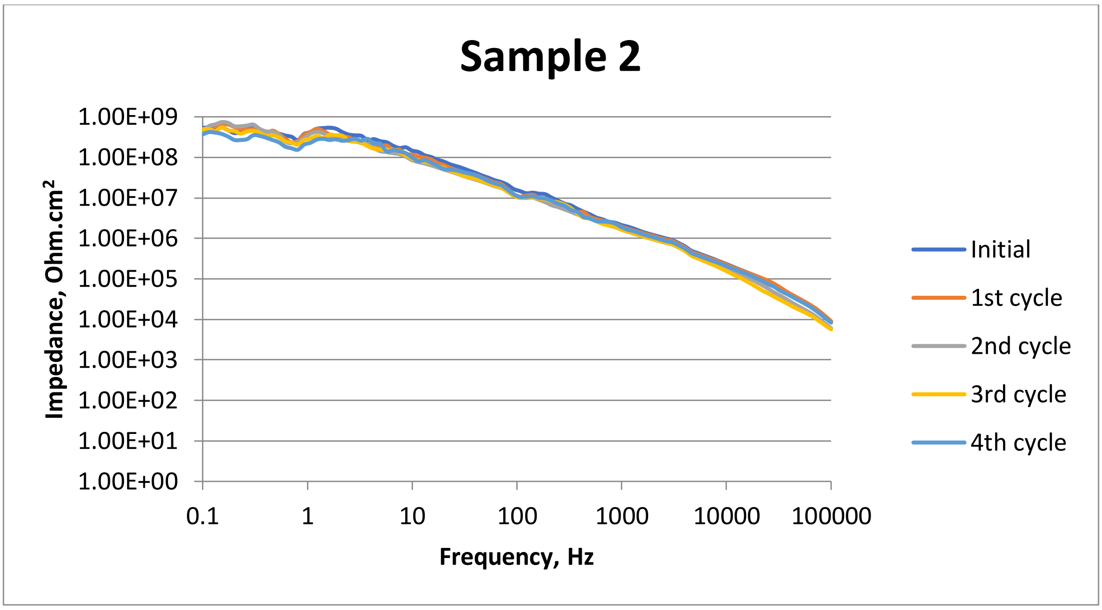
Bode plot

Below is the result (bode plot) for sample 1, 2 and 3:

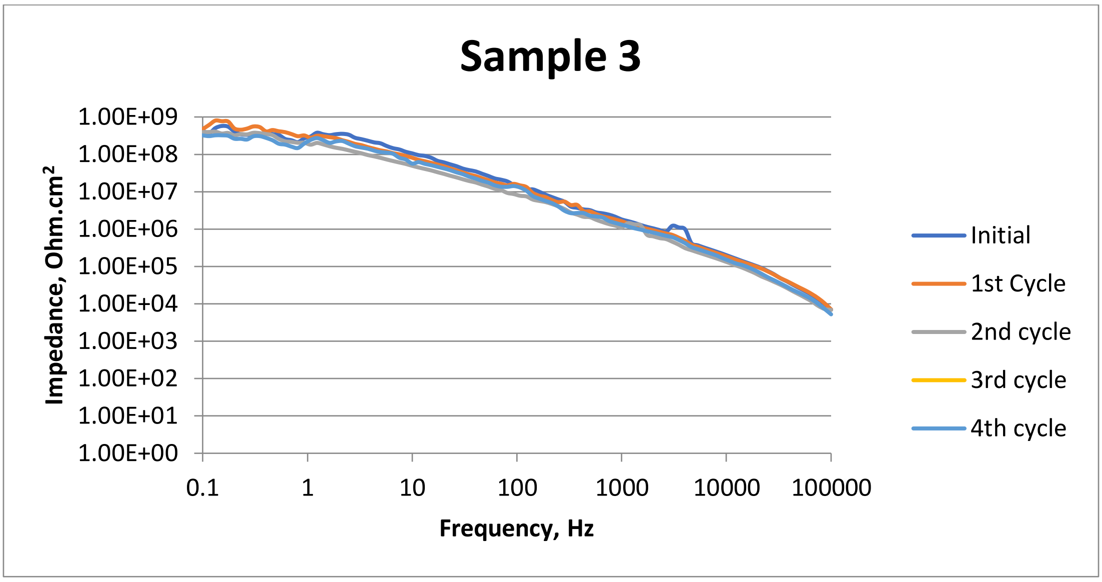
Sample 1



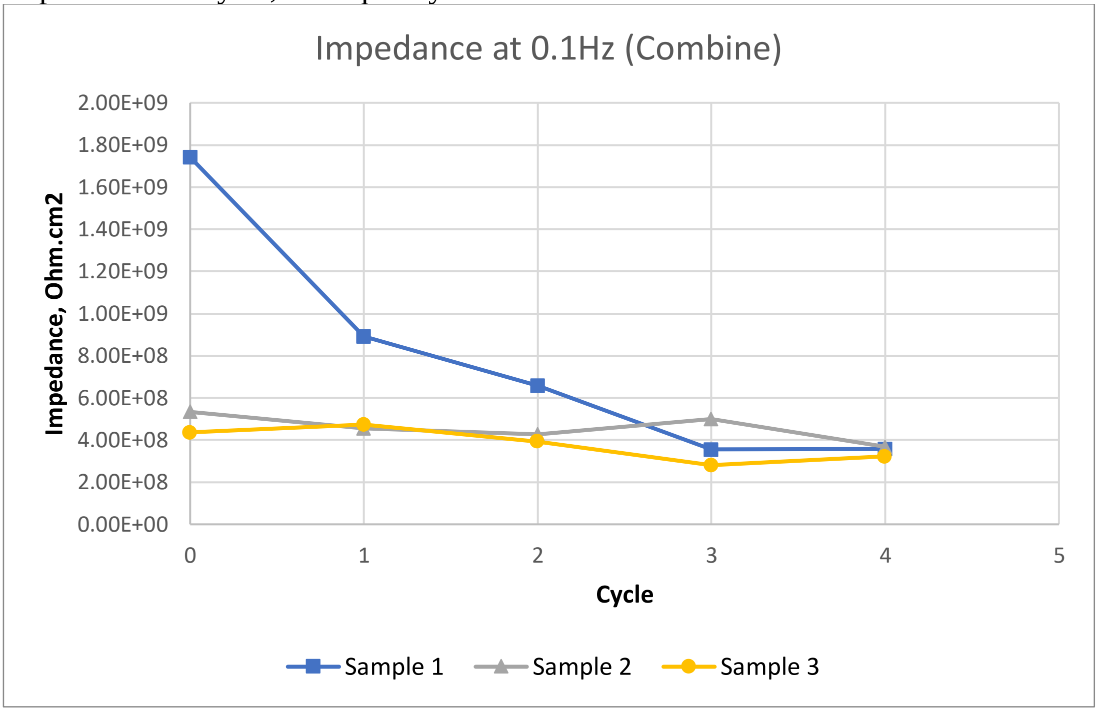
Sample 2



Sample 3



Impedance Vs Cycle, at frequency of 0.1 Hz

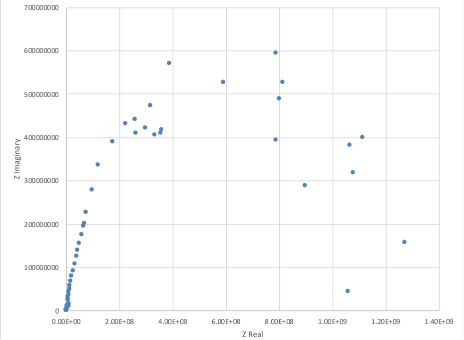
