

SHIBAURA INSTITUTE OF TECHNOLOGY

Corrosion Protection of Zinc Rich Paint Coating on Steels

by

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Declaration of Authorship

I, AZIZUL HELMI BIN SOFIAN, declare that this thesis titled, 'COROSSION PROTECTION OF ZINC COATING' and the work presented in it are my own. I confirm that:

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- Where I have consulted the published work of others, this is always clearly attributed.
- Where I have quoted from the work of others, the source is always given. With the exception of such quotations, this thesis is entirely my own work.
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“I begin by starting with the heart of beginnings, for it is the highest and noblest of beginnings”

Imam Maulud Matharat al-Qulub

Abstract

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Special attention has been paid since late 1950s to the studies aimed at improving and betterment the application of means of corrosion protection of metals as one of the methods for saving natural resources and increasing the durability of machines, building structures and other equipment. In order to protect metals against corrosion, coating is one of the promising method that can be employed. At the same time, insufficient attention has been given to the mechanism aspects of evaluating the efficiency of the protective coating. Recognising that there exist significant shortcomings in currently available information on corrosion mechanism, we are motivated to investigate the anti-corrosive protection by zinc rich paints (ZRP) using the commercial paints in the market. The research work was structured by coating metallic substrate with two different kind of ZRP with zinc content of 74 wt.% and 96 wt.%. Based on this coated materials, three main studies; specifically on corrosion performance in corrosive agent, comparison in different concentration of corrosive agents and evaluation on protective coating using electrochemical impedance spectroscopy (EIS).

1. Zinc rich paints (ZRP) are one of the most effective coatings used to protect steel from corrosion and they have been studied under severe environment like seawater, marine and industrial environments. A major problem in classic solvent-based paint is the emission of volatile organic compounds (VOC), which contribute to atmospheric pollution. In this study, the corrosion behavior of an epoxy based ZRP with less organic solvent so they abide by environment standards was studied. In this work, metal substrate was coated with various thicknesses of coatings of ZRP and the cross-section of the coating was observed by means of scanning electron microscopy (SEM), electrochemical behaviors were compared using potential corrosion measurement system and open circuit measurement. It was verified that both coatings with 74 wt.% and 96 wt.% showed good corrosion resistance mainly due to the cathodic protection and barrier effect, respectively. However, for single layer coating of 74 wt.% Zn, does not offer good corrosion protection. Based on

results from morphology characteristics of ZRP at initial stage, a probable current density inhibition model was proposed.

2. The second study deals on the evaluation of coated samples in two different concentration of corrosive agents, 0.5 and 1.0 M NaCl solution. The electrochemical behaviour were investigated based on polarization measurement, open circuit potential and electrochemical impedance spectroscopy (EIS). To confirm our coating is stable in thickness, SEM observation on the cross-section was conducted. The performance of the coating with different coating thickness varied particularly in coating system of 74 wt.-%-ZRP. Using Stean-Greary equation, the polarization resistance (R_p) was determined from the Tafel plots and we also calculate the corrosion rate (V_{corr} in millimetre per year) . In 0.5 M NaCl solution, coating system with 96%-5 shows the lowest corrosion rate. Coating systems with 74%-ZRP do performed well, and remarkably sample with 5 layers show the best performance in that system. There was a correlation between zinc content and corrosion resistance performance. Film thickness of the coated samples with 74% probably affected the electrochemical properties and the corrosion resistance performance.
3. The third study evaluates the corrosion performance of the coating systems by using electrochemical impedance spectroscopy (EIS). EIS was used to monitor, up to 7 weeks, the degradation kinetics of three different thickness under cathodic protection in NaCl solution were conducted. EIS in the 100kHz-1mHz frequency range was employed as the main electrochemical technique to study the corrosion behaviour of ZRP. The EIS results obtained at the open circuit corrosion potential have been interpreted using a model associate the impedance of parcel to particle contact to account for increasing resistance between zinc particles with immersion time, in addition to the impedance due to zinc surface oxide layer and the resistivity of the binder. From the results, we conclude that the loss of cathodic protection is due to the decreases of the zinc and metallic substrate area ratio due to zinc corrosion and the loss of electric contact between Zn to Zn particles, and this can be confirmed from SEM observation. Coated sample with 74 wt.-%-ZRP shows severe corroded zinc particles, while 96 wt.-% sample relatively still maintain the spherical shape of zinc particle. Even when cathodic protection effect by Zn particle became weak, the metallic substrate is still protected against corrosion by the barrier effect and reinforced by zinc corrosion products.

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Abbreviations

EEC	E lectrochemical E quivalent C ircuit
Fe	Iron
Fe(OH)₂	Ferum Hydroxide
Fe₂O₃	Ferric Oxide
H₂O	Water
NaCl	Sodium Chloride
O₂	Oxygen
SEM	S canning E lectron M icroscopy
Zn	Zinc
ZRP	Z inc R ich P aint

Symbols

C	absolute capacitance	F
C_{dl}	double layer capacitance	F
I	current	A
Q_{cc}	$s^n \Omega^{-1}$	
Q_f	constant phase element of coating film	Ω
Q_{dl}	constant phase element of double layer	Ω
R_c	resistance of charging circuit	Ω
R_{ct}	charge transfer resistance	Ω
R_f	resistance of coating film	Ω
R_s	resistance of solution or electrolyte	Ω
Y_{dl}	pre-factor of constant phase element Q_{dl}	$s^n \Omega^{-1}$
Z^*	complex electrochemical impedance	Ω
Z'	real part of electrochemical impedance	Ω
Z''	imaginary part of electrochemical impedance	Ω
Z_c	impedance of capacitor C	Ω
Z_q	impedance of constant phase element Q	Ω
Z_r	impedance of resistor R	Ω
ω	angular frequency	rads^{-1}

Dedicated to my Beloved Parents. . .

Chapter 1

Introduction

The application [1] of zinc rich paints (ZRP) metal substrates is a very efficient approach of corrosion resistance protection. They are used in many aggressive media such as sea water, marine and industrial environments. Today, thousands of industrial manufacturers depend on paint or coating for long lasting strength, protection and improve productivity. The main area zinc has been depicted to be more effective than other coatings types. Furthermore, the current *Clarke* number of zinc is 0.004% exceptionally very small value and the needs in reducing zinc consumption is very crucial [2]. As the global economy is expanding at a decent pace, manufacturing and construction development in BRICs countries and other major developed countries the usage of steel keep expanding. Therefore, the demands of zinc rich paint, zinc plating application are growing everyday. Compared to electroplating, not only the consumption of zinc can be reduced, power saving and shortening the manufacturing time also can be expected by using the paint. The protection of steel with epoxy based zinc rich paint is based on the general principle of cathodic protection by metallic zinc in contact with metal substrates. It is a common fact that in order to achieve a long life coating system, a zinc primer needs to be applied as the first coat. For solvent based zinc rich paints, it seems to be established that, at least at the beginning of immersion, zinc particles provide [3, 4]. Then, a long term protection develops due to the formation of zinc corrosion products, reinforcing the barrier effect of the paint [5].

The metallic zinc content in the dry film is a very important parameter to be emphasized in the technical specifications of zinc rich paints. However, as observed by Lindquist *et al.* [6] this parameter is not the only factor determining the performance of this kind of paint. For example, Fragata [7] Del Amo [8] and Pereira *et al.*[9] verified that the chemical nature of the binder and the zinc particle size are also very important. The zinc particle (spherical or lamellar shape, or a combination of both shape) is dispersed

in an inorganic (usually orthosilicates) or organic binder (usually epoxies) [10]. These particles must be in electrical contact between themselves and the metallic substrate in order to secure a well established electrical conduction within the coating. In such condition of percolation, a galvanic coupling is created between zinc and the metal substrates which is nobler than zinc. Then, zinc can preferentially dissolve, acting as sacrificial pigment, and allowing a cathodic protection of the metal substrate. Many studies [11, 12, 13, 14, 15, 16, 17, 18, 19] exist in literature and relate the protection mechanisms and degradation processes of such coatings. Physico-chemical properties and corrosion resistance of solvent based zinc rich paints strongly depend on pigment volume concentration (PVC), shape and size of zinc particle [4, 20]. In common liquid ZRP, zinc usually introduced as spherical particles with mean diameter ranging from 5 to 10 μm . To ensure good electrical contacts between zinc pigments and the steel substrates, a high pigment concentration is required (usually above 60 wt.% by volume in solvent based zinc rich paints) [20]. A major drawback of classic solvent based paint is the emission of volatile organic compounds (VOC), which contribute to atmospheric pollution. Since the 1970s, powder coatings are often preferred because they are composed of dry thermosetting powder (without organic solvent) and more environment abiding.

Another type of zinc rich paint was introduced in the middle of 1990s in the automotive industry with the intention of imparting weldability to organic coating [21]. The steel sheets were joined partly with each other at some sites during assembly into the automobile body. Since such overlapped areas of steel sheets were difficult to be treated with paint or phosphate solutions, they became highly susceptible to corrosion. As a solution for this problem, cavity wax spray was employed to seal overlapped sites of steel sheets to prevent corrosive factors from approaching the joint sites. However, this method caused low productivity and higher production costs. In consequence, pre-coated steel sheets with paints that allow the welding of coated metal was proposed as an alternative to overcome the problem. Much effort has been invested to improved the corrosion resistance and weldability of the coating incorporating.

1.1 Motivation and Objectives

The main problem with liquid ZRP concerns the emission of volatile organic compounds (VOC) into the atmosphere. That is the reason why powder coatings are often preferred, because they are composed of dry thermosetting powders. However, the zinc content in powder ZRP is usually well below the one reported in liquid ZRP. Indeed, above 70 wt.% of zinc particles, the powder (after extrusion and before application) is not homogeneous which induces problems of zinc dispersion into final coating (after application). In a zinc

rich paint with epoxy based with 90 wt.% zinc, the volume concentration of the zinc will be approximately 60 wt.%, due to the difference in specific gravity. Due to the lower zinc volume concentration usually found in epoxies and the insulating and protecting properties of the epoxy binder, one may ask whether zinc epoxy based coating systems are more susceptible to degradation in corrosive environments. Moreover, percolation and porosity are affected by low zinc content which means that effectiveness and interest of these "zinc rich" coatings can be discussed. The corrosion behaviours of zinc rich paint with various thickness ranging from $10\mu\text{m}$ to $50\mu\text{m}$, in two types of zinc rich paint with zinc contents of 74 wt.% and 96 wt.% was investigated to find out key factors of corrosion mechanism. In addition, the cathodic protection ability of zinc rich coating on metal substrate was evaluated.

1.2 Thesis Outline & Contributions

1.2.1 Chapter 4: Corrosion Performance of ZRPs on mild steel in 0.5 M NaCl solution

The chapter discusses on the preparation of coated samples using commercial ZRPs with different thickness. The corrosion behaviors/performances of zinc rich paint (ZRP) applied on steel substrates under NaCl solution environment were investigated by using electrochemical measurements, scanning electronic microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) and the results are presented in this chapter.

1.2.2 Chapter 5: Comparison of corrosion resistance in different concentration solution

The chapter consists of the electrical properties evaluation of coated samples with ZRP-74 wt.% and 96 wt.% in two different concentration solutions. The influence of the zinc content on the paint behavior has been studied, but little attention has been paid to steel/paint corrosion product, which simulates practical application conditions. In this chapter, we reports an evaluation of the corrosion behaviors/performances of zinc rich paint (ZRP) applied on steel substrates under NaCl solution as artificial seashore environment by using polarization measurements and Electrochemical Impedance Spectroscopy (EIS) in two different corrosive media. Understanding the coating behaviour in severe solution will lead to a new high corrosion protection coating design.

1.2.3 Chapter 6: EIS characterisation of ZRP coating

Characterization of coated ZRP as anti-corrosive coating for metallic substrate using EIS is presented in this chapter. The performance of the materials was investigated practically based on two different types of commercial ZRP, 74 wt.% and 96 wt.% with three different kind of thickness using open circuit potential and electrochemical impedance spectroscopy measurements. Comparison of these samples in different duration of immersion was also carried out and is presented in detail in this chapter. By utilizing EIS measurement, superior performance of ZRP in severe corrosive media could be understood deeply, as we fitted our data using the suggested electrical equivalent circuit.

1.2.4 Chapter 7: Conclusions & future works

The final chapter concludes all the studies that have been conducted and their remark contributions. In addition, extension studies on ZRPs optimum design, mathematical and circuitry analyses are suggested in this chapter.

Chapter 2

Background Theory

In this chapter introductory theory will be elaborate to give the reader a deeper understanding of the basic concepts of zinc rich paints and the application of zinc rich paints in anticorrosive paint systems for the protection of steel. The theory section is divided into 4 sections, each with their own subject area. Section 2.1 will be discussing general aspects of zinc rich paint, section 2.2 describes basic corrosion theory and mechanisms, and 2.3 describes type of corrosion. Sections 2.4 describes the composition and formulation of anti-corrosive paint systems.

2.1 Zinc rich paints

This section will describes the basic chemical and physical characteristic of zinc rich paint with silicate and epoxy based. In particular, the chemical structure and its importance for different physical and chemical properties are presented.

2.1.1 Introduction to zinc rich primer

What is a zinc rich primer and how is it possible to protect bare metal from corrosion?

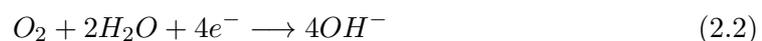
Zinc rich primer besides being a good barrier to oxygen and water may also protect the metal galvanically. For betterment in corrosion resistance the conductivity of the coating should be high and provide necessary conductivity for galvanic protection. High concentration of zinc, contributes to the film or coating's porosity and its poor internal adherence. The coating of silicate base of ZRP frequently do not bond well to each other and it is better to coat the metallic substrate using an organic zinc-rich paint. Inorganic zinc primers and, to a lesser extent, organic zincs have been effective in moderating

corrosion in extremely aggressive environment such as seashore and marine environment. Their pricing is tied to the current price of zinc in the markets. Paint formulators have used variety of additives to reduce the occurrence of pinholes and cracks. The major problem is air entrained in the metallic substrate during the paint application. Although most of the air escapes from the paint without causing problems, a compelling quantity remains as tiny bubbles until the film is in its final stages of drying process. Therefore, to achieve maximum performance, most researchers attempt to coat the metallic substrate with thin coat, in order to allow the coat to dry fast without occurrence of cracks. In many environments the presence of pinholes in film or coating does not result in excessive corrosion. This surprise is probably due to high surface tension of solution, causing it form droplets rather than flowing on hydrophobic resin surfaces. However, in certain device, for example in tank lining work, pinholes cannot be tolerated [22]

While zinc silicate is a typical "new building" coating, organic zinc rich paint is more of a maintenance primer. The epoxy base primer is far more easy to apply in higher thickness without cracking and can be applied with conventional airless spray, while alkali silicates normally need special equipment. Organic zinc rich coatings are not as electrically conductive as inorganic zinc rich coatings, thus, they have lower level of galvanic protection. We need to remind here that, organic zinc rich paints do not require as high a level of blast cleaned metallic surface as do inorganic coatings and they are easier to handle even for layman [23].

2.2 Corrosion of steel

Corrosion of steel is a well known problem, and can be recognized by the formation of red rust on the surface. In order for steel to corrode and form rust, anodic and cathodic reaction must take place. In the anodic reaction iron is oxidized and forms divalent cation Fe^{2+} with the liberation of two electrons (reaction 2.1). In reality, the most frequent cathodic reaction is the reduction of oxygen, as shown in reaction 2.2



The iron ions given in reaction 2.1 will subsequently react with the hydroxide ions and form the complex iron hydroxide:

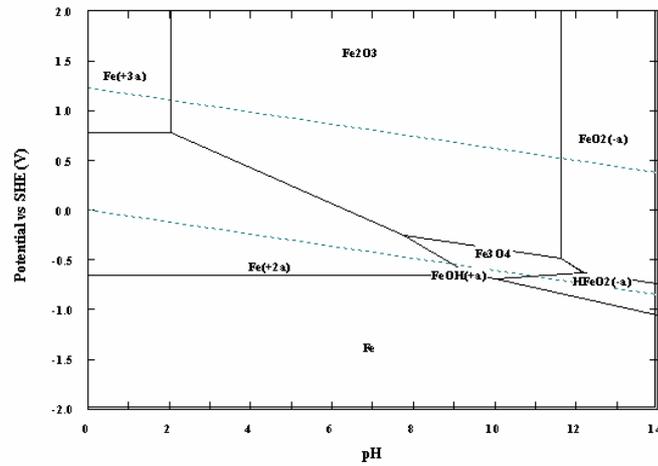
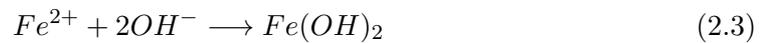


FIGURE 2.1: Pourbaix diagram for iron in water



Since oxygen dissolves readily in water, there is normally an excess of it. A further reaction with the formation of the well known red rust can therefore take place as shown in reaction 2.4



The stability of iron may be depicted by means of a Pourbaix diagram. Figure 2.1 shows the Pourbaix diagram for iron substrate in water at 30°C with an ion molarity of 1.0×10^{-6} . As depicted on Figure 2.1, iron is only immune at a potential below -0.65V. Above the immune area, iron will corrode in acidic environments with the formation of Fe^{2+} or Fe^{3+} . In neutral environments, iron will have tendency to form oxides normally as Fe_2O_3 or Fe_3O_4 . In strongly alkaline environments, iron will corrode and form either FeO_2^{-} or $HFeO_2^{-}$.

It is important to state that the presence of chloride ions in the environments has a big influence on the stability of iron metal and increase the risk of active corrosion. the ability of iron to form oxides will additionally decrease and the passive properties are harder to reach.

2.3 Corrosion of coated steel

The protective nature of corrosion resistance paint system is only valid for a given time and the destruction of the paint coating will eventually take place leaving free passage entrance for corrosive agents to penetrate towards metal substrates. normal failure mechanisms related to organic coatings include blistering and under cutting corrosion, which are fatal for the protective behaviour of the coating and chalking or fading, which are less risky. Blister paint are formed when water and other corrosive agents percolate the paint coating during time of wetness. Access of corrosive agents cause a corrosive reaction to take place underneath the coating and cause the paint film to swell, as illustrated in Figure 2.2. As the blister grows, it often be condusive to combine with other blister can be formed according to Table 2.1.

