EFFECTS OF GAMBIR EXTRACT TREATMENT ON THE RUSTED MILD STEEL

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EFFECTS OF GAMBIR EXTRACT TREATMENT ON THE RUSTED MILD STEEL

by

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LIST OF ABBREVIATIONS AND SYMBOLS

AA	Antioxidant activity
C_c	Coating capacitance
C_{dl}	Double layer capacitance
CE	Catechin equivalent
CR	Corrosion rate
CTC	Condensed tannin content
E_{corr}	Corrosion potential
EDX	Energy-dispersive X-ray spectroscopy
EIS	Electrochemical impedance spectroscopy
FTIR	Fourier transform infrared spectroscopy
I_{corr}	Corrosion current density
R_{ct}	Charge transfer resistance
R_{po}	Pore resistance
R_s	Solution resistance
RT	Rate of transformation
SEM	Scanning electron microscopes
TFC	Total flavonoid content
TPC	Total phenolic content
XRD	X-ray diffraction
β_a	Anodic Tafel slope
β_c	Cathodic Tafel slope
UV-Vis	Ultraviolet visible spectroscopy

KESAN RAWATAN EKSTRAK GAMBIR TERHADAP KELULI LEMBUT BERKARAT

ABSTRAK

Uncaria gambir telah diekstrak menggunakan enam pelarut yang berbeza dan kesan terhadap hasil pengekstrakan dan kandungan fenolik telah diselidik. Kandungan fenolik tersebut, iaitu, jumlah kandungan fenolik (TPC), jumlah kandungan flavonoid (TFC), kandungan tannin terkondensasi (CTC) dan aktiviti antioksidan (AA) ekstrak gambir telah ditentukan. Pelarut etil asetat didapati berjaya mengekstrak kandungan tertinggi bagi TPC (93% katecin setara), TFC (91% katecin setara) dan CTC (96% berat). Disamping itu, kandungan fenolik menunjukkan kemampuan gambir ekstrak sebagai antioksidan yang baik. Keupayaan ekstrak gambir sebagai penukar karat telah dikaji. Kesan kepekatan gambir, pH larutan, masa tindak balas dan penambahan asid fosforik dalam penukar karat telah diselidiki. Spektrum FTIR menunjukkan penukaran lepidokrosit (γ-FeOOH) adalah terpantas diikuti magnetit (Fe_3O_4) dan akhir sekali goetit (α-FeOOH). Keberkesanan salutan penukar karat ditentukan melalui spektroskopi impedans elektrokimia dan pengutuban potensiodinamik. Analisis daripada plot Tafel bersesuian dengan analisis daripada plot Nyquist iaitu semakin tinggi kepekatan gambir kadar pengaratan semakin berkurang. Campuran 10% gambir dengan 5% H_3PO_4 didapati lebih efektif sebagai penukar karat. Perubahan morfologi dapat dilihat dengan ketara apabila bentuk berduri karat telah berubah kepada permukaan yang lebih sekata dan padat selepas ditindak balas dengan penukar karat. Corak belauan x-ray menunjukkan pengurangan pada hasil karat selepas bertindak balas dengan penukar karat berasaskan gambir.

EFFECTS OF GAMBIR EXTRACT TREATMENT ON THE RUSTED MILD STEEL

ABSTRACT

Uncaria gambir was extracted using six different solvents and the effects on the extraction yield and phenolic contents were investigated. The phenolic contents, namely, total phenolic (TPC), total flavonoid (TFC), condensed tannin (CTC) and antioxidant activity (AA) of the gambir extracts were quantified. Ethyl acetate solvent was found successfully extracted the highest TPC (93% catechin equivalent), TFC (91% catechin equivalent) and CTC (96% weight). Besides, the phenolic content shows the ability of gambir extract as antioxidant. The performance of gambir extract as rust converter was evaluated. The effects of gambir concentration, pH solution, contact time and the addition of phosphoric acid in rust converter were studied. The FTIR spectra showed that the conversion of lepidocrocite (γ-FeOOH) was the fastest, followed by magnetite (Fe_3O_4) and goethite (α-FeOOH) was the slowest. The effectiveness of rust conversion coatings was studied via EIS and potentiodynamic polarization. The Tafel and Nyquist plots analyses were in agreement showing that increasing the gambir concentration decreased the corrosion rate and the mixture of 10% gambir and 5% H_3PO_4 produced a better rust converter. The changes in morphology of the rust were significant as viewed by SEM analysis. The spike-shaped rust was converted into a more homogeneous and compact surface after treatment with rust converter. XRD patterns showed a decrease of the rust products after being treated with gambir-based rust converter.

CHAPTER 1

INTRODUCTION

Corrosion is a common phenomenon in our daily life as we can see the rust spots on cars, the rusting of iron fences and rusty light poles along the highway. Corrosion is the result of reaction of materials with their environments (Ahmad, 2006). Corrosion can affect us in term of economics, safety and environmental damage. The idea of corrosion can also be applied in a broader sense, not only limited to metals but also includes the deterioration of non-metallic materials. Rusting, on the other hand, can only be applied on iron-based materials.