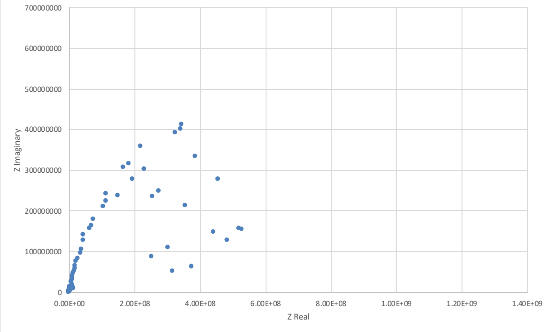
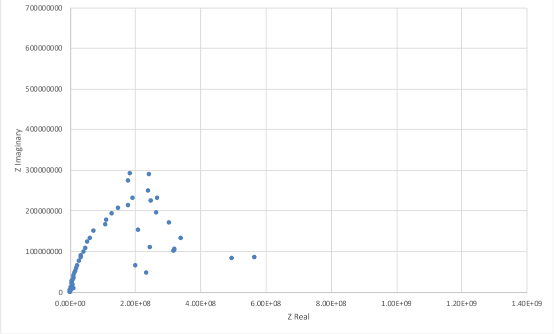
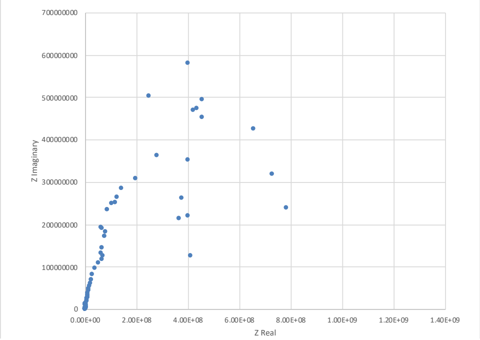
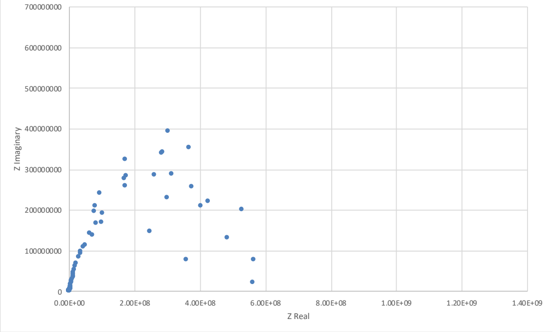
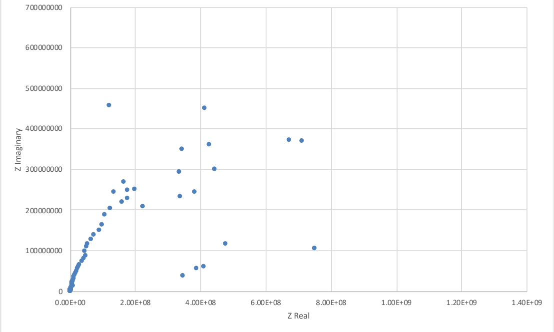