The osmotic blister is most common and is created near contaminants on the metal surface. An osmotic blister is the ordinary and created contaminants vicinity on the metal surface. An osmotic blister is conceived when water percolate the paint and



FIGURE 2.2: Schematic of a blister

TABLE 2.1: Types of blister

No	Type of blister
1	Osmotic blister
2	Anodic blister
3	Cathodic blister

dissolves soluble substances in the paint. This produce a dense fluid beneath the paint which is drawn to the solution outside the paint by osmosis. The blister is developed as an attempt to equalize the density between these two fluids. [24]. Undercutting corrosion is developed near scribe or sheared edges as illustrated in Figure 2.3. The corrosion will normally occur either by a chemical reaction in the interface between substrate material and paint, or by corrosion of the substrate metal itself. Both situations will decrease the adhesion, or unfavourable case, completely disconnect the paint film. The mechanism of undercutting corrosion can be described as a crevice corrosion scenario. Crevice corrosion is characterized by the presence of a small local anode and a large external cathode. Formation of an acidic environment and gaseous hydrogen in the crevice will further accelerate the corrosion [25]

Another kind of crevice corrosion is often present on painted aluminium and it is known as filiform corrosion. Filiform corrosion is initiated near defects and mechanical damages in the paint from which fine passageways containing corrosive products are spread in a smeared pattern. The mechanism behind filiform corrosion is directed by an active "head", which acts as an anode, while the "tail" and the surrounding regions act as a cathode. A potential difference of 0.1 to 0.2V is generally obtained between the head and tail region. The presence of oxygen is crucial for the maintenance of cathodic reactions, and therefore the motivation behind the mechanism of filiform corrosion. The cathodic reactions take place in the tail region, which is supplied with oxygen and condensed vapour through cracks and crevices in the coating. The head of the filament is filled with floating flakes of opal aluminium gel which are moving towards the tail region. Reactions between aluminium ions (Al^{3+}) and hydroxide ions (OH^-) will also take place in the tail region, producing aluminium trihydroxide ($\text{Al}(\text{OH})_3$) and aluminium

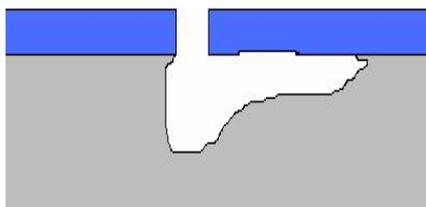


FIGURE 2.3: Schematic diagram of undercutting corrosion

oxide (Al_2O_3). Filiform corrosion is generally dependent on the relative humidity and the quality of the applied surface treatment. Serious attacks appear in warm coast regions, where high salinity and high relative humidity increase the development of filiform corrosion. Filiform corrosion is only present in the atmosphere and occurs especially at a relative humidity of 85% to 95%. [26]. Cathodic protection of steel by means of sacrificial anodes (eg. zinc) or impressed current can result in cathodic disbondment which decreases the adhesion of the paint coating. The loss of adhesion between the paint and substrate material, is caused by formation of cathodic reaction products (eg. OH^-) near flawed areas in the paint coating. Cathodic protection thus increases the risk of disbandment since cathodic polarised steel surface has a higher exposure to cathodic reactions. A model for the mechanism of cathodic disbandment is illustrated in figure, with the presence of cathodic reaction products beneath the paint coating.

Studies of the mechanism behaviour have shown that production of hydroxyl ions is the primary cause of cathodic disbondment. A direct proportionality is present between the OH^- concentration and the rate of disbandment. It is believed that the generated hydroxyl ions interact with the paint and thus weaken and break the bonds between the paint and the steel substrate. The oxygen concentration in the environment is another factor that enhances the risk of cathodic disbondment [27]

2.4 Anti-corrosive paint

An introduction to general aspects of paint composition and properties is needed in order to understand the mechanism of anti-corrosive paint systems. Paint is a complex formulation based on many different components which contribute to the overall efficiency of the system. This section describes the different components and their mode of operation.

2.4.1 What is paint?

Paint is an organic coating that primarily protects equipment and constructions from environmental damage and provides a decorative surface. For protection purposes, paint is used in a wide range of industrial applications such as ships, ballast tanks, drilling rigs and concrete constructions. Selecting the right kind of paint system requires a comprehensive knowledge about the environment and its demands. Protection is a wide area of expertise and requires information about problems related to corrosion, fouling, contaminations, wear and abrasion. Paint as a definition, composed of a liquid material which transforms to a thin coherent and adherent film when applied to a surface.

The composition of paint can generally be divided into four main components: binder, pigment, solvent and additive. The binder is the backbone of a paint system and is therefore used to classify the system.

Generally, organic solvent based paint can be divided into two groups: physically drying paint and chemically curing paint. This categorisation concerns the action of film formation and describes whether the transition from liquid to solid state takes place either by evaporation or by chemical reaction.

Physically drying paints form a film exclusively by evaporation of solvents. The binder molecules have therefore the same composition and size both before and after solidification of the film. The mechanism of physically drying paint is physical process where the solvents evaporate and leave behind long chains of resin molecules, which pack together and form a coherent plastic film. Chemically curing paint is based on a curing mechanism where the film formation takes place by a chemical reaction between the binder and a curing agent. The final binder molecules in the dry film are therefore different from the initial binder molecules. The final binder molecules are much bigger and contain a high degree of cross-linking, forming a strong and non-reversible paint film [28].

A description of the four main components is given in the following four sub-sections. Each section describes the most common components, their mechanism and application.

2.4.2 Binders

The binder is an essential component that provides uniformity and coherence to the paint system. It holds the pigments together when a dry film is formed, and provides adhesion to the substrate material. The type of binder often determines the durability of the final product. The ability of a binder to form a dense and tight film is directly related to its molecular weight and complexity. Binders with a high molecular weight often tend to form film by evaporation, while low-molecular binders generally will form film by a reaction in situ. A way to classify a binder is according to its chemical reactions. Table 2.2 lists some important binders, their grouping and chemical reactions.

2.4.3 Pigments

Pigments compose a broad group of dry powder materials which are added to the paint in order to provide functionality and appearance to the paint system. The pigments are insoluble in the paint system and range from naturally occurring minerals to synthetic organic materials. Besides the obvious purpose of providing colour and opacity, pigments

are also an important additive for corrosion protection, film reinforcement, coverage and adhesion. In anti-corrosive paint systems, pigments mainly provide protection by one or more of the following mechanisms; inhibition of corrosion, passivation of substrate metal, barrier against water permeability and cathodic protection. Certain pigments also elevate heat, abrasion, acid or alkali resistance to the final dry film. Important properties for all pigments are particle size and shape, wet ability by the binder and bulking. Some important pigments, their grouping and functionality are listed in Table 2.3.

2.4.4 Solvents

Solvents are volatile liquid substances with the purpose to dissolve solid paint fractions, reduce the viscosity and make the paint fluid for satisfactory application. After application, the solvent must evaporate to allow the coating to cure and achieve hardness. If a solvent has low volatility it can cause runs and sags in the drying coating film. In contradiction, solvents can not be too volatile and cause solvent pops, loss of gloss, dry spray, poor surface wetting and penetration, poor film flow and inhibit cure. A blend of different solvents is therefore normally used in order to achieve optimum properties. Solvents are usually categorized according to their chemical composition. Table 2.4 lists some important groups of solvents, their advantages and disadvantages.

TABLE 2.2: Classification scheme of binders according to their chemical reactions

Classification	Examples	Chemical reactions
Oxygen reactive binders	Alkyds, epoxy esters, urethane alkyds	The binder molecules react with oxygen and a cross-linking of the resin molecules takes place
Lacquers	Polyvinyl chloride polymers, chlorinated rubbers, acrylics	Drying mechanism by solvent evaporation. The long chain resins entangle with each other but no cross-linking exists
Heat conversion binders	Hot melts, Organosols and plastisol, powder coatings	Curing takes place upon heating as the components melt. Both cross-linked and non cross-linked coatings are possible
Co-reactive binders	Epoxies, polyurethanes	The film formed by a polymerisation between the resin and curing agent. A three-dimensional network is formed
Inorganic binders	Post-cured silicates, self-curing water silicates, self-curing solvent based silicates	The binders are usually used in zinc particles pigmented primers where a reaction between zinc and binder takes place forming a very hard film
Coalescent binders	Latex	Film formation by coalescence of binder particles dispersed in water

2.4.5 Additives

The final components in a paint system is the additives which normally make less than 1% of the entire paint formulation. Additive are used to balance the paint fluid and modify different physical and chemical properties such as viscosity, surface and interfacial tension, brightness and curing time. Addition of additives is only done when necessary since unwanted consequences on the paint properties are likely to obtain. The most common additives are listed in Table 2.5 with an explanation of their function.

2.5 Corrosion protection by zinc rich paints (ZRP)

The application of zinc metal particles for corrosion protection has been examined for more than 50 years [29]. This section will reviewed different protection mechanisms which are proposed by a number of researchers. According to several studies, zinc rich paints (ZRP) are well known as efficient organic coatings to protect metallic substrates from corrosion. Marchebois *et al.* [30] has reported solvent based ZRP with mixture of zinc pigment varies from 50 or 70wt.%. The zinc concentration was well reported with liquid ZRPs and for the third formulation, conductive pigments (carbon blacks) were added. Then, their electrochemical behaviours wee compared using electrochemical impedance spectroscopy (EIS) and micro-Raman spectroscopy. They found that porosity and electrochemical behaviour was intimately related to the conductive pigments presence in the coating. Two coatings presented behaviours which related to zinc bare

TABLE 2.3: Classification scheme of pigments according to functionality

Classification	Examples	Functionality
Colour pigments	Titanium dioxide, iron oxides, organic azo pigments	Provide colour to the paint. Titanium dioxide is the most popular white pigment because of its high refractive index
Inhibitive pigments	Zinc phosphate, aluminium phosphate, zinc molybdate	Provide active corrosion inhibition to the metal substrate. The pigments are slightly water soluble. Dissolved ion species thus react with the metal to form passivating reaction products
Barrier pigments	Aluminium flake, micaceous iron oxide	Increase the permeation path length to the substrate fro incoming moisture
Hiding pigments	Rutile titanium oxide	Pigments with a high light refractive index to provide good hiding
Extender pigments	Carbonate, silicates, sulphates, barytes and mica	Act as reinforcement and flow control pigments. They are relatively inexpensive

metal during a short period but not real cathodic protection and effective percolation were offered. This is due to the low zinc content, but the shape and the size of the zinc dust have strong influence. Marchebois *et al.* also discussed the influence of addition of conductive pigments like carbon blacks on the corrosion behaviour of ZRPs coated steel in artificial sea water [31]. Two different effects were pointed out, first, an increase of the porosity induced by carbon addition and a galvanic action between zinc and carbon pigments. The performance of the powder coatings, strongly improved if the carbon amount was sufficient, compared to the one reported for solvent based zinc rich paints. Then Jagtap [32] and Gergely [33, 34] improved the corrosion protection using zinc rich paints with various amounts of dispersed polypyrrole-deposited alumina monohydrate particles. They focused on investigation various hybrid formulations in order to gain valuable improvement by certain zinc rich compositions. Also, to find the optimal balance between inhibition of sacrificial action of the zinc and galvanic function of the hybrid coatings. They conclude that, advanced protection performance may be obtained by one preferred hybrid formulation comprising zinc particles and polypyrrole coated alumina inhibitor particles (PCAIPs). They also found that lamellar pigments have more surface area than spherical zinc pigments because of which it has better

TABLE 2.4: Classification scheme of solvents with a description of their application range

Classification	Examples	Solvent description
Aliphatic hydrocarbons	Naphtha, mineral spirits, hexane, heptane	Used with asphalt, oil and vinyl based coatings. Poor to moderate solvency and wide range of evaporating rates. Least expensive of all solvents
Aromatic hydrocarbons	Toluene, xylene	Used with chlorinated rubbers, coal tars and certain alkyds. Greater solvent power than the aliphatics
Ketones	Acetone, methyl ethyl ketone, methyl isobutyl ketone	Effectively used with vinyls and some epoxies. Exhibit varying evaporation rates and relatively strong solubility parameters. Strong hydrogen bonding and high polarity
Esters	Ethyl acetate, isobutyl acetate, ethylene glycol	Used as latent solvents with epoxy and polyurethane. Solvency power between aromatic hydrocarbons and ketones. Strong hydrogen bonding and a relatively high polarity.
Alcohols	Ethanol, isopropanol, n-butanol	Good solvents for highly polar binders such as phenolics. Alcohols are highly polar with a strong affinity for water
Ether and alcohol ethers	Ethyl ether	Excellent solvents for some of the natural resins, oils and fats
Water	Water	Used in latex

connectivity and conductivity. This connectivity resulted better corrosion protection because barrier as well as sacrificial cathodic protection to base metal. The leading ratio that provide best results was 25:75 for spherical shaped particles to lamellar shape particles, this also supported by the rheological measurements. From there, they design equation based on PVC and conductivity analysis could be a simple tool in predicting the salt spray resistance of the particles under consideration.

2.5.1 Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy, also known as *ac impedance measurement*, is most powerful analytical tool in investigating electrochemical behavior (corrosion mechanism) of paint/steel including the utilizable capacitance as well as the R_{esr} . The measurement is performed by applying small ac signal (several millivolts) to the coated samples within a frequency range, typically between mHz and kHz range. The R_{esr} value can be determined from the real part, $Z'(\omega)$ of the impedance data, $Z^*(\omega)$ in high frequency region. Meanwhile, if the measured capacitive is considered as a whole capacitor, as described by Meroufel, *et al.* [35], the impedance data can be expressed in terms of complex capacitance $C^*(\omega)$ as follows;

$$Z^*(\omega) = Z'(\omega) + jZ''(\omega) = \frac{1}{j\omega C^*(\omega)} \quad (2.5)$$

$$C^*(\omega) = C'(\omega) - jC''(\omega) = \frac{-Z''(\omega)}{\omega|Z^*(\omega)|^2} - j\frac{Z'(\omega)}{\omega|Z^*(\omega)|^2} \quad (2.6)$$

where the real part of $C^*(\omega)$, $C'(\omega)$ corresponds to the utilizable capacitance value and the imaginary part $C''(\omega)$ is related to the dispersion of zinc particles [36].

TABLE 2.5: Classification scheme of additives according to functionality

Classification	Examples	Functionality
Antifoam additives	Mineral oils, silicone oil, wax dispersions	Prevent the formation of foam eg. by coalescence of small bubbles to larger bubbles which increases the buoyancy of the bubbles
Thickness	Bentonite, cellulose derivates, polyacrylates	Increase the viscosity of the paint by creating a network between hydrophobic and hydrophilic parts of the paint
Dispersion additives	Tensides	Increase the wet ability of pigments to the binder phase by formation of micelles
Siccatives	Metals salts or organic acids	Used in paints with oxygen reactive binders. Improve the curing process
Cold stabilisers	Ethylene glycol, propylene glycol	Used in water based paint to improve the stability to freezing

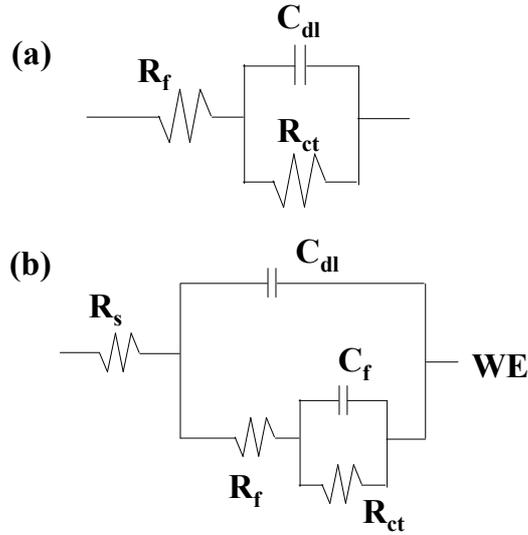


FIGURE 2.4: Basic approach of corrosion mechanism modeling; (a) before reaching the electrolyte to the metallic substrate and (b) after initiation of corrosion process due to electrolyte percolation

2.5.2 Equivalent circuit model

In order to interpret the corrosion mechanism of coated samples, it is necessary to obtain its electrical equivalent circuit. Figure 2.4(a) represents basic approach in modeling an equivalent circuit (EEC) by describing the layer with bulk solution resistance R_s and the polarizable zinc electrodes (charge accumulation area) with parallel-connected double layer capacitance C_{dl} and film/coating resistance R_f . In case of EDLC that comprises of symmetrical polarizable electrodes configuration, the model can be deduced as Figure 2.4(b).

Normally, equivalent circuit model for a corrosion mechanism is pre-determined based on its Nyquist plot behavior. Basic evaluation of Nyquist plot using electrical elements is shown in Figure 2.5. R , C and Q represent resistor, capacitor and constant phase element, respectively according to these impedance equations;

$$Z_r = R \quad (2.7)$$

$$Z_c = \frac{1}{j\omega C} \quad (2.8)$$

$$Z_q = \frac{1}{Y(j\omega)^n} \quad (2.9)$$

where Y and n are the pre-factor and exponent of the constant phase element Q . Constant phase element Q is an element that behave in between resistor and capacitor (non-linear capacitor) [37]. Depending on the exponent n value, the corresponded Nyquist plot of a constant phase element tends to; 1) slightly deviate from vertical-line behavior of capacitor for series connection with a resistor (refer Figure 2.5(iii)) and 2) suppress the capacitor semi-circle behavior for parallel-connected to a resistor (shown in Figure 2.5(vi)).

There is also another element that has been widely used to describe charge accumulation process into porous carbon electrodes, called Warburg impedance [38]. The element is expressed similarly based on the constant phase element as in equation 5.2, but with exponent n value of 0.5. Corrosion mechanism have been practically modeled using the combination of these elements in various configuration (series and parallel connection) [39, 40].