Rust products are complex materials that change continuously as the complex develops through the precipitation, evolution and transformation of chemical species in the iron-oxygen-water system. Under ambient condition, lepidocrocite (γ-FeOOH), geothite (α-FeOOH) and magnetite (Fe_3O_4) are the main constituents of rust and the specific composition each depends on the pH, temperature and the presence or absence of atmospheric pollutants (Nasrazadani, 1997). Rust converter is one of the efforts in controlling corrosion, preventing corrosion from further occuring. It can be applied on the steel surface, serves as barrier to protect the steel as well as a base for paint.

Recently, few studies had been conducted in order to evaluate commercial rust converter. Several factors affect the mechanisms of the conversion including the components of the converter, pH, reaction time of the converter with the rust and the method of application (Ocampo *et al.*, 2004). Besides rust converters that are based on phosphoric acid and chromate, researchers are now more interested into the study of natural inhibitors as more ecofriendly and biodegradable rust converters such as

gallic acid and tannic acid (Favre *et al.*, 1998; Rahim *et al.*, 2010). The naturally occurring polyphenols mostly in plants can react with iron ions lead to more stable, insoluble iron complexes so that no further reaction can occur between rust and the corrosive agents (Seavell, 1992).

Gambir (*Uncaria gambir*) consists of catechin as the most abundant polyphenolic constituent (Taniguchi *et al.*, 2007). It was found that due to its high catechin contents, gambir possesses high antioxidant capacities (Anggraini *et al.*, 2011; Apea-Bah *et al.*, 2009). Other researchers found other applications of gambir plant including inhibitors in preventing corrosion of mild steel in acidic solution (Hussin, 2010), as adsorbent of selected dye adsorption (Achmad, 2012), and one of the components in mouth antiseptic (Lucida *et al*., 2007). Study also had been conducted on the ability of gambir in phase transformation of rust (Suan, 2009).

Catechin belongs to the group of flavonoid. Catechin compounds are present in various natural foods, known to show some health-enhancing effects such as carcinogenesis reduction in the external and internal organs (Cao *et al.*, 1996; Huang *et al.*, 1992; Majima *et al.*, 1998) and reduction in atherosclerotic plaques (Chyu *et al.*, 2004). Catechin polyphenols have been demonstrated to act directly as radical scavengers of oxygen and nitrogen species besides having well established metal chelating properties (Mandel *et al.*, 2006).

Problem statements

1. Different solvent systems had been used for catechin extraction in various plant samples; however, the literature of extraction of gambir plant by different solvent systems is limited.

2. Previous works have shown that gambir is capable as good corrosion inhibitor and adsorbent for dye. Does gambir have the potential as rust converter as well?

3. Few studies had been conducted on commercialize rust converter via electrochemical analysis. Does rust converter based on gambir extract have the same impedance and polarization pattern as those commercialize rust converter?

Therefore, the aim of this work is to study the potential of gambir to be used as a rust conversion coating. The objectives of the present study are as follows:

1. To study the effects of solvent on the phenolic content, flavonoid content, condensed tannin and antioxidant activity of gambir extract.

2. To evaluate the performance of gambir extract on the transformation of rust by means of FTIR, SEM-EDX, XRD and electrochemical analyses.

CHAPTER 2

LITERATURE REVIEW

2.1 Definition of corrosion

Corrosion can be defined in many ways. The word corrosion is derived from the Latin word *corrodere* which means "to eat away" (Groysman, 2010; Davis, 2000; Sastri *et al.*, 2007). According to ISO 8044, corrosion is defined as an interaction between a metal and its environment that results in changes in the properties of the metal, and which may lead to significant impairment of the function of the metal, the environment, or the technical system of which these form a part (Mattson, 1996). Fontana (1986) defined corrosion as the deterioration of materials as a result of reaction with its environment while Revie and Uhlig (2008) outlined that corrosion is the destructive attack of a metal by chemical or electrochemical reaction with the environment. Generally, we can describe that corrosion is the degradation of material, especially metal, or its properties because of a reaction with its environment (Roberge, 2008).

The environment consists of the entire surrounding in contact with the material. The primary factors to describe the environment are as following (Davis, 2000):

1) physical state – gas, liquid or solid

2) chemical composition – constituents and concentrations

3) temperature

Other factors can be important in specific cases. Corrosion can affect us in everyday life in terms of economics, safety and environmental damage. Replacement of

corroded equipment, contamination of product and shutdown of plantation due to corrosion failure are some examples of economics' effects. Sudden failure which can lead to fire, explosion and construction failure as well as pollution are the consequences of corrosion that adversely affect our safety and health including environment damage that cause the depletion of natural resources.