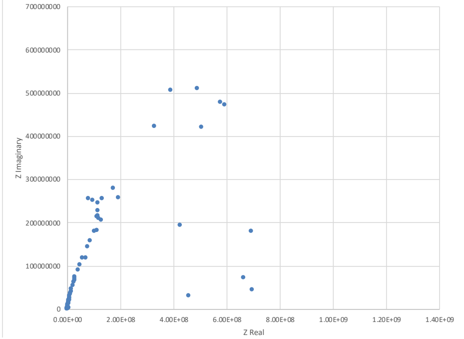
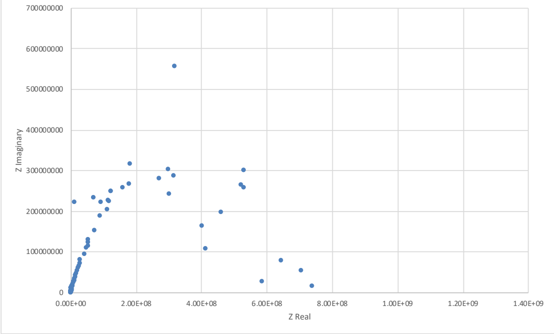
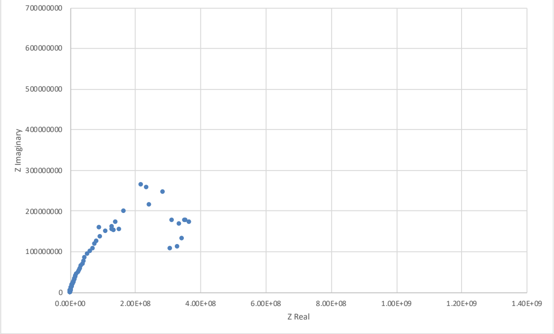
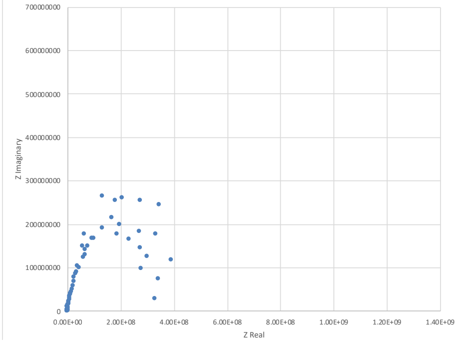
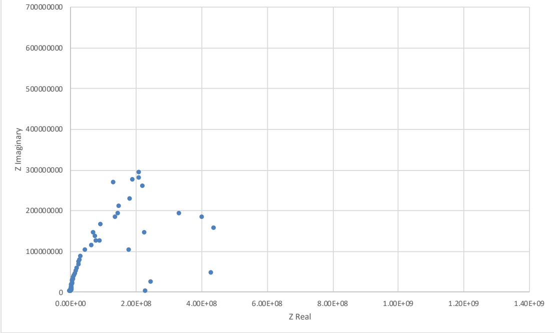
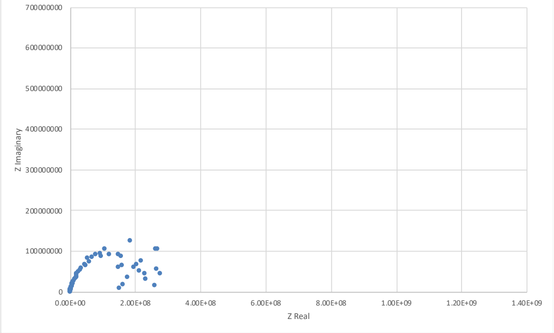
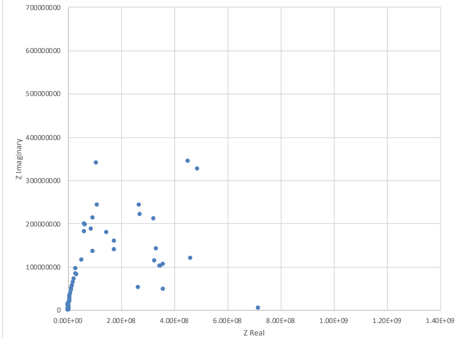
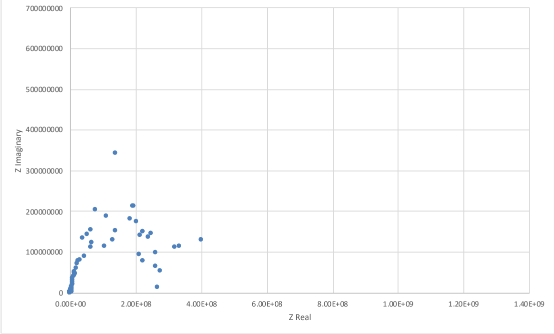
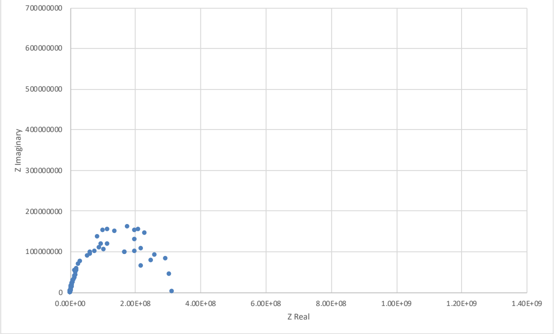
To conclude the bode plot result, sample 1 shows a quite significant of decrease in its impedance, while sample 2 and sample 3 shows a slight decrease of impedance. At cycle 4, all three sample have a impedance value of 3.2x10$_8$ to 3.7x10$_8$, which is still categorized as a good quality of coating as per stated by Gamry Instruments [18].