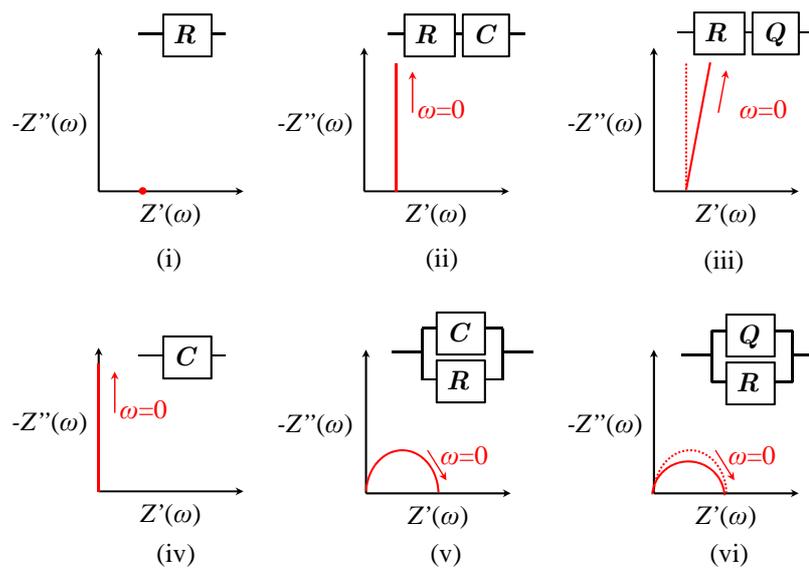


FIGURE 2.5: Circuit configuration with corresponded Nyquist plots.

Chapter 3

Apparatuses and Experimental Methods

This study is aimed to investigate the spraying method for zinc rich coating at room temperature using commercial zinc rich paints spray. The experimental work focuses on two main works. First, substrate treatment and spraying method. Second is material characterization and electrochemical properties investigation.

3.1 Substrate Pre-Treatment

In this study, a pure iron (Fe 99.5%) sheets are used as substrates for all coating substrates. The metallic sheet then cut into (10mm×20mm×0.5mm) in dimension. The metallic substrates are first serially polished with emery paper #600, #800, #1000 to produce mirror like surface. The metal substrates are then introduced into distilled water and rinsed using an ultra sonic bath. Ethanol is employed to degrease the surface of the metal substrates and they rinsed again with distilled water. The cleaned substrates then, dried at room temperature before spraying process.

3.2 Spray Painting technique

After the substrate is properly cleaned and dried, it is then ready for the spraying process. In order to reduce the duration of spraying process, we employed "wet on wet" spraying technique. In this technique, one coat is sprayed then the next coat immediately applied without and time left between coats. Spray that we employed are shown in Figure 3.1. To achieved optimum and similar coatings, spraying process is conducted in temperature

ranges between 20 - 25°C. While spraying, the spray can is held at a distance of 25-30 cm away from the metal surface and keep the hand moving to ensure the thin coats of paint will be deposited on the metallic substrate. After the spraying process the samples will be dried at ambient temperature for 1-2 hours. Schematic diagram of coated sample is shown in Figure 3.2.

3.3 Surface morphology and Composition by Scanning Electron Microscope (SEM)

Morphology of the coated substrate was studied using Field Emission Scanning Electron Microscope (FE-SEM) JEOL JSM-7400F fitted with Energy Dispersive Analysis X-ray (EDAX) for chemical composition analysis of the coating. Actual setup as shown in Figure 3.3.



FIGURE 3.1: Commercial zinc rich paint

3.4 Electrochemical Polarization Curve Measurements

Corrosion behaviour of coated substrates at various coating thickness are studied using electrochemical polarisation curve measurements. In order to investigate the electrochemical behaviour of the coated substrate polarization measurement was performed using electrochemical measurement system (Hokuto Denko HS-5000). The coated substrate sample is used as the working electrode. The sample is mounted on epoxy resin and exposed only the test surface. Then the sample is connected using copper wire. Platinum is employed as a counter electrode, and Ag/AgCl/KCl/KCl (saturated) is used as a reference electrode. Then, the reference electrode was connected to the test solution or electrolyte and secured using saturated KCl bridged. Polarization curve measurements of a sample are obtained in 0.5 and 1.0M NaCl solution from -1.0 V until 1.0V. The actual measurement setup and experimental diagram as shown in Figure 3.4 and 3.5 below.

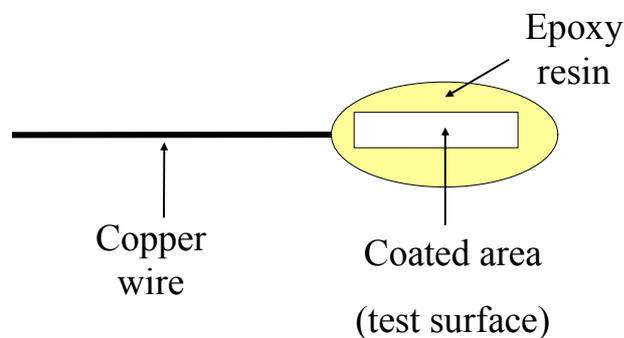


FIGURE 3.2: Schematic diagram of coated sample



FIGURE 3.3: The FE-SEM fitted with EDAX capability

3.5 Electrochemical Impedance Spectroscopy

The electrochemical impedance of the coated metal substrates were characterized by electrochemical impedance spectroscopy measurement. The applied ac voltage amplitude is $\pm 5\text{mV}$ with the frequency range between 10kHz and 10mHz. The measurement was carried out at the rest potential of the tested capacitors using the same electrochemical measurement system (Hokuto Denko HZ 5000 and NF FRA5022) (refer Figure 3.5).

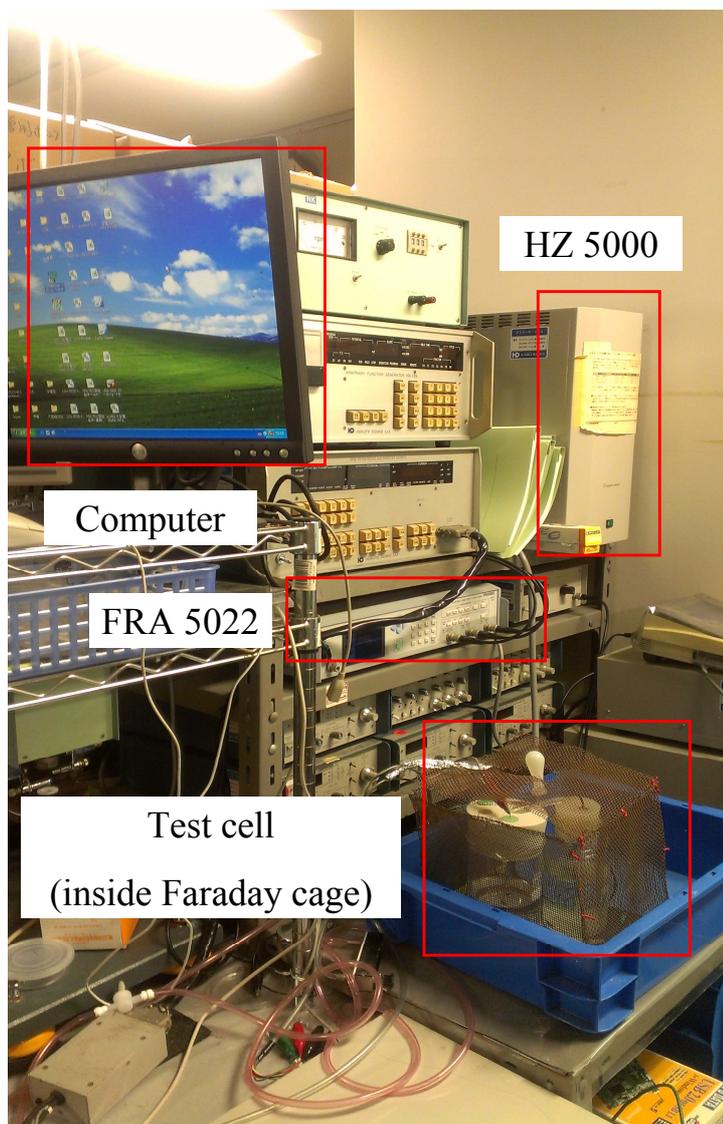


FIGURE 3.4: Actual measurement setup

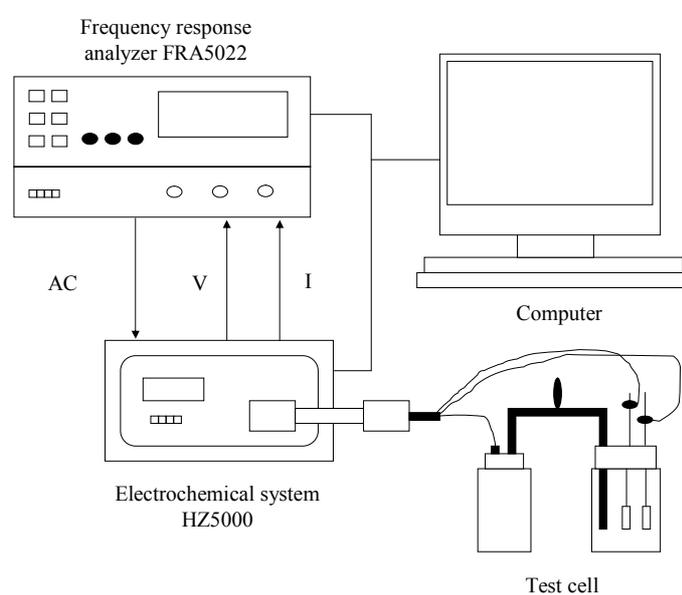


FIGURE 3.5: Polarization and electrochemical impedance measurement system

Chapter 4

Corrosion Performance of ZRPs on mild steel in 0.5 NaCl solution

4.1 Background

Steel is one of the predominantly used metals. However, exposure to humidity and salinity in atmosphere will accelerate the corrosion protection of steel. Today, thousands of industrial manufacturers depend on paint or coating for long lasting strength, protection and improved productivity. Zinc is one of the most important elements for commercial application in the corrosion protection and improved productivity. Zinc coating displays its leadership and innovation on protecting the metal surfaces against corrosion and fouling usually caused by seawater. The protection of steel with epoxy based zinc rich paint is basically contributed by the sacrificial elements of paint, which is zinc that promotes cathodic protection to the metal substrate. Since late 1950s, the development of epoxy based zinc rich paint for corrosion resistance application has drawn much attention [29]. The main application area of ZRP is in the anti corrosion protection for industrial construction, for example pipelines, bridges, petrochemical or power industries, also for marine applications. Several studies have been carried out in order to elucidate the influence of the zinc content on the electrochemical properties of these paints. Romagnoli *et al.* have reported that paint with Zn concentration larger than 60 wt.% is recommended in order to achieve a good protection towards corrosion [41]. Ji Hoon Park *et al.* has reported that with 60 wt.% of zinc in the paint, the performance of coating can be improved when the surface modified zinc particles were applied in the coating film [40]. Under immersion conditions, the time of cathodic protection depends on the zinc content in the coating film and they verified coatings with 60 volume percent of zinc powder showed good corrosion resistance mainly due to the cathodic protection. Since

then, the effect of the surface morphology of zinc particle towards the coating film was reviewed significantly. The influence of chlorides, sulfates and nitrates on the steel/paint surface in terms of the underfilm corrosion was also investigated [42]. Vilche and Giudice *et al.* [20, 33, 43] studied the influence pigment shape and content of zinc primers by designing and manufacturing several series of coatings to obtained adequate pigment volume concentration in order to enhance the anticorrosive performances. In atmospheric condition, the anticorrosive mechanism of zinc rich paint is dominated by the coating behavior of zinc corrosion products which inhibit further corrosion activity [44]. The influence of the zinc content on the paint behavior has been studied, but most researchers show less concern to steel/paint interfacial structures which simulates practical application conditions. This paper reports a study of the corrosion behaviors/performances of zinc rich paint (ZRP) applied on steel substrates under NaCl solution environment by using electrochemical measurements, scanning electronic microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX).

4.2 Experimental

Test specimens were pure iron 99.5% ($10\text{mm} \times 20\text{mm} \times 0.5\text{mm}$), abraded with #600, #800 and #1000 emery papers. In order to ensure the absence of dust, oil and foreign matters on specimens were cleansed with ethanol using the ultrasonic bath. Commercial zinc 74wt% and 96wt% (Atom Paint Co. Ltd., Japan) content epoxy-ZRP was applied onto specimen by air spraying following the manufacturers instructions under control conditions in a laboratory. The specimens were coated with 1, 3 and 5 layers coating respectively. After the coatings were applied, the specimens were allowed to cure at ambient temperature. The specimens were exposed to a 0.5 M sodium chloride (NaCl) solution, and the corrosion potential was recorded. A three electrode systems was used, in which a silver-silver chloride electrode Ag/AgCl/KCl (sat.), a platinum electrode and coated samples were used as a reference, counter and working electrodes, respectively. Polarization curve measurement behavior of ZRP coated steel and non-coated steel were measured. Before the measurement, the specimens were cathodically polarized at -1.0V for 15 min to remove the pre-existing oxide film. The potentiodynamic polarization tests were conducted at scanning rate of 1.0 mV/s from -1.0V to 1.0V. From the polarization curves measurement, we obtained corrosion potential and corrosion current density. The specimens were immersed for 50 days and the open circuit potential was measured for each sample every day during the test period. Adhesion tests were performed on ZRP coatings after the spraying process and after immersion in 0.5 M sodium chloride (NaCl) solution. The initial stage of cross-section of coated steel was observed by SEM. The cross section analyses towards coated samples were performed under SEM observation.

The cross section surface of specimens were polished and washed by ethanol prior to drying by using cold air and stored in a desiccator to avoid corrosion at the paint or steel interface. A JEOL JSM-7400F SEM fitted with a source for energy dispersion X-ray analysis (EDX) was used to study the morphology and element distribution on the specimens cross-section area.

4.3 Results and Discussion

4.3.1 Adhesion test

Adhesion test were performed on ZRP coatings after the spraying process and immersion in 0.5 M NaCl solution to determine the efficiency of the coatings. By taking into account the results of cross-cut performed on ZRP coatings exposed to the salinity solution the appropriate failure mode can be determine and the lifetime of this kind of the binder can be understand. Cross-cut tests represented the additional criteria which were included in the failure time assessment presented in this work. The cross-cut area of the paint coatings and the stain marks left on the sticky tape after its removal were scanned and are shown in Figure 4.1 and Figure 4.2. Detailed of the results from the cross-cut tests is shown in Table 4.1 and Table 4.2. This layer may susceptible to the loss of binding from its degradation, enabling accurate detection of changes in the efficiency of the coatings, i.e. the cohesion of coatings by performing standard cross-cut [45]. This test seems to non-sophisticated, the stains left on the sticky tape can be an indicator for loss cohesion between the coatings and the metal substrate. For example, coatings before exposed to the solution did not show any signs of removal of coatings regardless of thickness and zinc contents. However, after exposed in 0.5 M NaCl solution in 1 week, slightly some black stain can be observed on the sticky tape. This showed that the paints established relatively highly air tight coatings, which completely inhibited the oxidation of the metal substrate.

TABLE 4.1: Adhesion properties of ZRP coatings after spraying process (Initial state)

Samples	1 layer	3 layers	5 layers
74%	10/10	10/10	10/10
96%	10/10	10/10	10/10

*Above 5/10: Passed Test Below 5/10: Failed Test

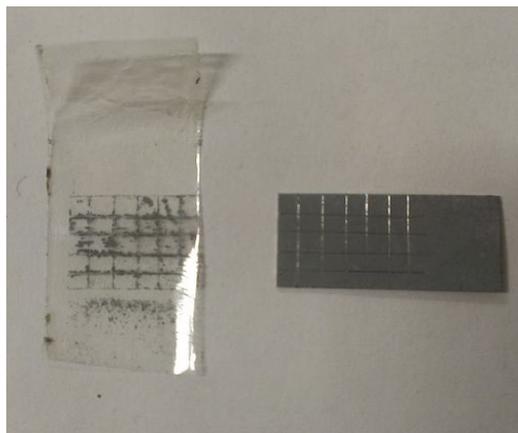


FIGURE 4.1: Cross-cut test after spraying process (Initial state). The stain left on the sticky tape after the cross-cut test is shown on the hand left side



FIGURE 4.2: Cross-cut test after immersion in 0.5 M NaCl for 1 week. The stain left on the sticky tape after the cross-cut test is shown on the hand left side

4.3.2 Cross-section morphologies

Figure 4.3 depicted a specimen with one layer of ZRP coating including distribution of Zn, Fe and C, respectively. As shown in Figure 4.3 (a), the Zn layer was compact and spherical in structure with thickness ca. 10-18 μ m. From the observation, it can

TABLE 4.2: Adhesion properties of ZRP coatings after immersion in 0.5 M NaCl solution for a week

Samples	1 layer	3 layers	5 layers
74%	8/10	8/10	8/10
96%	7/10	7/10	7/10

*Above 5: Passed Test Below 5: Failed Test

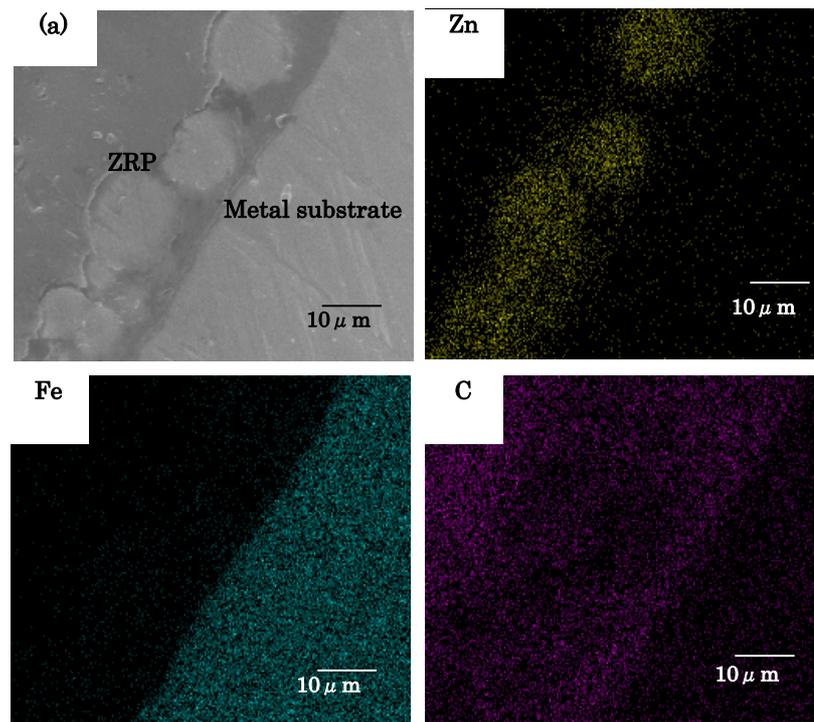


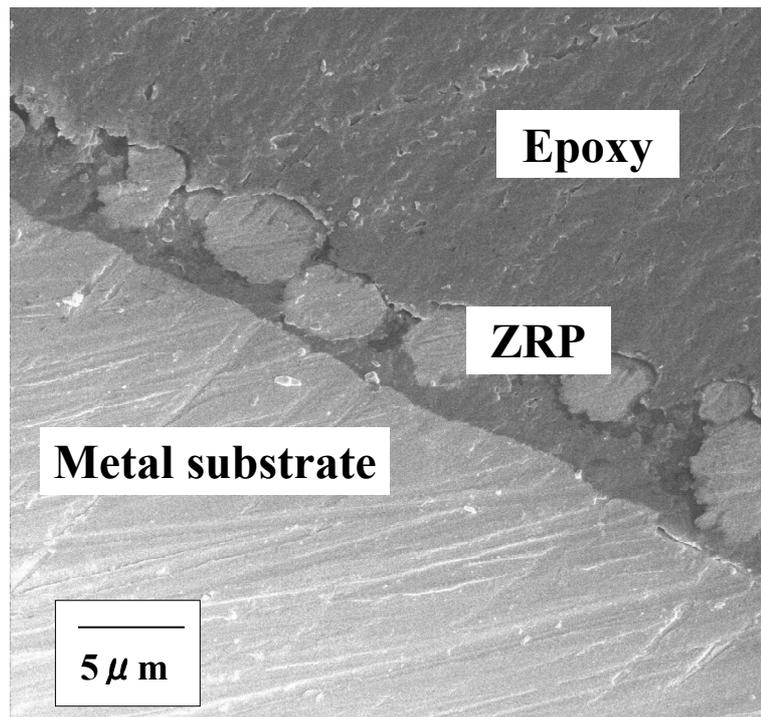
FIGURE 4.3: Cross-section of SEM micrograph of 1 layer coating and distribution of Zn, Fe and C at initial stage

be noted, the layer of the spray is constant and the distribution of zinc particles is homogeneous. Also from this observation, the boundary between metal substrate and ZRP is clear. EDX maps of cross sections for (a) was performed to determine the element distribution. A large amount of Zn was detected at the paint/steel interface and scattered on metal substrate and ZRP is clear.