The cost of corrosion in industrialized countries has been estimated to be about 3 - 4% of the gross national product (Sastri *et al.*, 2007; Roberge, 2008; Bardal, 2004). The studies of better understanding in corrosion have taken from 10% to 40% of the total cost in other words; this is the demand for applied research, education, information, transfer of knowledge and technology, and technical development. Corrosion costs could be divided into direct costs and indirect costs (Sastri *et al.*, 2007; Ahmad, 2006; Roberge, 2008; McCafferty, 2010).

Replacement parts (capital cost); maintenance, repairing, painting (control cost); protective coatings and corrosion inhibitor (design cost) are considered as direct costs (Revie and Uhlig, 2008) .While the in direct costs may involve shutdown of power plants and manufacturing plants, leakage of pipelines (loss of product) and clogging of pipes with rust (loss of efficiency). Indirect losses are more difficult to estimate, but briefly survey of typical losses of this kind compels the conclusion that they add several billion dollars to the direct losses already outlined.

2.2 Corrosion of iron

Corrosion is considered to be an electrochemical process (Sastri *et al.*, 2007). The most common form of corrosion is rusting of iron or steel. Iron is the most versatile, least expensive and most widely applied of the engineering metals. Iron has a natural tendency to combine with other chemical elements to return to its lowest energy

state. Thus, iron frequently combines with oxygen and water (which are present in most natural environments) to form hydrated iron oxides (rust), similar in chemical composition to the original iron ore (Davis, 2000). Figure 2.1 illustrates the corrosion cycle of a steel product.

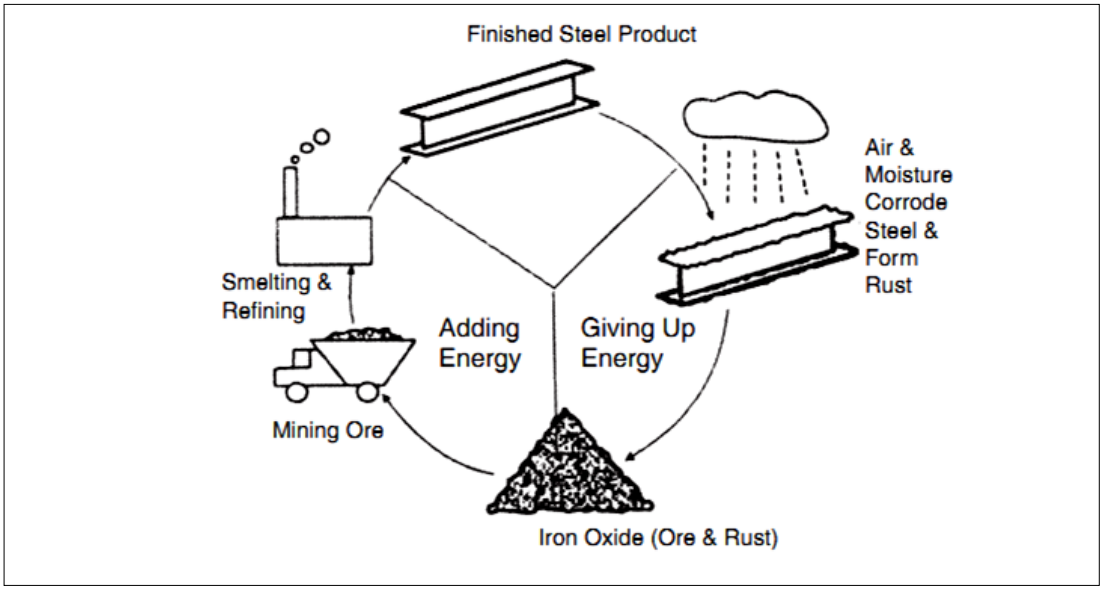

Figure 2.1 The corrosion cycle of steel (Davis, 2000)

2.2.1 Formation of corrosion products of iron

Most metals corrosion occurs via electrochemical process which requires the presence of anode, cathode and aqueous solution or electrolyte which contains positively or negatively charged ions, also a conductor. Oxidation occurs at anodic site while reduction occurs at cathodic site. During corrosion more than one oxidation and one reduction may occur. The electrochemical mechanism of corrosion of iron is depicted in Figure 2.2.