Nyquist plot

Below are the result for electrochemical impedance test, using Nyquist plot:

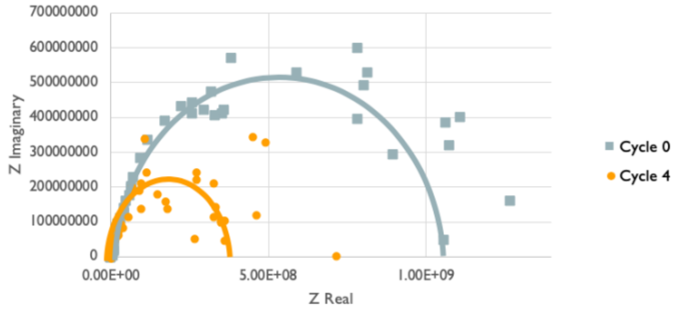
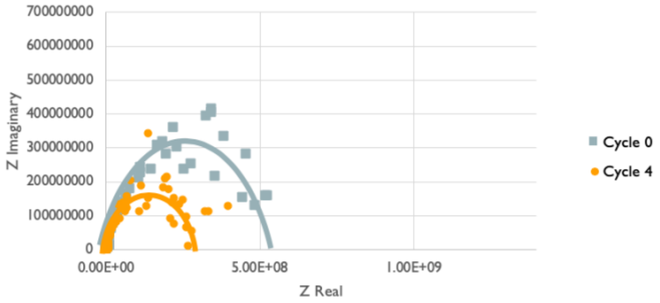
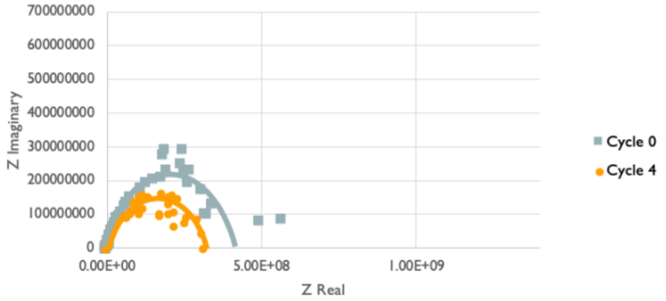
Table 4.2 Nyquist plot result

<table>
<tr><th>Cycle</th><th>Sample 1</th><th>Sample 2</th><th>Sample 3</th></tr>
<tr><td>0</td><td>
</td><td>
</td><td>
</td></tr>
<tr><td>1</td><td>
</td><td>
</td><td>
</td></tr>
</table>

2	Z Imaginary 700000000 600000000 500000000 400000000 300000000 200000000 100000000 0 0.00E+00 2.00E+08 4.00E+08 6.00E+08 8.00E+08 1.00E+09 1.20E+09 1.40E+09 Z Real	Z Imaginary 700000000 600000000 500000000 400000000 300000000 200000000 100000000 0 0.00E+00 2.00E+08 4.00E+08 6.00E+08 8.00E+08 1.00E+09 1.20E+09 1.40E+09 Z Real	Z Imaginary 700000000 600000000 500000000 400000000 300000000 200000000 100000000 0 0.00E+00 2.00E+08 4.00E+08 6.00E+08 8.00E+08 1.00E+09 1.20E+09 1.40E+09 Z Real
3	Z Imaginary 700000000 600000000 500000000 400000000 300000000 200000000 100000000 0 0.00E+00 2.00E+08 4.00E+08 6.00E+08 8.00E+08 1.00E+09 1.20E+09 1.40E+09 Z Real	Z Imaginary 700000000 600000000 500000000 400000000 300000000 200000000 100000000 0 0.00E+00 2.00E+08 4.00E+08 6.00E+08 8.00E+08 1.00E+09 1.20E+09 1.40E+09 Z Real	Z Imaginary 700000000 600000000 500000000 400000000 300000000 200000000 100000000 0 0.00E+00 2.00E+08 4.00E+08 6.00E+08 8.00E+08 1.00E+09 1.20E+09 1.40E+09 Z Real
4	Z Imaginary 700000000 600000000 500000000 400000000 300000000 200000000 100000000 0 0.00E+00 2.00E+08 4.00E+08 6.00E+08 8.00E+08 1.00E+09 1.20E+09 1.40E+09 Z Real	Z Imaginary 700000000 600000000 500000000 400000000 300000000 200000000 100000000 0 0.00E+00 2.00E+08 4.00E+08 6.00E+08 8.00E+08 1.00E+09 1.20E+09 1.40E+09 Z Real	Z Imaginary 700000000 600000000 500000000 400000000 300000000 200000000 100000000 0 0.00E+00 2.00E+08 4.00E+08 6.00E+08 8.00E+08 1.00E+09 1.20E+09 1.40E+09 Z Real

Below is the combined Nyquist plot for cycle 0 and cycle 4:

Table 4.3 Combined Nyquist plot (cycle 0 and cycle 4)

Sample	Combination of Nyquist plot (cycle 0 and cycle 4)
1	
2	
3	

All the sample have a semi-circle shaped for Nyquist plot, meaning water have start absorbing into the coating. The Nyquist plot also can be used to read the impedance of coating. The size of the semi-circle have decreased from cycle 0 to cycle 4, meaning the impedance of the coating have decreased.