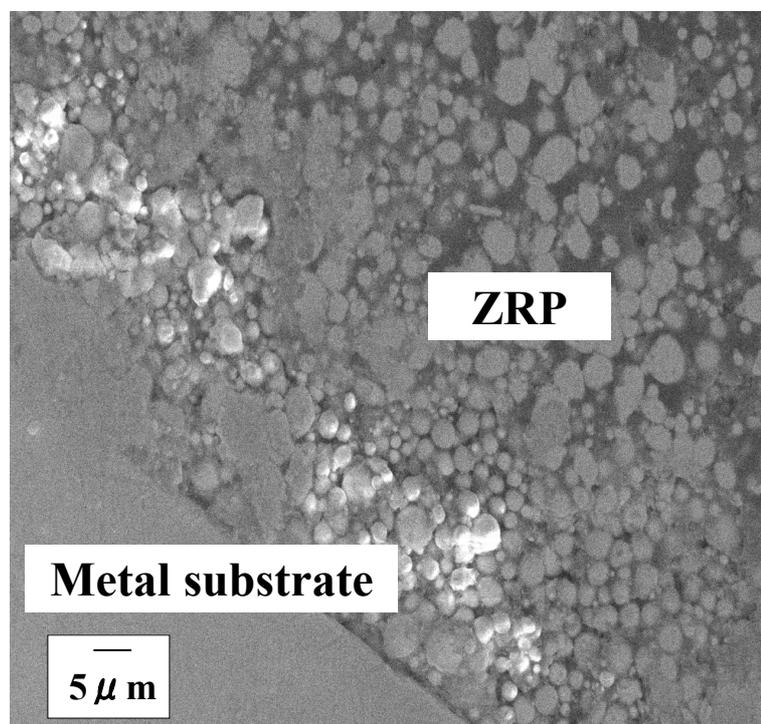
Figure 4.4 shows the cross-sectioned of 1 layer coating (a) and 5 layers coating (b) at initial stage. For (a), its thickness was about 10-18 μm . Obviously, the zinc layer was compact and homogeneous. In contrast, for (b) the zinc particles along the metal interface was compact but porous and loose at the paint surface.

4.4 Open Circuit Measurements

The evolution of the free corrosion potential E_{corr} allows to follow the electrochemical activity of the coatings system. It is generally assumed that the electrochemical processes transaction in such systems (ZRP) are the oxidation of zinc particles and the reduction of the dissolved oxygen.



(a) Cross-section of 1 layer coating specimen



(b) Cross-section of 5 layer coating specimen

FIGURE 4.4: Cross-section of 1 layer coating specimen (a) and 5 layers coating specimen (b)



According to Abreu *et al.* [17] the E_{corr} evolution is in close relationship with the variation of the ratio of active areas which is between zinc and metallic substrate (zinc/metal). In other words, the increase in the potential correlates to the decrease of the electroactive zinc area which means the decrease of the cathodic protection. This is commonly, Zinc rich paints can protect the steel cathodically when zinc particles in the coatings have electric connection to steel substrate. Figure 4.5 shows variation in corrosion potential with time for samples coated with 74wt% ZRP exposed in 0.5 M NaCl solution. The potential increased to about -0.64V and tend to maintain, which means that the steel was corroding approaching the end. Probably the zinc concentration was low that zinc particles were consumed and the steel started to corrode or we may say that there is no electrical contact and thus there is no protection of the substrate. According to visual observation after the test, particularly for sample coated with 1 and 3 layers of coating covered with white zinc corrosion products more than 5 layers coating sample. Thus, these results suggest that the numbers of coating do improve the anticorrosive performance.

On the other hand, there were large differences in the performances of 96 wt.% ZRP as shown in Figure 4.6. The potential of zinc in sodium chloride is approximately -1.05 V, while the steel substrate approximately -0.65 V. This shows that the zinc particles in the paint were galvanic connection to the steel substrate. The potential increased during the test period from -1.0 V in the beginning to -0.55 V in the end. This result exhibit that the zinc particles were consumed or that galvanic contact was lost with the time. It is interesting to note that the potential for 96 wt.% ZRP coated samples were close to that of zinc and exhibited hardly any differences in appearances. The potential of the sample increases when the amount of zinc particles in the coating layer with the steel decreases. The galvanic may be lost due to corrosion of the zinc particles, either by total depletion of the particles or formation of isolating corrosion products between particles and the steel substrate.

Figure 4.7 shows the polarization curve measurement result of ZRP coated specimens, pure iron and pure zinc, respectively. The presence of zinc powder in the coating , shift the corrosion potential of the steel into less noble potential and make it immune to corrosion compared to pure iron. Even the samples were coated with 1, 3 and 5 coatings, the corrosion potential shows almost the same behavior of pure zinc. As numbers of

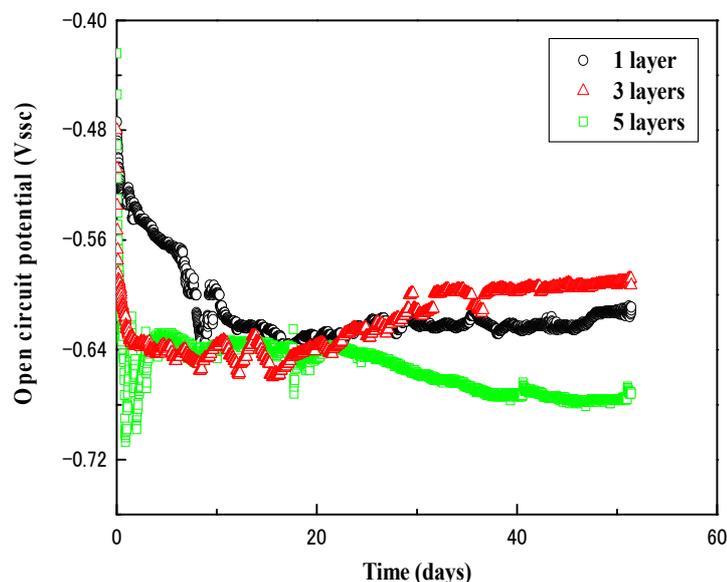


FIGURE 4.5: Variations in corrosion potential with time for samples coated with 74wt.% ZRP exposed in 0.5 M NaCl solution at ambient temperature.

coatings were increased, the anode current shifted to lower current density compared to one layer coating, which indicates that numbers of coatings have significant effect on anodic current.

Figure 4.8 shows the polarization curves of 74 wt.% ZRP coated samples in 0.5M NaCl solution. There is a cathodic oxidation peak at -0.85V which attributes to the zinc potential. It is found that polarization curves have the similar trends with 96 wt.% ZRP coated samples. They are characterized by corrosion potential shifted to less noble potential as numbers of coatings are increased. This also implied that zinc particles inside the coating and steel substrates are properly contact. On the other hand, the current density become lower as numbers of coating increased. This may be explained, as numbers of coating increased epoxy thickness also increased which formed a barrier coat. Therefore, the process of corrosion may be inhibited.

4.5 Current density inhibition model

Figure 4.9 illustrates schematics of the probable inhibition mechanism for ZRP coatings. Diagrams show the structures of 1, 3 and 5 layers of ZRP coatings, respectively. For

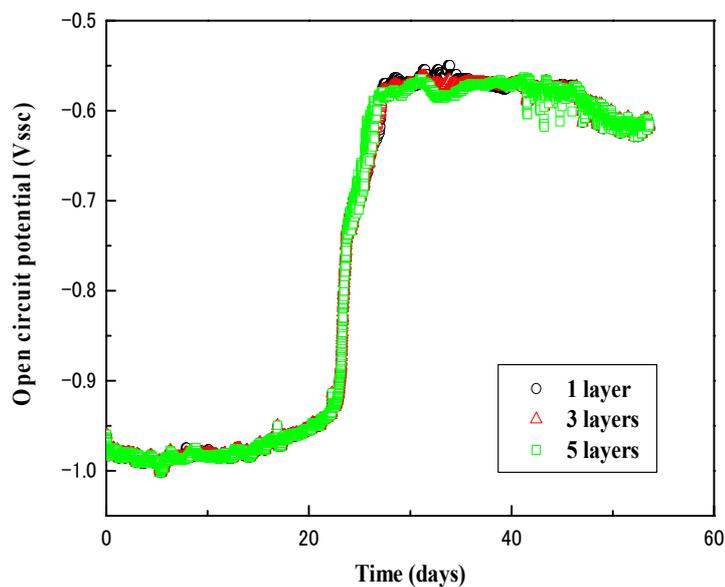


FIGURE 4.6: Variations in corrosion potential with time for samples coated with 96 wt.% ZRP exposed in 0.5 M NaCl solution at ambient temperature.

sample with 1 layer, the zinc particles are deposited homogeneously. As we apply the paint continuously without letting the first layers to be dry enough. Therefore, when we apply the second and the next layer, the tendency for the zinc particles to settle down and left the epoxy to the surface are high due to the atomic weight of zinc is higher than epoxy. The zinc particles will be beneath the top layer of epoxy. When the epoxy layer became thicker it will act as barrier, thus, the current density become lower too. As a whole, the protection performance of ZRP coatings may be though depend on the barrier effect of epoxy layers and the sacrificial effect of zinc. In reality, it may well rely on producing the maximum resistance properties of zinc layers as outlined previously. Commonly, epoxy layer with high thickness have lower porosity, but microcracks may occur due to the stronger tensile stress existed in thicker epoxy layers. However, this attributed to the improvement corrosion performance provided by epoxy layer.

4.6 Chapter Conclusion

Sample with high content of zinc and have more layers, show a better corrosion performance than that of a single or 1 layer of ZRP coatings. Results obtained from open

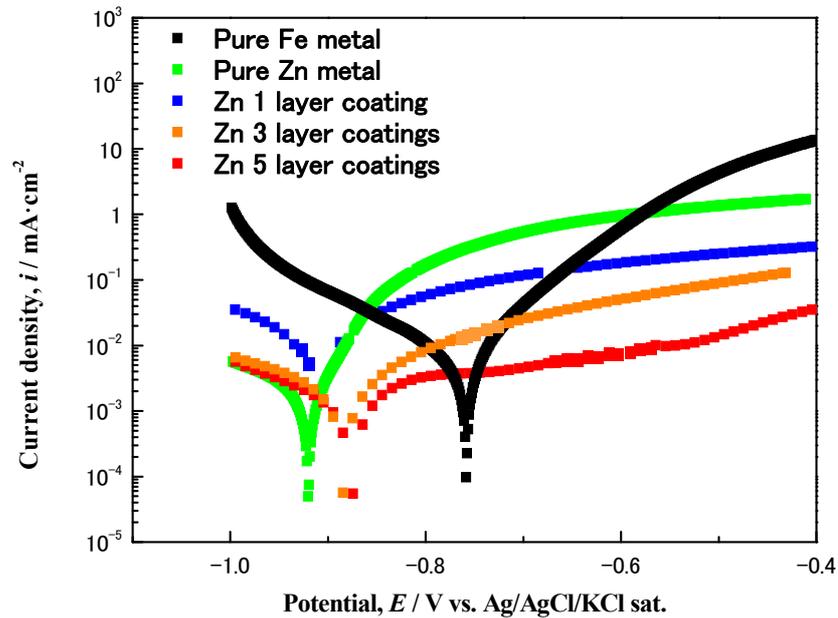


FIGURE 4.7: Polarization measurement result for pure iron, zinc and coated samples in 0.5M NaCl solution

circuit measurements and polarization measurements suggest that adequate galvanic protection of epoxy based zinc rich paints was achieved at 96 wt.% Zn on dry coatings. Remarkable galvanic protection performance was achieved when the Zn content in the commercial zinc rich coatings exceeds 80 wt.% [32]. Surprisingly coating containing 74 wt.% of zinc with 3 and 5 layers also exhibit good corrosion protection behavior which mainly comes from barrier protection mechanism coming mainly from the epoxy resin. However, for single layer coating of 74 wt.% Zn, does not offer good corrosion protection. Based on results from morphology characteristics of ZRP at initial stage, a probable current density inhibition model was proposed.

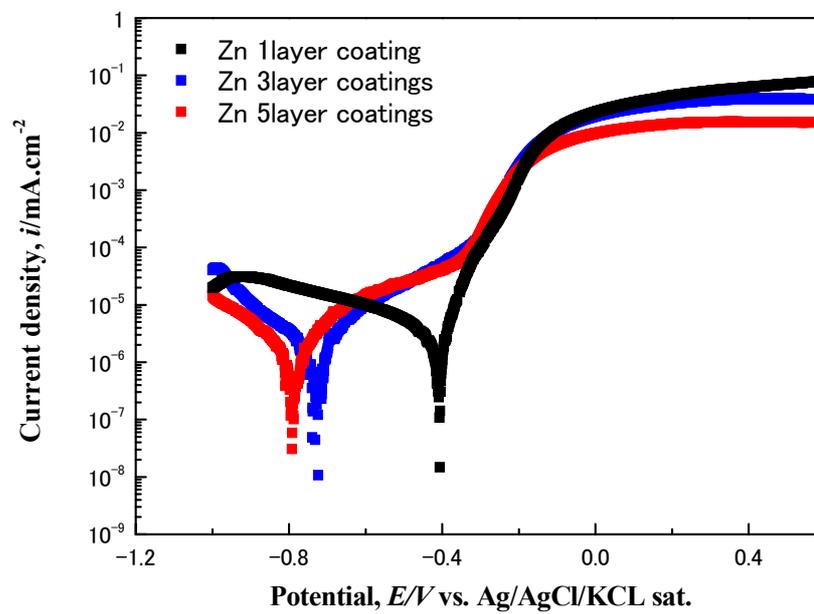


FIGURE 4.8: Polarization measurement result for coated samples with 74% ZRP in 0.5M NaCl solution

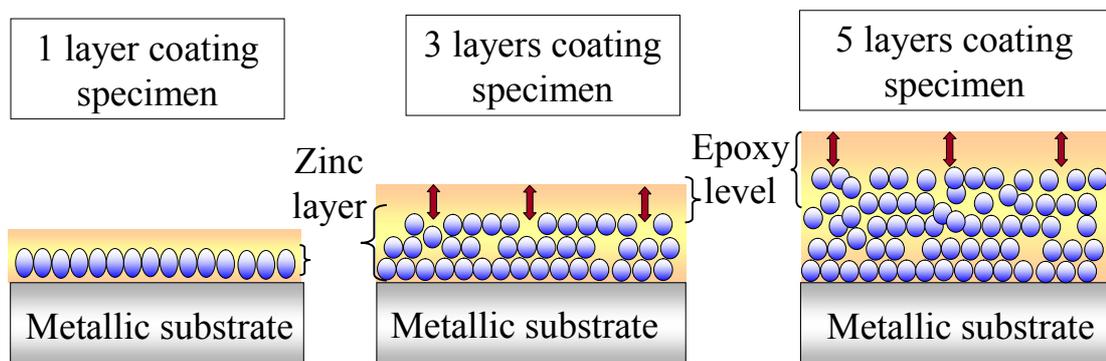


FIGURE 4.9: Suggested current density inhibition model

Chapter 5

Comparison of corrosion resistance in different concentration solution

5.1 Overview

Usage of metallic materials in process industries is inevitable. Corrosion has become a major problem especially in gas and oil industries. Corrosion in metal pipes, valves and other parts of constructions has caused so many losses to the industries. According to US Federal Highway Administration (FHWA) and National Association of Corrosion Engineers (NACE) on study of corrosion costs and preventive strategies in United States claimed that the total annual estimated direct cost of corrosion in US approximately around 276 billion US dollar equivalent to 3.1% nation gross domestic products (GDP) [46]. Therefore, the study of corrosion is relevance and important in order to eliminate this kind of loss. Exposure to humidity and salinity in the atmosphere will accelerate the corrosion of steel. Today, thousands of industrial manufacturers depend on paint or coating for long lasting strength, protection and improved productivity. Many coatings have been used to attain that purpose, some of them, however, show less satisfactorily than expected. Zinc is one of the most important components for commercial application in the corrosion protection and improved productivity. Zinc has been depicted to be more effective than other coating types. The protection of steel with epoxy based zinc rich paint is based on the general principle of cathodic protection by metallic zinc in contact with ferrous substrate. The positive effects of epoxy based zinc rich paint (ZRP) and on metal substrate towards corrosion resistance of paints have drawn much attention since late 1950s [1]. In the film of ZRP, the particles of pigments are close contact

with each other and with the substrate to be protected. Theoretically, the mechanism of inhibition is similar to a continuous layer of zinc applied by galvanization, however, with some differences since at the initial stage of the exposure the film is porous and acts mainly by cathodic protection [43]. During the earlier stages of its life time, zinc provides good sacrificial protection. At the later stages, the alkaline nature and low solubility of corrosion products of zinc provides additional barrier protection [5]. The main application area of ZRP is in the anti corrosion protection for industrial construction, for example, pipelines, bridges, petrochemical or power industries, also for marine applications. Several studies have been carried out in order to elucidate the influence of the zinc content on the electrochemical properties of these paints. Paint with zinc content higher than 60 wt.% by weight is recommended to achieve good protection [5]. Ji Hoon Park *et al.* investigating the effect of zinc rich organic coating by incorporating surface modified zinc particle [5]. Under immersion conditions, the time of cathodic protection depends on the zinc content in the coating film, and they verified coatings with 60 volume percent of zinc powder showed good corrosion resistance mainly due to the cathodic protection. A great deal of effort has also been dedicated to reviewing the studies related to contamination at the metal/paint interface before 1999. The influence of chlorides, sulfates and nitrates on the steel/paint surface in terms of the under film corrosion was also investigated [20]. EIS is widely used to evaluate the efficiency of organic coatings and the mechanism of corrosion resistance [47]. In Bode modulus diagram of EIS, a high performance barrier coating gives a straight curve with unit negative slope (pure capacitive action). Modulus of impedance digresses from its straight line path, when solutions penetrate through the coating followed by corrosion initiation. Much literature suggests that when the resistance of the coating (low frequency impedance) is $< 10^7 \Omega \text{ cm}^2$ then such coatings are not protective [47]. Such judgment of EIS data can mislead a paint formulator who does not have good knowledge in electrochemistry. An appropriate example in this case is a ZRP (>90% zinc on dry coating) having superior corrosion resistance properties exhibits low frequency. The influence of the zinc content on the paint behavior has been studied, but little attention has been paid to steel/-paint corrosion product, which simulates practical application conditions. This paper reports an evaluation of the corrosion behaviors/performances of zinc rich paint (ZRP) applied on steel substrates under NaCl solution as artificial seashore environment by using polarization measurements and Electrochemical Impedance Spectroscopy (EIS).