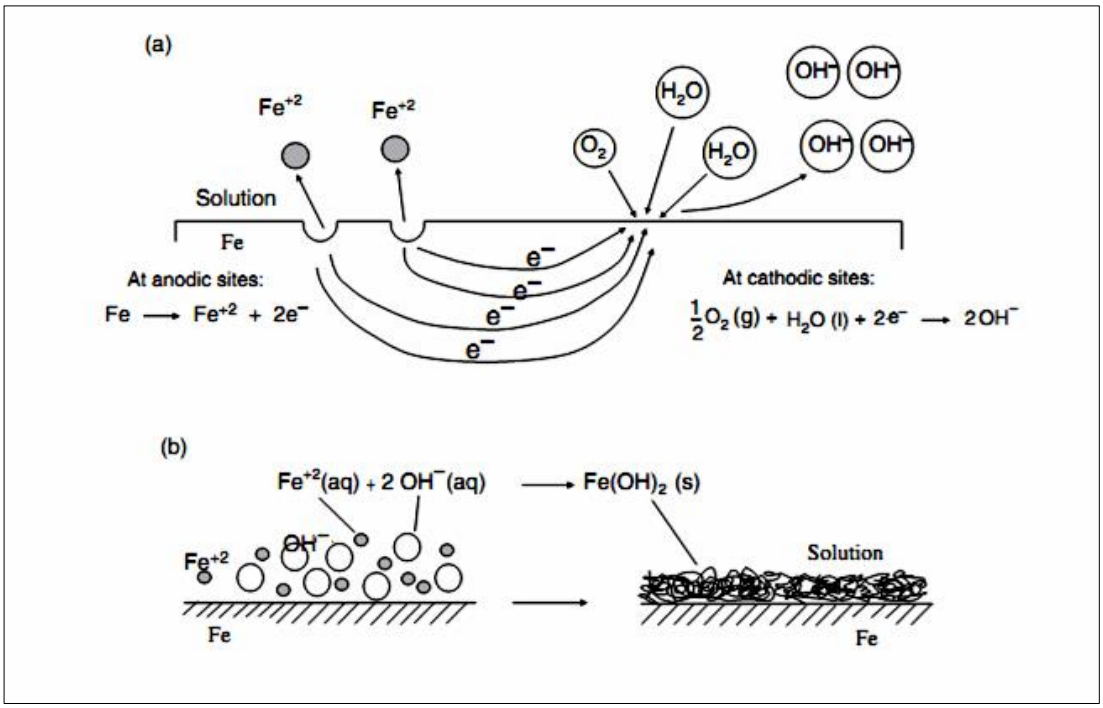

Figure 2.2 (a) Electrochemical reaction of iron and (b) The precipitation of iron(II) hydroxide on metal surface (McCafferty, 2009)

Anodic reaction, the iron ionizes:

$$Fe \rightarrow Fe^{2+} + 2e^{-} \quad (2.1)$$

Cathodic reaction, hydroxyl ions are produces:

$$H_2O + \tfrac{1}{2}O_2 + 2e^{-} \rightarrow 2OH^{-} \quad (2.2)$$

If no other oxidation or reduction reaction occurs, the OH^- ions react with Fe^{2+} ions deposited to iron(II) hydroxide, $Fe(OH)_2$:

$$Fe^{2+} + 2OH^{-} \rightarrow Fe(OH)_2 \quad (2.3)$$

The colour of $Fe(OH)_2$ is normally greenish black due to incipient oxidation by air. With more excess to oxygen in the air, $Fe(OH)_2$ oxidises to iron(III) hydroxide, $Fe(OH)_3$ of reddish brown colour (Revie and Uhlig, 2008):

$$Fe^{2+} + OH^- + \tfrac{1}{4}O_2 + \tfrac{1}{2}H_2O \rightarrow Fe(OH)_3 \quad (2.4)$$

The oxidation rate is very fast, and the $Fe(OH)_2$ formed by corrosion is likely to turn into $Fe(OH)_3$ immediately at the site of corrosion (Tamura, 2008). The deposition of $Fe(OH)_3$ would lead to good adherence of the precipitates to the corrosion sites. The aging of $Fe(OH)_3$ leads to dehydration even in the presence of water and forms oxyhydroxides, FeOOH:

$$Fe(OH)_3 \rightarrow FeOOH + H_2O \quad (2.5)$$

Tamura (2008) also reported, after dehydration, lepidocrocite, γ-FeOOH which is dominant at early stage will gradually transformed into more stable goethite, α-FeOOH. The α-FeOOH formed at the initial stage of corrosion would be tightly aggregated due to the small repulsion between particles.

In deficiency of oxygen, $Fe(OH)_2$ is reduced to magnetite, Fe_3O_4:

$$3Fe(OH)_2 + \tfrac{1}{2}O_2 \rightarrow Fe_3O_4 + 3H_2O \quad (2.6)$$

For the formation of Fe_3O_4, either a reducing condition near the metal surface or an insufficient supply of oxygen due to thick $Fe(OH)_2$ is necessary. Later, the magnetite produced is re-oxidized in by oxygen in the presence of water to regenerate γ-FeOOH:

$$Fe_3O_4 + \tfrac{1}{2}O_2 + \tfrac{3}{2}H_2O \rightarrow 3\gamma\text{-}FeOOH \quad (2.7)$$

From the reactions above, it serves to illustrate that the electrochemical nature of rusting and the essential parts played by moisture and oxygen. Evans proposed the effect of wet-dry-wet cycles on the growth of rusts, and assumed the reaction

depends on the dry or wet conditions for steel with inner Fe_3O_4 and outer FeOOH layers as shown in Figure 2.3 (Tamura, 2008).