Percentage coating water uptake

Referring to the Nyquist plot, the most suitable equivalent circuit for all of the sample would be as follows:

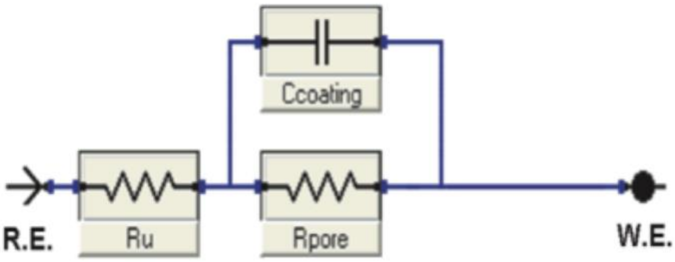


Figure 4.2 Equivalent Circuit based on results obtained.

Once the equivalent circuit is attained, coating capacitance is obtained and Brasher and Kingsbury's equation is used. Below is the result for percentage coating water uptake for all three samples from cycle 1 to cycle 4.

Table 4.4 Percentage coating water uptake result.

Cycle	Coating water uptake (%)		
	Sample 1	Sample 2	Sample 3
1	13.28	7.48	1.14
2	14.62	10.81	9.45
3	15.14	11.99	11.66
4	15.29	13.11	11.66

At cycle 1, sample 1 have the highest percentage coating water uptake (13.28%), followed by sample 2 and 3 which have 7.48% and 1.14% respectively. However, as the cycle increases until cycle 4, sample 1, 2, and 3 have a percentage coating water uptake of 15.29%, 13.11% and 11.66% respectively.

4.2 Discussion

Firstly, for the measurement of DFT (before and after the ageing test), all of the sample have decreased approximately by 1% from its initial thickness. Hence, the coating may have experienced degradation when the experiment is running. As for the degree of blistering and degree of rusting, all the samples have a rating of 10, meaning no blister or rust is visually seen.

As for electrochemical impedance measurement, in general, the impedance for all coated samples have decreased after 4 cycles. Based on the Nyquist plot, the all the coating have a semi-circle-shaped, meaning the coating are developing low pore resistance, and water starts absorbing into the coating. The coating is, however, still reliable since it have not been categorized as damaged coating based on Nyquist plot. Moving on to the percentage coating water uptake, all of the coating have increased its percentage coating water uptake approximately between 11% to 15%. This correlates with the Nyquist plot, since the it have a ‘semi-circled’ shape.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

5.1.1 Visual inspection

All samples have a rating of 10 for both degree of blistering and degree of rusting since it does not have any blistering or rusting seen on the coating.

5.1.2 Electrochemical impedance test

Up until cycle 4, the impedance for all of the samples have decreased. As for the Nyquist plot, the coating have started to develop low pore resistance, and water starts absorbing since it have a semi-circle-shape. This correlates with the calculation of the percentage water uptake whereby the value is between 11% to 15%. Hence, up until 4 cycle (28 days), introducing electrochemical impedance test is able to detect coating's degradation when running long term accelerated weathering test for coating.

5.2 Recommendation

To have more credible result, it is recommended that the ageing test should be extended until result for impedance and Nyquist plot are categorized as damaged coating as per Table 2.2. Once the coating are categorized as damaged coating, it should then be compared visually through blistering and rusting.

Moreover, it seems that when running EIS experiment, the result have some unexplainable noise. One of the factor may be due to disturbance from surrounding area such as air conditioning, vibration, noises etc. So, to avoid these noises, Faraday's cage should be used when running EIS. The main function of Faraday's cage is to reduce noises from the surrounding, which can lead to a better and convincing result.

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