5.2 Experimental

5.2.1 Materials and experimental set-up

All chemicals were reagent grade and used as received without purification. Distilled water was employed in order to prepare the solutions. The electrochemical measurements were carried out by using the conventional three electrode setup. The cell was connected to 5000 Autolab potentiostat. Test specimens were pure iron 99.5% (10mm×20mm × 0.5mm), abraded with #600, #800 and #1000 emery papers. In order to ensure the absence of dust, oil and foreign matters, specimens were cleansed with ethanol using the ultrasonic bath. Commercial zinc 74% and 96% (Atom Paint Co. Ltd., Japan) content epoxy-ZRP was applied onto specimen by air spraying following the manufacturers instructions. The specimens were coated with 1, 3 and 5 layers respectively. After the coatings had been applied, the specimens were allowed to cure at ambient temperature.

5.2.2 Characterization of ZRP coating

To avoid the sample from corrosive media, except for the test surface, the sample was protected with epoxy resin. All corrosion test were carried out at room temperature and repeated two or three times, to ensure the reliability of the data and checking reproducibility. Three electrodes system was used, in which a silver-silver chloride electrode Ag/AgCl/KCl (sat.), a platinum electrode and coated samples were used as a reference, counter and working electrodes, respectively. Polarization curve of ZRP coated steel and non-coated steel were also measured. Prior to the measurement, the specimens were cathodically polarized at -1.0V for 15 min to remove the pre-existing oxide film. The potentiodynamic polarization tests were conducted at scanning rate of 1.0 mV/s from -1.0V to 1.0V. From the polarization curves, we obtained corrosion potential and corrosion current density. The impedance measurements were carried out with FRA5022 Model at frequencies 100 KHz to 10 mHz, and the applied signal amplitude was 1mV. We applied three electrodes system, consists of the prepared coated sample, as the working electrode, platinum rode as the counter and silver-silver chloride Ag/AgCl/KCl as the reference. The measurement were carried out using a potentiostat/galvanostat coupled to frequency analyser (FRA-5022). Electrochemical Impedance Spectroscopy (EIS) data were recorded after immersing in 0.5M NaCl solution for 30min, and the impedance data obtained between 100kHz and 100mHz at 5mV as the applied sinusoidal perturbation. Imaging and elemental analyses of the coatings and corrosion products were performed using (JEOL, JSM-7400F) Scanning Electron Microscope (SEM).

TABLE 5.1: Average of coating thickness after spraying process

Number of coating	Coating thickness (μm)
1	30-35
3	40-45
5	65-70

5.3 Results and Discussion

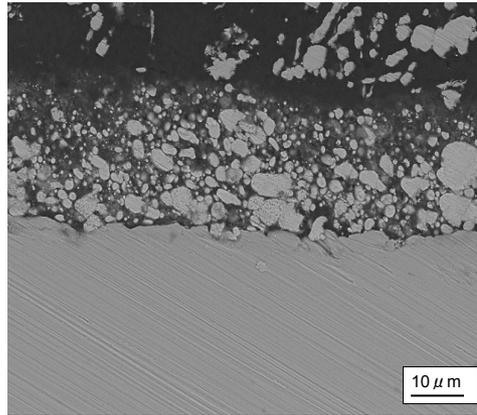
In previous chapter, Figure 4.4 shows SEM images that show that the Zn coated homogeneously the surface of the metallic substrate after the spraying process. The average diameter of the zinc particles was about 3-5 μm . Average thickness for 1, 3 and 5 layer coating is shown in Table 5.3

The cross-section micrographs show the zinc rich paints based on epoxy with coating layer 1, 3 and 5 respectively on metal substrate. From Figures 5.1 and 5.2 it seen that zinc particles are closely packed on the metallic substrate surface and porous toward the coating surface.

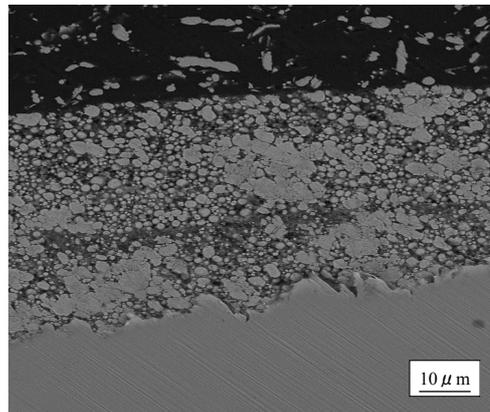
5.3.1 Effect of concentration in NaCl solution

The polarization measurement was carried out for coated metallic substrates in 0.5 and 1.0 M NaCl solution at scan rate of 1.0 mVs^{-1} at room temperature. It is obvious from Figure 5.3 show that the corrosion potential for all coated samples is more positive than that marked in the case of 96% in 0.5 M NaCl solution. It is observed that, the corrosion current density, I_{corr} , values of ZRP coating

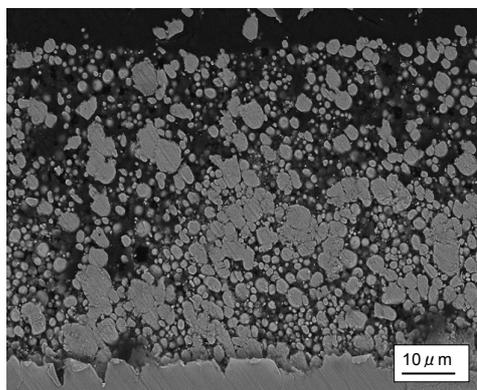
The polarization measurement was carried out for coated metallic substrate in 0.5 M NaCl solution at a scan rate of 1.0 mVs^{-1} at 25. It is obvious from Figure 5.3 show that the corrosion potential for all coated samples is more positive than that marked in the case of 96%-5. It is observed that, the corrosion current density, I_{corr} , values of ZRP coatings gradually decrease as the coating thickness increase up to 5 layers and the 96%ZRP-5 has the lowest value of I_{corr} (0.0218 $\mu\text{A}/\text{cm}^2$). Also the most negative value of E_{corr} (-742mV versus Ag/AgCl/KCl) signifies that 96%ZRP-5 sample act as sacrificial coating and has the lowest tendency to corrode. However, in contrast samples coated with 74%-ZRP exhibit less definite shift in E_{corr} (-463 to -502mV versus Ag/AgCl/KCl) and I_{corr} (6.13 $\mu\text{A}/\text{cm}^2$ to 6.72 $\mu\text{A}/\text{cm}^2$) which implied that samples coated with 74%ZRP, enhance the barrier effect and protect the samples from corroding.



(a) 74%-1

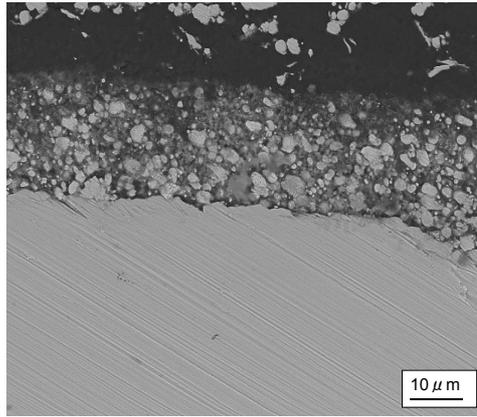


(b) 74%-3

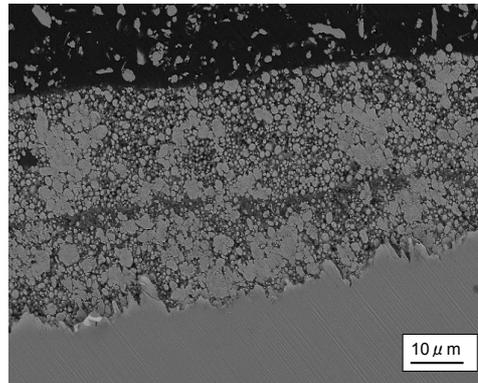


(c) 74%-5

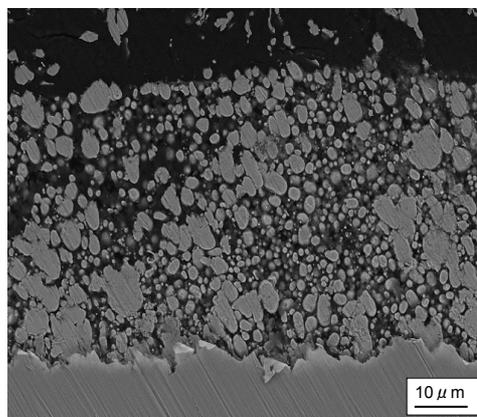
FIGURE 5.1: SEM microstructure of coated samples for (a) 74%-1, (b) 74%-3, (c) 74%-5



(a) 96%-1



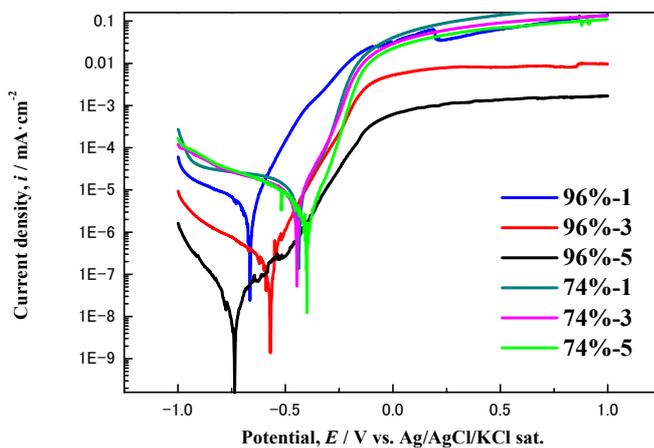
(b) 96%-3



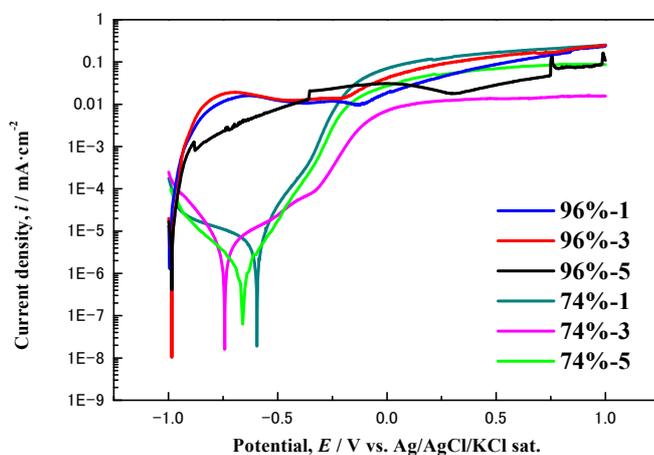
(c) 96%-5

FIGURE 5.2: SEM microstructure of coated samples for (a) 96%-1, (b) 96%-3, (c) 96%-5

While for samples measured in 1.0M NaCl solution, samples coated with 96% Using Stern-Geary equation 5.2 [25, 48, 49] the polarization resistance (R_p) was determined from the Tafel plots:

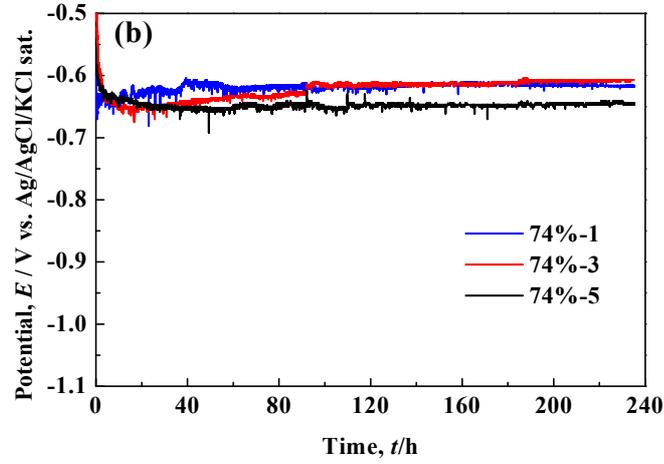


(a) 0.5 M NaCl solution



(b) 1.0 M NaCl solution

FIGURE 5.3: The polarization test was carried out for ZRP coated samples in (a) 0.5 M and (b) 1.0 M NaCl solution



(a) 74%-ZRP

FIGURE 5.4: Evolution of the free corrosion E_{corr} with immersion time for 74%-ZRP coated samples

$$R_p = \frac{\beta_a \beta_c}{2.3031 I_{corr} (\beta_a + \beta_c)} \quad (5.1)$$

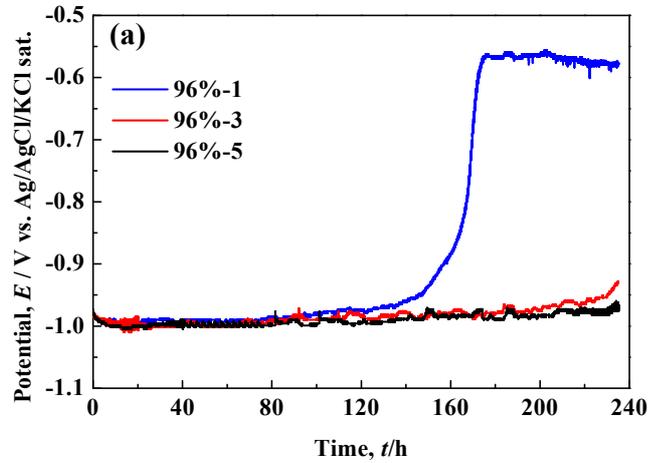
Where I_{corr} , β_a and β_c are the corrosion density, anodic Tafel slope and cathodic Tafel slope respectively. We also calculate the corrosion rate (V_{corr} in millimetre per year) by using the following equation 5.2 [25, 49]. Where I_{corr} , M.W, n and d are corrosion current density ($\mu\text{A}/\text{cm}^2$), molar mass (g/mole), charge number and density (g/cm^3) of tested metal, respectively.

$$V_{corr} = \frac{0.0032 \times I_{corr} \times (M.W)}{n \times d} \quad (5.2)$$

The samples coated with 96%-5 have the most negative E_{corr} value with respect to the zinc contents. For instance, the 74%ZRP-5 shows a corrosion potential of -0.45V versus Ag/AgCl/KCl which indicates that the 74%ZRP-5 is noble toward the electrochemical corrosion with good barrier effect instead of galvanic protection compared to the 96%-ZRP coated sample with E_{corr} value of -0.76V versus Ag/AgC/KCl. The electrochemical parameters from Tafel plots (anodic Tafel slope (β_a), cathodic Tafel slope (β_b), I_{corr} , E_{corr} , R_p , V_{corr}) are summarized in Table 5.2.