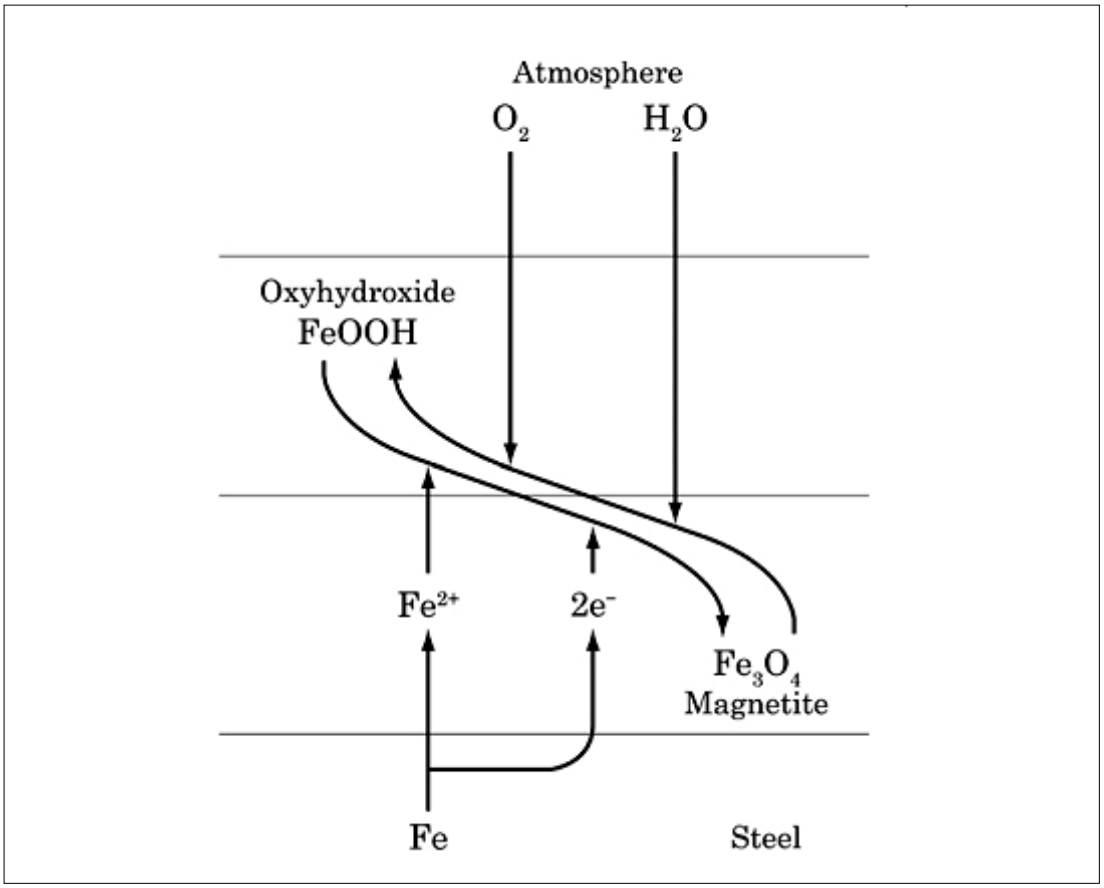

Figure 2.3 Evans model of corrosion (Tamura, 2008)

However, in the presence of electrolyte such as sodium chloride, the reaction is altered. Under the remaining rusts, the corrosion starts with water and oxygen being transported through channels due to defects in the rust causing iron(II) chloride, $FeCl_2$ is formed at the anode and sodium hydroxide, NaOH is formed at the cathode (Tamura, 2008):

$$Fe^{2+} + 2Cl^-(\text{contaminant}) \rightarrow FeCl_2 \quad (2.8)$$

$$OH^- + Na^+(\text{contaminant}) \rightarrow NaOH \quad (2.9)$$

The two components diffuse away from the sites of formation and react at a distance from the metal surface to form $Fe(OH)_2$, or basic salt, which then combines with oxygen to form rust with the regeneration of NaCl:

$$FeCl_2 + 2NaOH \rightarrow Fe(OH)_2 + 2NaCl \quad (2.10)$$

$$4Fe(OH)_2 + O_2 \rightarrow 4FeOOH + 2H_2O \quad (2.11)$$

γ-FeOOH, α-FeOOH and Fe_3O_4 are the main constituents of corrosion products of steel under normal ambient conditions. The specific composition depends on the pH, temperature and the presence or absence of atmospheric pollutants (Nasrazadani, 1997).

2.3 Corrosion control

There are five essential ways of corrosion control (Groysman, 2010; Davis, 2000; Ahmad, 2006; Bardal, 2004):

i) Appropriate material selection

ii) Suitable design

iii) Use of inhibitors

iv) Electrochemical, i.e. cathodic and anodic protection

v) Application of coatings

Material selection is critical to engineering design. The material selected has to meet the criteria for mechanical strength, corrosion and erosion resistance for specific service conditions. It involves many factors that have to be optimized for a particular application. The selection is a requirement to a good design. Materials and design are

complimentary and performed in connection with each other.