TABLE 5.2: Electrochemical parameters obtained in different NaCl solutions of the coated samples

Sample	E_{corr} (mV)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	β_c (V/dec)	β_a (V/dec)	R_p ($\text{k}\Omega \text{ cm}^2$)	V_{corr} (mm/year)
0.5M-74%-1	-460	6.72	0.11	0.722	6.16	0.075
0.5M-74%-3	-500	6.13	0.069	0.126	3.16	0.068
0.5M-74%-5	-440	2.75	0.117	0.224	12.1	0.031
0.5M-96%-1	-690	3.82	0.123	0.530	11.3	0.042
0.5M-96%-3	-610	0.265	0.103	0.503	14.0	0.0029
0.5M-96%-5	-740	0.0218	0.124	0.162	139	0.00024
1.0M-74%-1	-610	1.61	0.08	0.15	1.41	0.015
1.0M-74%-3	-750	5.21	0.24	0.25	10.1	0.058
1.0M-74%-5	-670	1.46	0.23	0.11	22.0	0.016
1.0M-96%-5	-1020	5.74	0.06	0.12	2.07	0.064



(b) 96%-ZRP

FIGURE 5.5: Evolution of the free corrosion E_{corr} with immersion time for 96%-ZRP coated samples

In order to evaluate the efficiency of the zinc rich paint coating containing different contents zinc, three different kinds of coated specimen were prepared; the coating with 74 wt.% and 96 wt.%. The electrolytes could not readily immerse through the organic coating to the steel substrate presumably because the coating had much fewer pores than the coating layer containing zinc particles. When zinc particles were blended into the coating layer, a substantial number of pores formed that could stimulate the solution uptake could form due to the bad bonding between the organic matrix and metallic materials. The cathodic protection duration of the substrate can be efficiently determined by measuring the corrosion protection. Corrosion potential for zinc in sodium chloride solution is approximately -1.050V while steel has the potential of approximately -0.650V [50]. According to thermodynamics, cathodic protection of steel is obtained when potential is lower than -0.850V. Measured potentials are mixed potentials between the metal substrate and the active zinc pigments. If only few zinc pigments are active, the anode area will be small, and the potential will be close of that steel. On the contrary, if the area of active zinc particles is large, the potential will be close to that of zinc. The open circuit potentials, for example, E_{corr} for the coated samples, are plotted vs. the immersion time in days (Figure 5.4 and Figure 5.5). For samples coated with 74wt% ZRP the initial corrosion potential are close to that of the metal substrate in the early days of immersion. Corrosion products are formed on the surface, but the protective resistance decreases with time hence the corrosion potential increases. E_{corr} increases

rapidly to positive values indicating the inefficiency in resisting corrosion. However, the plot shows that for higher thickness of zinc coatings, the corrosion potential was slightly negative, thus large anodic areas are accessible to the solution leading to small current density being drawn from active zinc. On the other hand, for samples coated with 96 wt.% ZRP, the corrosion potentials of coatings are initially close to that zinc metal what indicates that the coatings provide a cathodic protection to the metal substrate in the early days of immersion. In contrast to samples coated with 74wt%, the thickness of 96wt% coating did not show any difference. The packing density of 96 wt.% ZRP was better compared to 74 wt.% which implies that the compactness of zinc particle was enhancing the corrosion protection.

5.3.2 EIS measurement

Based on the amount of zinc and binder type, Nquist diagrams of solvent generate ZRPs, exhibiting one, two [8] or in some cases three semi-circle [30]. These Nquist plots are accordingly interpreted using different equivalent circuit models. In this work, Nquist plots of the coating show different behaviours reflecting different zinc concentrations in the coatings. Detailed physical interpretation of Nquist plots was not the main objective of this study. Nonetheless, an attempt was made to fit the impedance data with suitable equivalent circuit models. When the zinc content in the coating below 60 wt.%, classical models like Randles or Randles with additional double layer capacitor and charge transfer resistor connected parallel could successfully fit the curves. However, none of the existing models (both classical and transmission line [8, 30]) could fit the data with meaningful values of circuit parameters when the zinc content is above 70wt.%. Therefore, equivalent circuit modelling will not be discussed here. Nquist plots for ZRP containing 74 wt.% and 96 wt.% zinc are shown in Figure 5.6. When the zinc content is 74%, coatings show single loop indicating purely capacitive behavior of the coating. These coatings provide a barrier type of protection to the metal substrate. The diameter of the loop decreases as the coating thickness increases (Figure 5.6 (a)). When the zinc content in the ZRP is 96%, two or three overlapping loops appear, and their total diameter is much smaller than coatings embedded with 74% zinc (Figure 5.6 (b)). This illustrates that galvanic protection mechanism is attained when zinc content in the coating is 96%, which have been confirmed, earlier by OCP measurements. Figure 5.6 (b) displayed that ZRPs offer galvanic protection to the metal substrate when zinc content is 96%, whereas they offer efficient barrier protection when zinc content is 74%. Evolution of Bode plot frequency profiles for 74 wt.% and 96 wt.% ZRP as a function of coating thickness are shown in Figure 5.7. At the early stages, Bode plot of 74% ZRP exhibits curved like lines with unit negative slope. Minor deviations from the plot

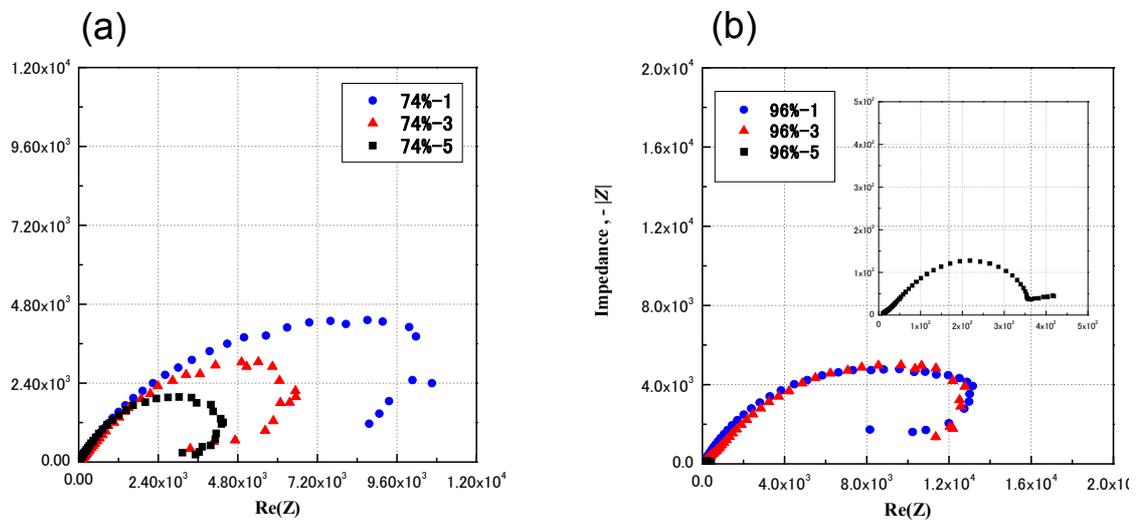


FIGURE 5.6: Nyquist diagrams for coated samples of (a) 74% and (b) 96% in 0.5 M NaCl solution

lines path are due to solution penetration through the coating [51, 52]. Low frequency impedance of 74% ZRP with 1 and 5 layers coating was in the order of $10^5 \Omega \text{ cm}^2$, however, for a sample with 3 layers coating the impedance slightly drops to $10^4 \Omega \text{ cm}^2$, in 0.5 M NaCl solution. This indicates that increase in coating thickness does enhance the barrier protection efficiency. This can be distinguished from 74% ZRP, when the zinc content is 96% (Figure 5.6 (b)). The impedance for 96% ZRP is in the order of $10^2 \Omega \text{ cm}^2$ of immersion in 0.5 M NaCl solution. It is clear from Figure 5.5 (b) that samples with more coatings offer more barrier protection, whereas, in the later stages, corrosion protection may come through galvanic protection mechanism. Therefore, in case of 74% ZRP, EIS alone could not indicate whether galvanic protection is offered or not. In the other hand, 96% ZRP shows very low values of high frequency impedance ($10^2 \Omega \text{ cm}^2$) in 0.5 M NaCl solution. Such low values of impedance are generally observed for zinc coating or good electronic conductors [53]. Thus, it is fair to conclude that 96 wt.% ZRP could provide galvanic protection to the metal substrate.

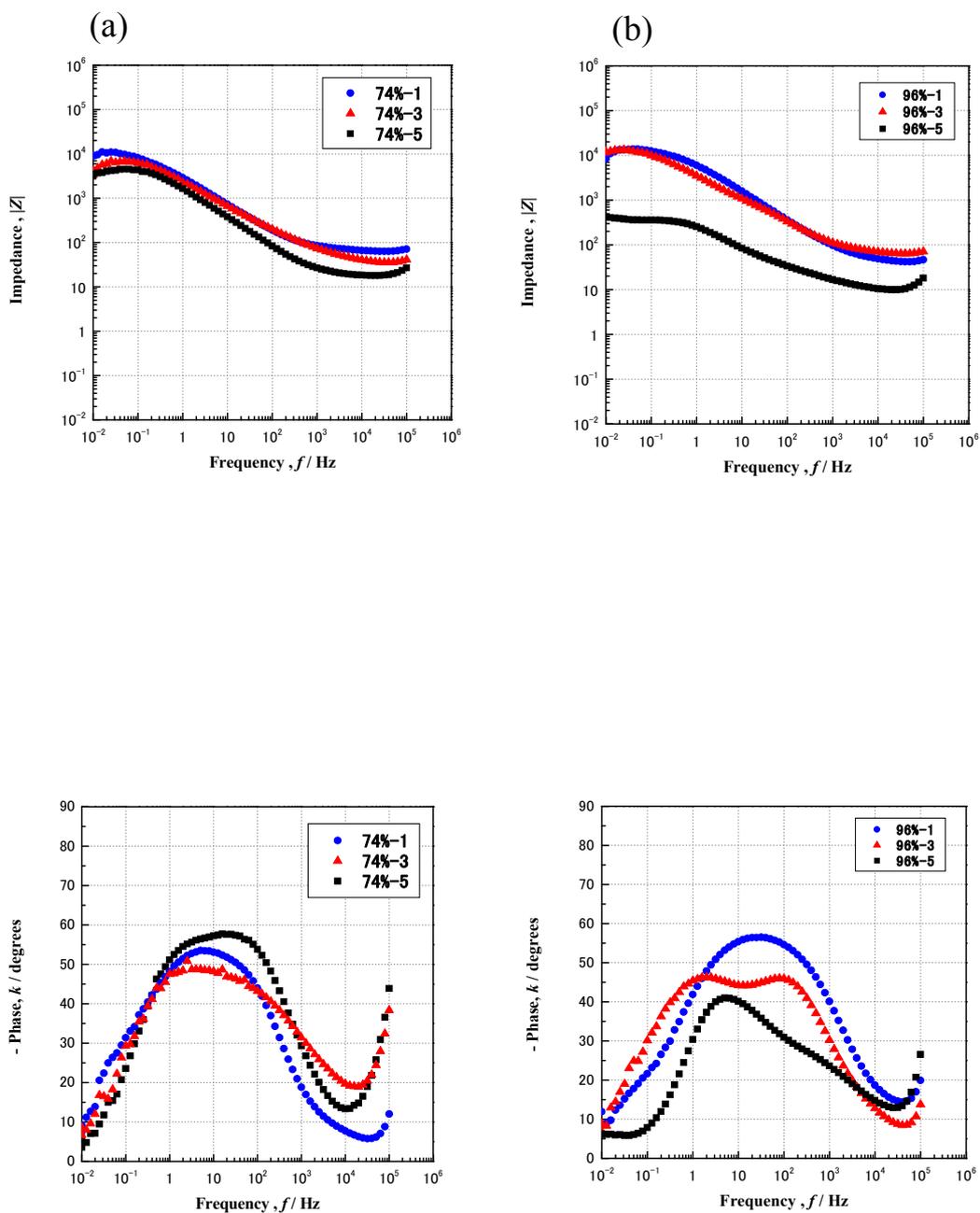


FIGURE 5.7: Bode plot for (a) 74% and (b) 96% as a function of different coating thickness

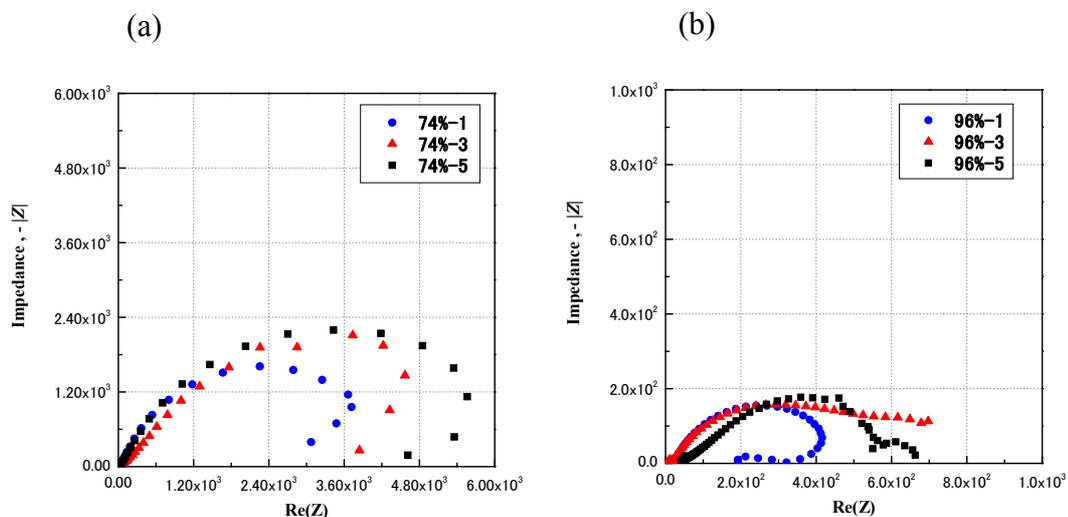


FIGURE 5.8: Nyquist diagrams for coated samples of (a) 74% and (b) 96% in 1.0 M NaCl solution

5.4 Chapter Conclusions

OCP studies indicate that penetration limit for providing sufficient barrier protection of epoxy zinc rich paints was attained at 74 wt.% zinc on the coating film. However, excellent galvanic protection efficiency was achieved with coating of 96 wt.% zinc regardless of the coating thickness. Interestingly coating containing 74 wt.% zinc does not exhibit galvanic protection; however, do shows good barrier protection performance mainly from the epoxy resin. The barrier and galvanic type of protection could be distinguished using OCP by monitoring the corrosion potential during the immersion in NaCl solution. Data obtained from EIS measurements demonstrate that ZRP coating with low coating thickness and low content of zinc than the corresponding ZRP coating deteriorate relatively faster in NaCl solution than those coatings with high content of zinc particle. From this study, we found that galvanic protection efficiency only depends on quantity of zinc particles in paint formulation but not the thickness of the coatings. However, the film thickness of the paint seems to be important for the performance of the coating system in paint with low concentration in paint formula. The sample with thickest coating (74 wt.%) performed best in the measurement and there seemed to be correlation between

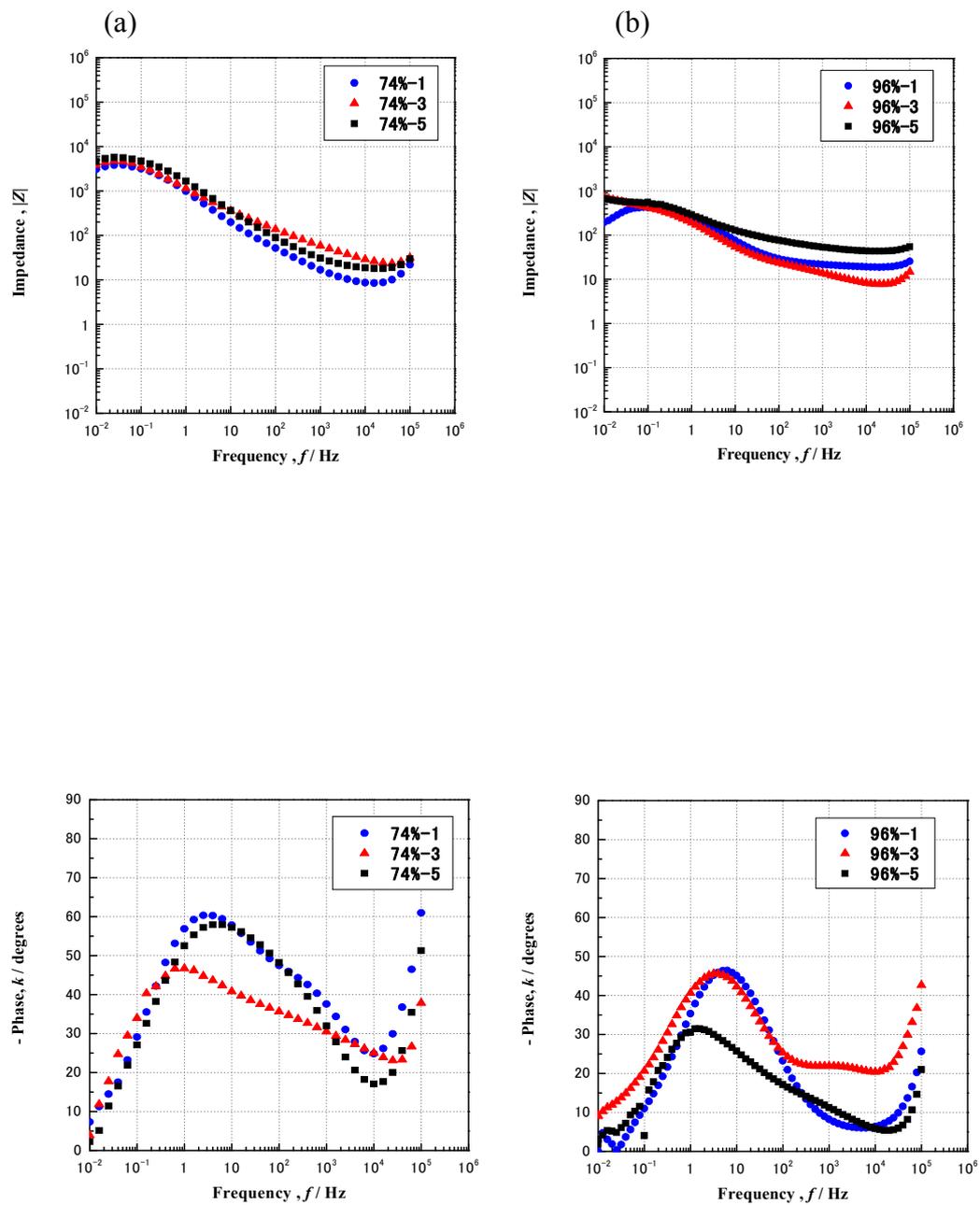


FIGURE 5.9: Bode plot for (a) 74% and (b) 96% as a function of different coating thickness

film thickness of the paint with low concentration zinc and electrochemical properties. The results suggest that there is a connection between electrochemical properties ZRP and the corrosion resistance of the coating system. This implies that the electrochemical properties of ZRP to some extent predict their performance when exposed in corrosive atmosphere.

Chapter 6

EIS characterisation of ZRP coating

6.1 Background

As early as 1940s zinc rich paints (ZRP) has been demonstrated as excellent anti-corrosive particles for protecting steel from corrosion. Zinc particles regardless the shape (spherical or lamellar shape or combination of both shape) is dispersed in an inorganic (usually orthosilicates) or organic binder (usually epoxies) [35]. To achieve galvanic effect, these particles must be conductive between themselves and the metallic substrate in order to establish electrical conduction with the coating. In that situation, galvanic coupling is constructed between zinc and the metallic substrate which is more noble as compared to the zinc. Therefore, zinc will preferentially dissolve and act as sacrificial particles and conceding a cathodic protection of the metallic substrate. Many studies [11, 54, 55, 56] have been conducted, relating the protection mechanisms and degradation processes of such coatings. Morcillo *et al.* [5] mentioned, a network of capillaries or ionic conduction paths between anodic (zinc particles) and cathodic area (metallic substrate) is a second basic condition for the cathodic protection mechanism in ZRPs. Finally, zinc corrosion products form and fill the pores, then, the coating will act as an inhibition or pore sealing process provides a subsequent longer period of protection (passive protection). As reported by Abreu *et al.* [4], a high zinc concentration (commonly > 60 vol. %, i.e. 90 wt.%) is required to ensure a good electrical connection. This chapter is focused on the cathodic protection by investigating the electrochemical behaviour of commercial ZRPs (74 wt.% and 96 wt.%) using EIS. The research is based on on systematic scanning electron microscope (SEM) observation of cross-section of different

ZRP coatings. The main objective is to propose a model of EIS results accounting for the zinc particles distribution and mechanisms of water entrance within coating.

6.2 Experimental

The metallic substrate was pure iron with purity of 99.5% (Nilaco Corporation, Japan). Before spraying process, metallic substrate were abraded with emery paper #600, #800, #1000, respectively. Then, degreased with ethanol and dried at ambient temperature. Copper wire was attached in order to allow electrochemical measurements and embedded with epoxies resin except for test surface area with dimension of (2cm×1cm) Figure 6.1. The coatings were sprayed according to the manufacture's direction with coating thickness of 1, 3 and 5 layers, respectively. Coated samples were exposed to the electrolyte 0.5 M and 1.0 M of NaCl solution at room temperature. Polarization measurements and impedance measurements were performed using FRA 5022 (NF Corporation, Japan). EIS data were obtained using a classical three electrode cell, with Ag/Ag/KCl (saturated) as reference electrode and platinum as counter electrode. EIS spectra were collected at room temperature in the frequency range between 100kHz to 10mHz by applying 5mV perturbation signal. Surface of different samples were observed by SEM (JEOL JSM-7400F) at 20kV.

6.3 Results and Discussion

6.3.1 SEM analysis

The SEM study revealed that zinc coatings covered homogeneously the surface of the steel right after the spraying process. The average diameter of the zinc particle was about 3-5 μ m. In order to get a better sight of the corroded surface appearance of all specimens after 7 days immersion testing were conducted. Figure 6.2 (a) and (c) showed the SEM surface morphologies of coated samples of 74 wt.% and 96 wt.% before the immersion test. As can be seen in Figure 6.2 (b), the surface of 74 wt.% collapsed severely and showed needles-like structure constituted by micro-spherical grains. While, Figure 6.2 (d) presented the surface appearances of 96 wt.%, where the original shape of zinc still can be recognized which implied the corrosion rate is less compared to 74 wt.%.

6.3.2 Corrosion potential with immersion time

Figure 6.3 presents the evolution of the corrosion potential during the immersion of the coated ZRP. After 50 days of immersion some small spot of red rust can be noticed on the coating surface, indicating that the iron corrosion process started some days before. If the above mentioned thermodynamic criterion is applied, the cathodic protection effect fade after 30 days of immersion. According to the data in Figure 6.3 three main periods can be categorized in the lifetime of the ZRP [4]:

1. Period 1. The corrosion potential shifts to more negative values, reaching the zinc magnitude in this medium.
2. Period 2. The corrosion potential increases to approximately $-0.9V$ vs. $Ag/AgCl/KCl$ (sat.) where a short stabilization is reached. This stabilisation is called the "transition" period.

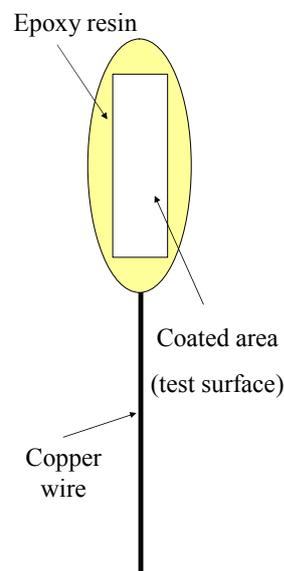


FIGURE 6.1: A schematic figure of coated sample

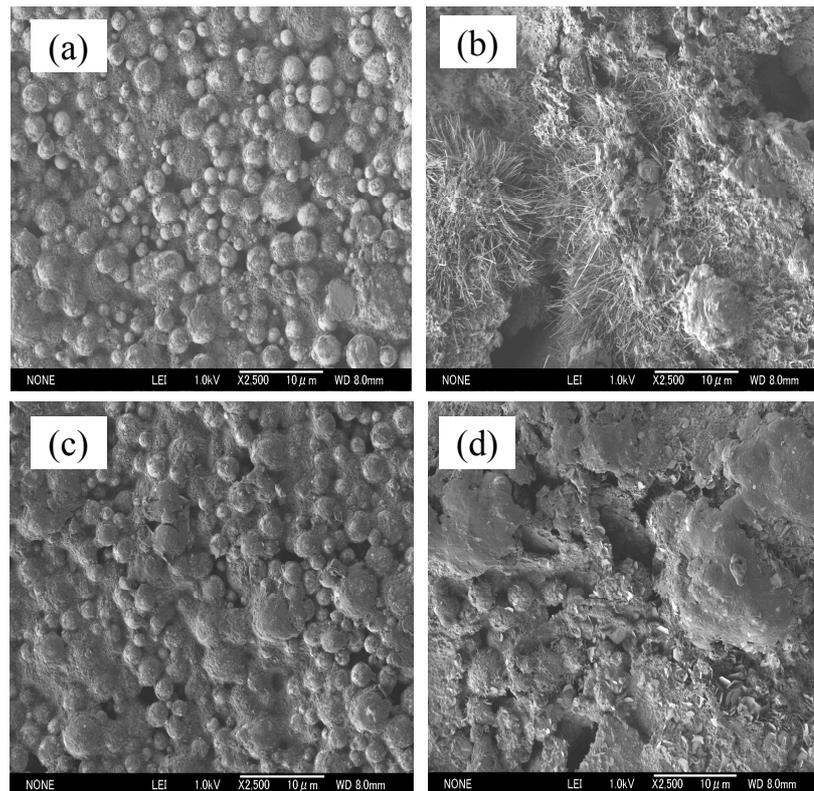


FIGURE 6.2: SEM micrograph of zinc coating samples before and after immersion in 0.5 M NaCl solution for 7 days (a) 74%-before test (b) 74%-after test (c) 96%- before test (d) 96%-after test

3. Period 3. After the transition period, the corrosion potential continues to rise reaching the potential -0.65V over which cathodic protection is no longer efficient. After some period, the potential starts to fluctuate and small iron rust are detected on the coating surface.

The evolution of the corrosion potential at the beginning of the immersion of the ZRP samples into corrosive agent, can be explained by the variation of zinc to steel area ratio. The zinc oxide covering the zinc particles reacts with NaCl solution, leading to a superior electrical connection established between the zinc particles themselves and with the metallic substrate. As the thickness of the zinc oxide is different for the different particles and the polymer binder them in different ways, the activation of the zinc particles takes some time to complete. Therefore, the zinc to steel increases continuously during this period: Period 1.

Period 2 and 3 correspond to a decrease of zinc to steel area ratio due to zinc corrosion. It is also possible that corrosion products themselves change their structure slowly and

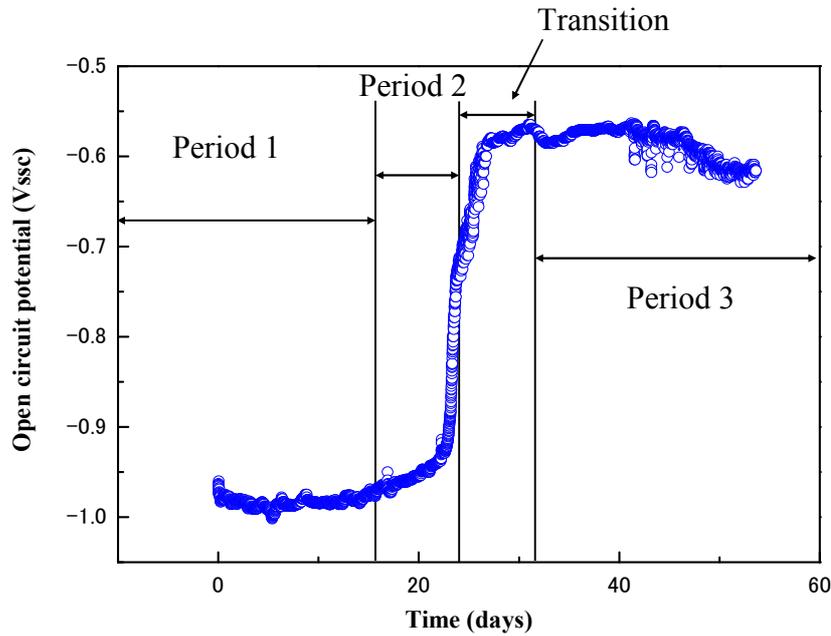


FIGURE 6.3: Evolution with immersion time of the corrosion potential of the ZRP coating system

come to protect the zinc particles as reported by Philips during the corrosion of galvanic steel covered with a varnish layer [57]. These phenomena result in the increase of the corrosion potential. The number of zinc particles in contact with each other changes consequently with evolution of time. When the concentration of zinc particles relatively high, the potential fluctuation thus generated is small since a large surface area is involved in the system. The corrosion of zinc particles results in a decrease of both contact number and diffusion surface of the metallic substrate. This phenomena show therefore to a smooth change towards a more positive (anodic) value (Period 2). When the number of particle to particle contacts decreases significantly, the change of this number generates considerable potential fluctuations (end of Period 3) since the diffusion surface area of zinc particles is small.

A standard used experientially for ZRP to protect metallic substrate is to maintain corrosion potential more negative than -0.65V [58]. Above this potential, ZRP simply behave as barrier layer. Figure 6.3 shows the evolution of the corrosion of samples coated with 96 wt.% ZRP immersed in 0.5 M NaCl solution for 50 days. From this result, three periods should be noticed as been described in the literature [4]. In this work, red rust spots were observed after immersion of 26 days. It can be seen from the corrosion

potential - time curves that cathodic protection was no longer effective after that time. Compared with the paints with more coatings i.e. 5 layers, the corrosion potential of 74 wt.% fluctuated at values negative to -0.72V in the initial 2 days of immersion, then were maintained around -0.71V, indicating cathodic protection ability during the immersion period of 6 days (as been discussed in Chapter 5). As reported by Shi *et al.* [1], the period of cathodic protection for ZRP containing 60 wt.% zinc particles can be up to 20 days. In our study, the period was only 6 days, which was much shorter as compared to their results. We need to remind here, that the coating thickness was only 55 μm , however, the coating thickness reported by Shi *et al.* was approximately double the values.

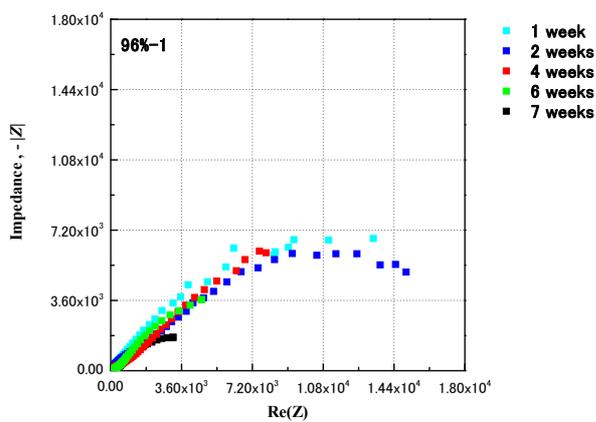
1. Prior to immersion, the coating behaves as a dielectric which suggests a poor electrical contact between zinc particles. This contact lean on the nature of the zinc corrosion products.
2. As a galvanic system, the anodic and cathodic reactions are partially separated.
3. As Figure 6.3 the cathodic reaction is controlled by a diffusion process.

6.3.3 EIS analysis during immersion in corrosive agent

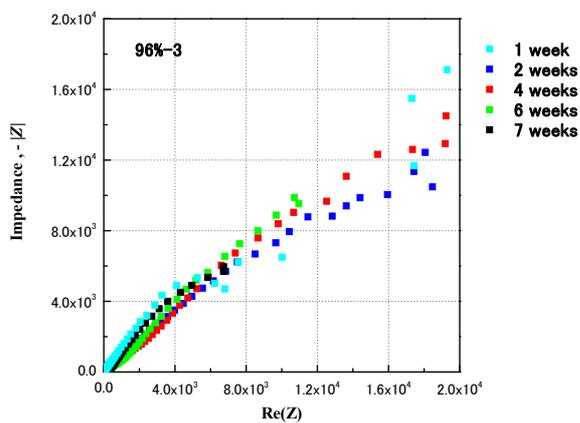
EIS spectra obtained at different immersion time are presented in Figure 6.4 for coatings 96%-1, 96%-3 and 96%-5, respectively. Typical EIS spectra, obtained with sample 96%-1 are shown in Figure 6.4 (a) with impedance values around 10^3 - $10^4 \Omega \text{ cm}^2$. In the Nyquist diagram, single semi-circle was clearly defined at beginning of the exposure. After 2 week immersion, the two half-circles presented lower values impedance which can be explained by the activation of the zinc particles and the progression of the solution into the coating. For longer immersion time, the semi-circle shrank with the increase of corrosion degree. For 96%-5 6.4 (c), the diameter of the semi-circle is much larger than those 96%-1 and 96%-3, indicating better protective ability of the coating. The diameter of the semi-circles in the Nquist plots for all paints decreased rapidly from 4 weeks to 7 weeks, which implied that the rapid penetration of solution into ZRP with high zinc content. The decrease of the diameter of the semi-circles in the early stage of immersion is in agreement with the rapid decrease of corrosion potential as shown in Figure 6.4

A better interpretation of the electrochemical properties of the studied ZRP can be obtained if some basic results concerning these systems are taken into consideration [4]:

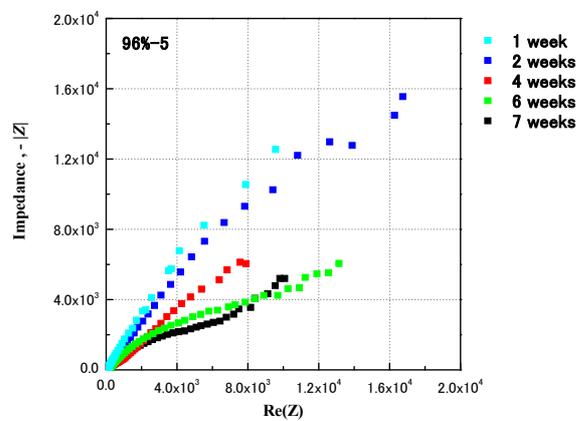
1. The coating has a porous nature which suggests the application of some kind of transmission line model.



(a) 96%-1



(b) 96%-3



(c) 96%-5

FIGURE 6.4: EIS data resulted from specimens in various immersion time in 0.5 M NaCl solution

2. Prior to immersion, the coating behaves as a dielectric which suggests a poor electrical contact between zinc particles. This contact lean on the nature of the zinc corrosion products.
3. As a galvanic system, the anodic and cathodic reactions are partially separated.
4. As Figure 6.3 the cathodic reaction is controlled by a diffusion process.

Here, it must be reminded that with liquid base ZRP, EIS spectra usually show, one, two [18], or three [1, 11, 19] time constants with low impedance values and are related to the intense electrochemical activity due to the oxygen reduction and zinc dissolution. From our results, it is clear that three different behaviours have to be considered for three coatings under examination. First, ZRP 96%-3 and 96%-5 in particular show a barrier-type behaviour in the early stage of immersion since cathodic polarisation of the metallic substrate is measured. Oxygen reduction and zinc dissolution are then supposed to follow and a strict barrier-type behaviour without Faradic process cannot explain the impedance spectra [30]. Abreu *et al.* however, considered, that the charge transfer resistance R_{ct} (Faradaic due to reaction of zinc with electrolyte) and double layer capacitance C_{dl} overlapped with contact impedance (R_m and C_m , parameters related to contact impedance between zinc particles) [4]. Therefore, there was only one time constant at the beginning of immersion. The EIS spectra at 1 week can be fitted using the equivalent electrical circuit as shown Figure 6.5. In this circuit, R_s represents the electrolyte resistance, R_f the film resistance. Since dispersion effect occurred, a constant phase angle element (CPE) Q_f is install to describe C_f (film capacitance). The impedance of CPE can be described by the following expression 6.1 [59]:

$$Z = Y_0^{-1}(J\omega)^n \quad (6.1)$$

where ω represents the angular frequency, J the complex operator $(-1)^{1/2}$, Y_0 the general admittance function and n the coefficient related to deviation ($0 < n \leq 1$, $n=1$ when CPE is "pure capacitance"). The matched transmission line model is shown in Figure 6.5. The values of the various parameters obtained by numerical fitting are listed in Table 6.3.3. As shown in Table 6.3.3, the fitted values show R_f decreases from $7.15 \times 10^3 \Omega\text{cm}^2$ at 1 layer to $2.28 \times 10^3 \Omega\text{cm}^2$ at 5 layer and Y_0 decreases from $1.73 \times 10^{-4} \text{ F cm}^{-2}$ to $4.76 \times 10^{-6} \text{ F cm}^{-2}$. In the proposed equivalent circuit, R_f imply the film or coating resistance; R_{ct} and C_{dl} represent the charge transfer resistance and the double layer capacitance, respectively. Therefore we proposed transmission line model as depicted in Figure 6.5. Samples with 5 layers showed the capacitive loop is composed with a small semi-circle in the high frequency domain, a large semi-circle in the low frequency domain, which are similar to those reported by Abreu and Shi *et al.* [1, 4].