Any addition of chemicals into the environment results in its chemical change and, as a result, influences its aggressiveness, diminishing or increasing the corrosion of metals. One of the most widespread methods of changing the chemistry of the environment is the use of corrosion inhibitors. A corrosion inhibitor can function in two ways, modify the corrosion environment into a noncorrosive or less corrosive environment through its interaction with the corrosive species, or interacts with the metal surface thus inhibits the corrosion of metal (Sastri *et al.*, 2007).

Besides using corrosion inhibitors, cathodic protection has been applied in combination with a coating in order to protect the steel. Cathodic protection can be described as elimination or reduction of corrosion of metal surface by making it the cathode (negative), using either galvanic or an impressed current (Sastri *et al.*, 2007; Ahmad, 2006; Bardal, 2004). Anodic protection is based on phenomenon of passivity, only applied on metals or alloys with a well-defined and reliable passive region and low passive current density. The material is polarized in the anodic direction so that the potential is lifted to the passive region (Bardal, 2004; Groysman, 2010).

Coatings can be classified in the following categories according to corrosion resistance (Ahmad, 2006). Barrier coatings consist of four types – anodic oxides, inorganic coatings, inhibitive coatings and organic coatings. Conversion coatings involve the surface metal to be converted into compound having desired porosity to act as a good base for paint. Anodic coating, generally called sacrificial coatings, meant that a coating which is anodic to the substrate and cathodic coatings imply the metals deposited are electropositive to the substrate.

2.4 Rust converter

Rust converters are chemical formulation that can be applied on rusted steel to penetrate and react with the rust, converting it to nonporous, stable compound that serves as a barrier layer to protect the steel (Bradford, 2001). It is also a layer where painting systems can be applied on. The protection efficiency of rust converters are varied due to several factors including appropriate components of the rust converter and its concentrations, pH, reaction time of the converters with the rust, the presence of other products, application method as well as the corrosion and contamination grades of the rusted steel (Ocampo *et al.*, 2004). Another variable is the type and concentration alcohol used as a solvent (Barrero *et al.*, 2001). However, very few works have been reported on this matter.

According to Favre *et al.* (1998), rust converters are able to convert 'active' rust into water-insoluble compounds, coherent, and corrosion resistant. The insoluble ferric complex is responsible for the protection of the surface where it acts as an electrical insulator or as a diffusion barrier for oxygen. DesLauriers (1987) concluded that the performances of a rust converter depend more on the properties of the paint/rust system and the amount of rust present than on its ability to form chelates.

2.4.1 Reaction of rust converter with iron

Most rust converters are based on tannins and phosphoric acid. Such products are not harmful to the environment and tannic acid is obtained from renewable sources (Singh and Yadav, 2008; Almeida *et al.*, 1997; Nasrazadani, 1997; Rahim *et al.*, 2008; Rahim *et al.*, 2010). Several studies have been described on the mechanisms of reaction for each acid with the most common iron phases, giving a strong base for the correct interpretation of most of the result (Ocampo *et al.*, 2004; Beltran *et al.*,

2010; Nasrazadani, 1997; Matamala *et al.*, 2000).

The rust converter transformed the corrosion products of iron into iron compounds that are more stable so that no further reaction between the rust and the corrosive agents hence hindered the steel corrosion. This mechanism is claimed to involve chemical reactions with rust to form an inert compound that stabilized the reduction-oxidation reactions between iron(II) and iron(III). Therefore, the cathodic cycle in the atmospheric corrosion process will stop and corrosion should be prevented (Seavell, 1992).

2.4.1.1 Reaction of phosphoric acid with iron

Phosphoric acid alone is not recommended as a rust converter because of its poor performance (Almeida *et al.*, 1997). However, combination of tannin and phosphoric acid produced a coating which gave better corrosion resistance (Pardini *et al.*, 2001, Rahim *et al.*, 2008). In a formulation containing phosphoric acid alone, it was found to migrate and react with the surface steel hence produced metal phosphate complexes such as $Fe(H_2PO_4)_2$, $FeHPO_4$, $Fe_3(PO_4)_2$ and $FePO_4$. These compounds can provide the proper functionalities for the condensation reactions with binder (Pardini *et al.*, 2001). Nasrazadani (1997) reported that phosphoric acid reacts with γ-FeOOH, α-FeOOH and Fe_3O_4 to form mainly ferric phosphate. The reaction is fastest with γ-FeOOH, a little slower with Fe_3O_4, and slowest with α-FeOOH.

Phosphoric acid solution with low concentration reacts with corrosion product of iron to form iron phosphate precipitation, which act as corrosion protector, according to reaction (2.13) and (2.14).

$$6H_3PO_4 + 3Fe \rightarrow 3Fe(H_2PO_4)_2 + 3H_2 \quad (2.13)$$

$$3Fe(H_2PO_4)_2 \rightarrow Fe_3(PO_4)_2 \downarrow + 4H_3PO_4 \quad (2.14)$$

However, if phosphoric acid with medium and high concentration were applied, the iron seems to be unable to allow the iron phosphate precipitation (Gust, 1991). Rahim *et al*. (2008) also reported that the phosphoric acid initially dissolves the iron products and proposed the following phosphate precipitation:

$$H_3PO_4 + FeOOH \rightarrow FePO_4 + 2H_2O \quad (2.15)$$

and

$$2H_3PO_4 + 3Fe_3O_4 + 5H_2O \rightarrow Fe_3(PO_4)_2 + 8H_2O + 3Fe_2O_3 \quad (2.16)$$

$$3Fe_2O_3 + 3H_2O \rightarrow 6FeOOH \quad (2.17)$$

$$2H_3PO_4 + 3Fe_3O_4 + 8H_2O \rightarrow Fe_3(PO_4)_2 \cdot 8H_2O(\text{vivianite}) + 6FeOOH \quad (2.18)$$

2.4.1.2 Reaction of catechin with iron

Catechin is polyphenolic antioxidant plant metabolites. In addition to its radical scavenging action, catechin possesses well established metal chelating properties. Structurally important features defining its chelating potential are the 3',4'-dihydroxyl group in the B ring, as well as the gallate group, which may neutralize ferric iron to form redox-inactive iron (Mandel *et al.*, 2006).

Chobot and Hadacek (2010) investigated the redox chemistry of iron complexes with (±)-catechin. The (±)-catechin shifted the redox potential of iron in the complex to the cathodic direction which led to more easily oxidised iron. The study concluded that the redox chemistry of iron in the complex or chelate was determined by catechin as ligand. Figure 2.4 shows iron formed complexes with (±)-catechin.

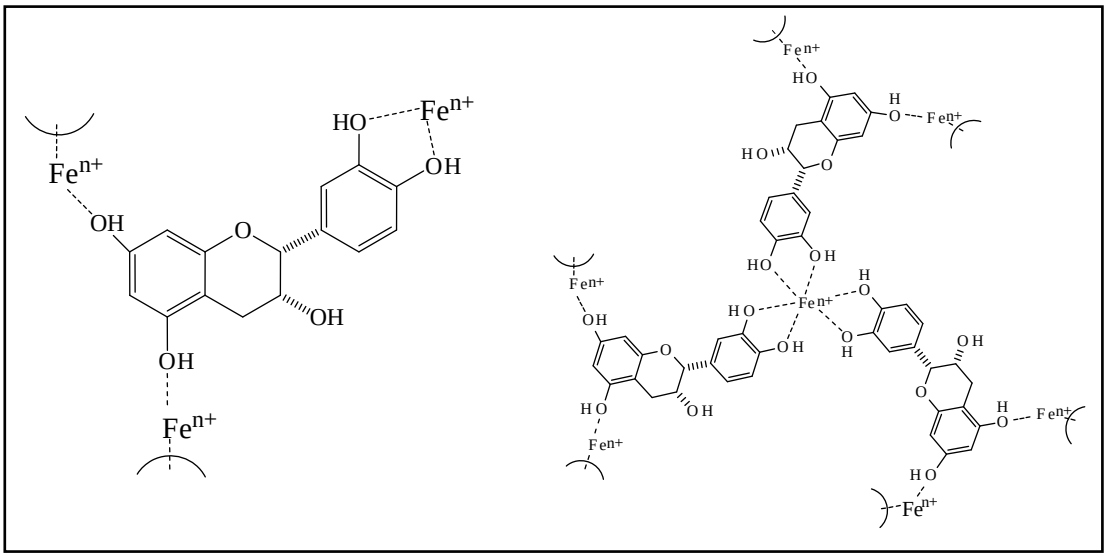

Figure 2.4 Iron complexes with catechin (Chobot and Hadacek, 2010)

The formation of iron(II)-catechin proposed by Mario *et al.* (2001) is shown in Figure 2.5. The iron-catechin complex is easier to form in the presence of a base.