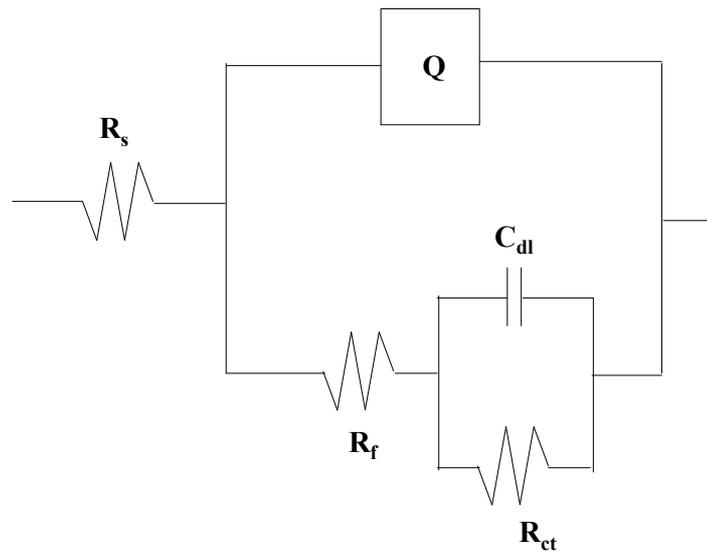


FIGURE 6.5: Equivalent circuit used for numerical fitting of the impedance plots obtained for the different immersion time

R_f has been generally explained as the pore resistance of the coating due to electrolyte penetration [40] or as area where solution easily uptake, particularly, pre-existing holes or porous areas [60]. When zinc particle was integrated into the organic binder, the pore could be created around the particle due to weak adhesion between the particle and binder. Through the pore, solution could percolate into the coating film easily decreasing the value of R_f . However, after 7 weeks of immersion, the value of R_f slightly increased as the coating thickness increased. This may occurred because of the zinc particle strongly adhered with binder matrix as solution percolation become severed. Generally, C_{dl} is accepted as a measurement of the area over which the coating has disbonded [60, 61]. In contrast, Amirudin recognized C_{dl} as a measurement of the electroactive area rather than degradation area [62]. The integrated of zinc particles in the coating increases the electroactive area in the coating because zinc particles have their own active surfaces [40]. For that reason, as coating thickness increase, the integrated of active zinc particles increased the double layer capacitance remarkably. Finally, R_{ct} (charge-transfer resistance), for coating 96%-ZRP, was considerably decreased with the increment of coating thickness. In theory, the value of R_{ct} would be the most applicable parameter for monitoring the protective properties of the coating as the corrosion rate of the primary metal can be estimated from the Stern-Gear equation [62]. Therefore, we may express R_{ct} as directly related to the corrosion activity of the coated sample.

As mentioned earlier, the characteristic of EIS spectra is related to the activity of zinc

dissolution and oxygen reduction on metallic substrate. The presence of the red rust layer at corroded coating/steel interface will accelerate zinc dissolution for the following reason.

1. Electrolyte will rapidly percolate into the coating at location of rust area due to higher osmotic pressure
2. High chloride concentration due to corrosion will promote zinc corrosion along paths saturated with electrolyte.

In this work, the zinc content is as high as 96 wt.%, thus it can be considered that zinc particles were in good contact. If good contact between the zinc particles and the metallic substrate is ensured, the zinc particles will be the only area of the anodic reaction and the bare area on metallic substrate will be the only area of the cathodic reaction. As a result, the zinc corrosion products will form at locations apart from zinc particles between the anodic and cathodic area [5]. Unlike in this work, if there was no contact between zinc particles and metallic substrate due to the existence of corrosion products, the anodic and cathodic reaction would be located on the same surface of the isolated particles saturated by the electrolyte. Hence, the zinc corrosion products would form at locations close to zinc particles [63]. The main reason that the contamination undermined the barrier effect and promoted blistering of the ZRP is the location of the zinc corrosion products. It is because, the zinc corrosion products cannot fill the pores within the ZRP [64]. Therefore, the cathodic protection capability of the ZRP decreased.

In the present work, electrolyte was present in the whole ZRP relatively fast after the immersion. Dissolution of the zinc particles and corrosion products occurred simultaneously. The former may occurred rapidly, however, the latter had been always progressing during the immersion period. As a result, the diffusion process because of insoluble zinc corrosion products just appeared at the early stage of immersion and from then on can be over sighted, and being replaced by the diffusion of iron corrosion products. By the end of immersion, the iron corrosion products had diffused into the ZRP.

According to our results, it is found that even if the deposited salts represented one day of deposition, the corrosion protection of ZRP with the minimum corrosion products 96%-5 was relatively reduced. Hence, in order to apply ZRP on metallic substrate in a salinity environment, the period between surface treatment and coating application should be as short as possible to ensure to lower down the influence of saline deposit on the degradation of ZRP.

TABLE 6.1: Fitted values of the parameters of EEC for 96 wt.% when immersed in 0.5 NaCl solution

Immersion time (week)	R_s (Ω cm 2)	Q (Y_0 S cm $^{-2}$ s n)	n ($0 < n < 1$)	R_f (Ω cm 2)	C_{dl} (F)	R_{ct} (Ω cm 2)
96%-1						
1	10.73	1.73E-04	0.58	7.15E 3	2.96E-06	2.56E 4
2	9.78	8.75E-05	0.53	1.26E 4	2.85E-05	1.87E 4
4	9.06	2.82E-04	0.42	8.39E 4	1.91E-05	1.34E 4
6	14.35	4.63E-04	0.37	1.05E 3	1.32E-04	1.16E 6
7	18.11	7.42E-04	0.35	1.56E 4	3.79E-05	1.27E 6
96%-3						
1	14.71	1.10E-04	0.65	4.03E 3	3.43E-06	6.06E 4
2	20.42	5.51E-05	0.62	1.25E 4	1.84E-04	1.84E 4
4	21.47	1.13E-04	0.48	7.62E 4	2.93E-03	1.05E 3
6	31.61	1.99E-04	0.41	6.23E 3	3.16E-05	6.63E 6
7	42.54	4.04E-04	0.43	7.82E 4	1.28E-04	1.77E 5
96%-5						
1	37.57	4.76E-06	1	2.28E 3	6.18E-06	3.04E 4
2	37.34	9.07E-05	0.61	2.55E 4	4.81E-05	4.34E 4
4	33.70	8.63E-05	0.57	4.26E 4	1.51E-05	2.91E 4
6	42.03	1.08E-04	0.46	2.46E 4	9.12E-04	2.11E 5
7	42.35	1.18E-04	0.44	3.79E 5	6.01E-04	1.84E 4

6.4 Chapter Conclusions

Using EIS and other electrochemical measurements, to investigate the corrosion behaviour of ZRP in artificial sea water at the metallic substrate and paint interface has been studied. A model accounting for zinc particles connection allows us to give a physical interpretation on the impedance spectra.

From the surface morphologies of the samples show that the zinc particles severely deformed after the immersion test, especially for samples with less coating. Corrosion potential measurement results indicate three main periods can be differentiated in the ZRP lifetime. Duration time of cathodic protection of the ZRP with lower contents of zinc and coating thickness was much shorter compared with that ZRP with higher content of zinc. This work suggests that the exposure time of metallic substrate before paint application should be short and higher contents of zinc in paint formulation is crucial to avoid degradation of ZRP coating due to high salinity environment.

Chapter 7

Conclusions & Future Works

7.1 Conclusion of Research Work

Generally, the research work was wholly based on Zinc Rich Paint (ZRP); the mechanism and the application. The discovery has led to three main researches or contributions in this research work: 1) the factors affecting the cathodic protection of ZRP, 2) ZRP formulation, and 3) relevant coating thickness application. Hence, the conclusion of the research work are particularly described as follows:

1. *ZRP mechanism on corrosion protection*: The zinc particles behaviour depending on whether or not they are in electrical contact with the metallic substrate base. The zinc particles can be in the site of anodic reaction of corrosion process, being carried out the cathodic reaction in the metallic substrate. This involves corrosion products forming at the area in between zinc particles, where the system full with electrolyte that contribute ionic condition between anodic and cathodic area. Conditions contribute to this establishment of network (high zinc contents and binders) also favour active anodic dissolution of the zinc particles in the cathodic protection process. However, a zinc particle electrically disconnect from the metallic substrate cannot be the exclusive site of the anodic reaction. The two reactions of the corrosion process (cathodic and anodic) will be located on the same surface of the isolated particle wetted by the electrolyte. Corrosion products will form in the immediate area of the metal, which will increase electrode polarization and reduced zinc corrosion rate. The reason of attacking the zinc particles when they act as anodic electrode, providing cathodic protection to the metallic substrate, remain to be explained. Some zinc particles clearly show a series of porosities or cavities in the original ZRP coatings. Hence, these work highlight that ZRP coatings are complex systems where the electrolyte penetration is non-uniform.

2. *ZRP formulation*: A major drawback of classic solvent-based paint is the emission of volatile organic compounds (VOC), which contribute to atmospheric pollution. Since 1970s, powder coatings are often preferred, because they only composed of dry thermosetting powders without organic solvent so they meet the environmental standards. Zinc particles is cemented with an organic binder which can be epoxy-type and zinc represents 70wt% and above of the paint formulation. These kind of paint can be considered as porous coating due to the metallic content and they have been studied for many years. ZRP with zinc content above 70 wt.%, the powder is not homogeneous which induces problems of zinc dispersion into final coating (after application). Moreover, percolation and porosity are affected by this low zinc content which means that effectiveness and interest of these ZRP coatings can be discussed. For this work, commercial ZRP with epoxy-base paint have been studied and we found that, 74 wt.% shows less cathodic protection compared to 96 wt. %.
3. *Coating thickness*: Good performance of cathodic protection was achieved with samples coated with 96 wt.% regardless of the coating system thickness. The coating thickness seems to be important for the paint formulation, relatively with low zinc content. The coating systems with the thickest zinc coating (74 wt.%-5 layers) shows a better performance and there seemed to be a correlation between coating thickness of the ZRP and electrochemical properties.

7.2 Future Works

7.2.1 Supplementary evaluation measurements

In additional to polarization measurement and electrochemical impedances, ; there are some supplementary measurements should be considered to further evaluate the coated samples performance. As mentioned by Shon *et al.* [64] zinc can easily change to white rust, therefore, weathering test such as condensation chamber test and salt spray test need to be conducted.

1. *Adhesion strength test* Coating breaks and surrounding disbondment crevice may also result when the coated structure is mechanically bent to fit necessary pattern or form; for example, zinc coated steel reinforcing bar (rebar). Severe fabrication bending may induces coating to breaks and separate from the metallic substrate, creating a crevice where corrosion take place. Even though, there are specifications in manufacturing area to avoid such damage, but tests with samples to bent more

severely are necessary to reveal the limits and reduce any accident in the future. Various guidelines on standard test method available from international standard on strength of coatings. [65]

2. *Accelerated life testing* - In real practical application, zinc containing paints are being used in a variety application such as offshore drilling rigs, smoke stacks, chemical plants and other heavy industry. In order to reduce any damage or accident, the ability to maintain the coating lifetime is vital. Protection duration are depend on the environment condition such as humidity, temperature, coating thickness and many other factors. Accelerated testing is an approach for obtaining more information from a given test time than would normally possible. It does this by using a test environment that is more severe compared to the lab environment. Since higher stresses are used, accelerated testing should be approached with caution to avoid any failures modes that will not be encountered in normal use. The level at which accelerated test is performed is very important. some accelerating techniques are appropriate only for part level testing, while others can be used only for higher levels of assembly. Thus, the results need to be carefully interpreted. It is used to identify relevant faults and to ensure that the coating have sufficient margin of strength above the required to survive the normal operating environments.

7.2.2 Mathematical analyses and circuit modelling

Further mathematical analyses as well as modelling on the fabricated coated samples have to be carried out in order to obtain extensive understanding on interrelationship between the coated zinc, material properties and their evaluated electrical characterization. Precise circuit modelling describing physical properties of zinc particles, metallic substrate and between coating interface is necessary for reliable explanation of the coating protection mechanism.

Appendix A

List of Publication

Journals

1. Azizul Helmi Sofian, Kazuhiko Noda: "Evaluation of Zinc Rich Paint (ZRP) Efficiency on Mild Steel in Seashore Environment", *ECS Transactions*, Vol. 50 (50), 2013
2. Azizul Helmi Sofian, Atsumu Tanaka, Kazuhiko Noda: "Corrosion Performance of Zinc-Rich Paints(ZRP) on Mild Steel in NaCl Solution", *ECS Transactions*, Vol. 45 (19), 2013
3. Jun-ichi Nozawa, Junko Suda, Azizul Helmi Bin Sofian, Hiroshi Hagiwara, Hiroshi Suda, Takahiko Kawai, Tadashi Komoto, Hiroyuki Kumehara: "Tribology of Polymer Injection-molded Stainless Steel Hybrid Gear", *Journal of Wear*, Vol 266, 2009

International Conference Proceedings

1. Azizul Helmi in Sofian, Kazuhiko Noda: "The investigation of Zinc Rich Paints (ZRP) Behavior in NaCl Solution by Electrochemical Methods", *International Proceedings 2013 of Malaysia-Japan Academic Scholar Conference*, 2013, Tokyo, Japan.
2. Azizul Helmi Bin Sofian, Kazuhiko Noda: "Corrosion Analysis of Zinc Rich Epoxy Coatings on Steel in NaCl Solution", *PRICM 8: 8th Pacific Rim International Congress on Advanced Materials and Processing*, 2013, Hawaii, USA.

3. Azizul Helmi Sofian, Kazuhiko Noda: "Corrosion Prevention by Zinc Rich Paint (ZRP) on Steel in Artificial Sea Water Solution", *Proceedings of the 7th South East Asian Technical University Consortium Symposium*, 2013, Bandung, Indonesia.
4. Azizul Helmi Sofian, Kazuhiko Noda: "Anticorrosive Performance of Zinc Rich Paint (ZRP) Coating on Pure Iron in NaCl Solution", *Proceedings of the Sixth Japan-China Joint Seminar on Marine Corrosion and Control - Memorial Symposium for the Retirement of Prof. Tooru Tsuru*, pp. 202-206, 2012, Tokyo, Japan.
5. Azizul Helmi Bin Sofian, Kazuhiko Noda: "Corrosion Performances of Organic Coating Particles on Mild Steel in NaCl Solution", *Proceedings of the 6th South East Asian Technical University Consortium Symposium*, 2012, Bangkok, Thailand (ISSN 2186-7615).

International Conference Presentations

1. Azizul Helmi Sofian, Teguh Dwi Widodo, Youhei Hirohata, Kazuhiko Noda, "Electrochemical Behavior of Steels Coated by Zinc Rich Paints (ZRP)", *International Conference on Surface Engineering (ICSE)*, 2013, Busan, Korea.
2. Ryoji Suzuki, Azizul Helmi Sofian, Youhei Hirohata, Kazuhiko Noda, "Corrosion Analysis of Co-Cr Alloy in Neutral Solution", *International Conference on Surface Engineering (ICSE)*, 2013, Busan, Korea.
3. Teguh Dwi Widodo, Azizul Helmi Bin Sofian, Ryouji Suzuki, Youhei Hirohata, Kazuhiko Noda, "Characterization of Mechanical Surface Treated 304 Stainless Steel by Electrochemical Impedance Spectroscopy", *International Conference on Surface Engineering (ICSE)*, 2013, Busan, Korea.
4. Azizul Helmi Sofian, Kazuhiko Noda, "Corrosion Resistance and Mechanism of Zinc Rich Paint in Corrosive Media", *224th ECS Meeting*, 2013, San Francisco, USA.
5. Azizul Helmi Sofian, Teguh Dwi Widodo, Kazuhiko Noda, "Application of EIS to Evaluate the Efficiency of Zinc Rich Paint (ZRP) Coating on Steel", *9th International Symposium on Electrochemical Impedance Spectroscopy*, 2013, Okinawa, Japan.
6. Azizul Helmi Sofian, Muhammad Zaimi, Kazuhiko Noda, "Electrochemical Analysis of Electroless Quaternary Nickel Alloy in 3.5 wt.% NaCl Solution", *9th International Symposium on Electrochemical Impedance Spectroscopy*, 2013, Okinawa, Japan.

7. Teguh Dwi Widodo, Azizul Helmi Sofian, Kazuhiko Noda, "Electrochemical Behaviors Observation of Shot Peened 304 Stainless Steel in 0.5 M Sodium Chloride Solution", *9th International Symposium on Electrochemical Impedance Spectroscopy*, 2013, Okinawa, Japan.
8. Atsumu Tanaka, Azizul Helmi Sofian, Kazuhiko Noda "Evaluation of Corrosion Protection of Zinc Rich Paint Coated Steel", *222nd ECS Meeting*, 2012, Hawaii, USA.

Domestic Conference Presentations

1. Azizul Helmi Sofian、八木雄太、鈴木良治、野田和彦、「中性溶液におけるジंकリッチペイントの電気化学特性」、(第24回傾斜機能材料シンポジウム) Tottori, 2013
2. Azizul Helmi Bin Sofian、野田和彦、「Electrochemical Properties and Corrosion Protection of Zinc Coatings in Corrosive Media」、(表面技術協会・第128回講演大会) Fukuoka, 2013
3. Azizul Helmi Bin Sofian、田中集、野田和彦、「電気化学インピーダンスによるジंकリッチペイントコーティングの耐食特性評価」、(表面技術協会・第126回講演大会) Hokkaido, 2012
4. 田中集、Azizul Helmi Sofian、野田和彦、「塗装鋼板における亜鉛顔料の防食効果」、(表面技術協会・第126回講演大会) Hokkaido, 2012
5. Azizul Helmi Bin Sofian、田中集、野田和彦、「Corrosion Performance of Organic Coatings Particles on Mild Steel in NaCl Solution」、(表面技術協会・第124回講演大会) Nagoya, 2011
6. 田中集、Azizul Helmi Sofian、野田和彦、「ジंकリッチペイントを施した鋼板の電気化学挙動解析」、(表面技術協会・第126回講演大会) Nagoya, 2011
7. Azizul Helmi Bin Sofian、田中集、野田和彦、NaCl溶液中におけるジंकリッチペイントコーティングを施した純鉄の耐食特性」、(金属学会・第149回講演大会) Okinawa, 2011

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