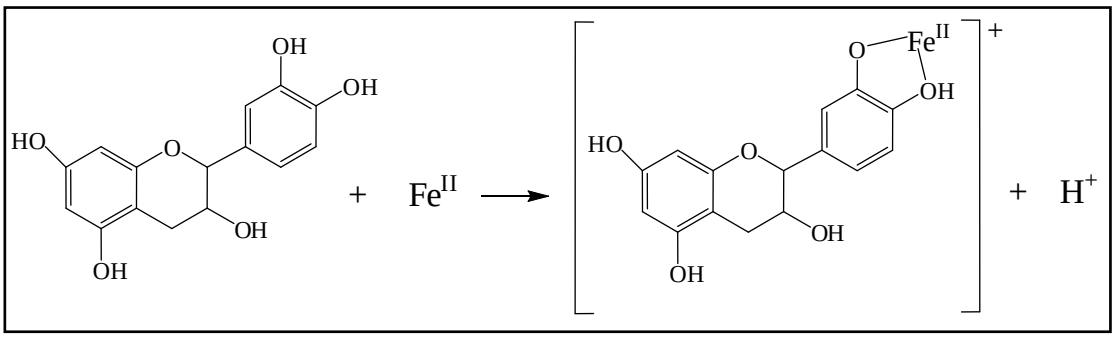

Figure 2.5 The chemical reaction of catechin with iron(II) (Mario *et al*., 2001)

The complexation of iron and catechin in various pH had been studied by Faizah and Afidah (2007). The most stable complexation of Fe-catechin began at pH 3 and at pH 8, ion hydrolysis occurred, leading to other complexation products being formed. However, ferric-catechin remained as the major product. UV-Vis analysis showed that ferrous ions were oxidized into ferric ions and catechin was possibly oxidized to quinone. Ferric-catechin complexes were formed when catechin reacted with either ferrous chloride or ferric chloride.

2.4.2 Electrochemical methods of rust converter study

The main idea of electrochemical test methods is to control and measure the fundamental properties of electrochemical reactions. Knowing these properties will gives a clear understanding on the effects of material and environmental changes on corrosion, as well as the mechanisms of corrosion.

2.4.2.1 Electrochemical impedance spectroscopy

Electrochemical Impedance Spectroscopy (EIS) is based on alternating currents (AC) which can be used to obtain insights into corrosion mechanisms and to establish the effectiveness of corrosion control methods, such as inhibition and coatings (Revie and Uhlig, 2008). The goal of the EIS technique is used to determine the electrical impedance of the metal–electrolyte interface at various AC excitation frequencies and then analyze the resulting spectrum to estimate the corrosion rates and the mechanism that might give rise to the spectra (Groysman, 2010; Revie and Uhlig, 2008). The impedance is affected by the interaction between frequency and all of the physical and chemical processes that respond to that frequency change within the electrochemical cell and across the corroding interface (Groysman, 2010). EIS is capable of characterizing the corrosion interface more comprehensively and with good quality equipment specifications of achieving measurements in lower conductivity solution or high-resistivity coatings (Revie and Uhlig, 2008).

In EIS analysis, three different types of plots are commonly used. Nyquist plot (complex plane, showing –Z' versus Z"), where Z' is real impedance while Z" is imaginary impedance; and two different types of Bode plots, showing the impedance magnitude versus log frequency and phase angle versus log frequency. Figure 2.6 and 2.7 show a typical of Nyquist plot and Bode plot, respectively.

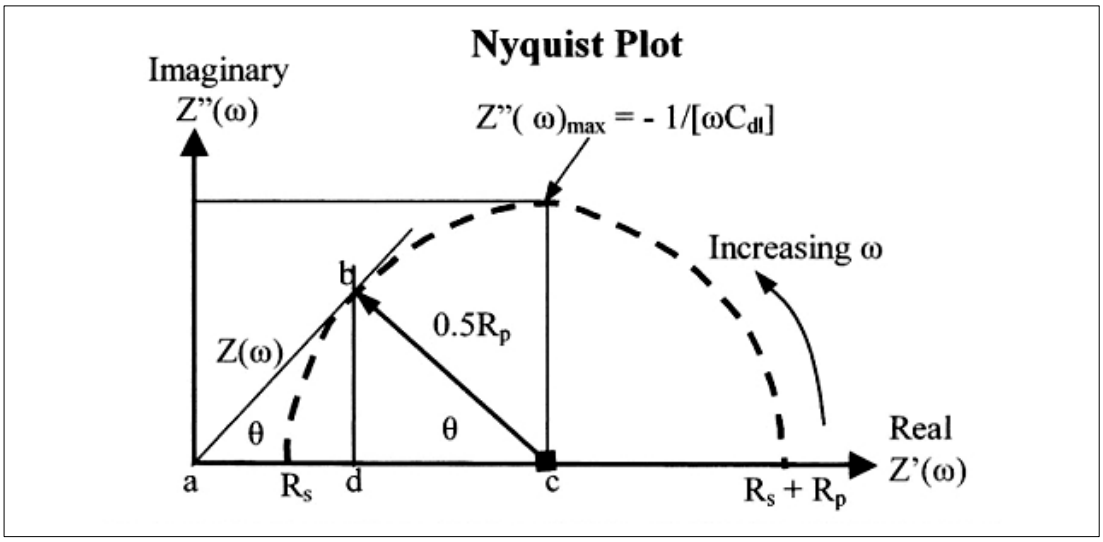

Figure 2.6 A typical Nyquist plot (Perez, 2004)

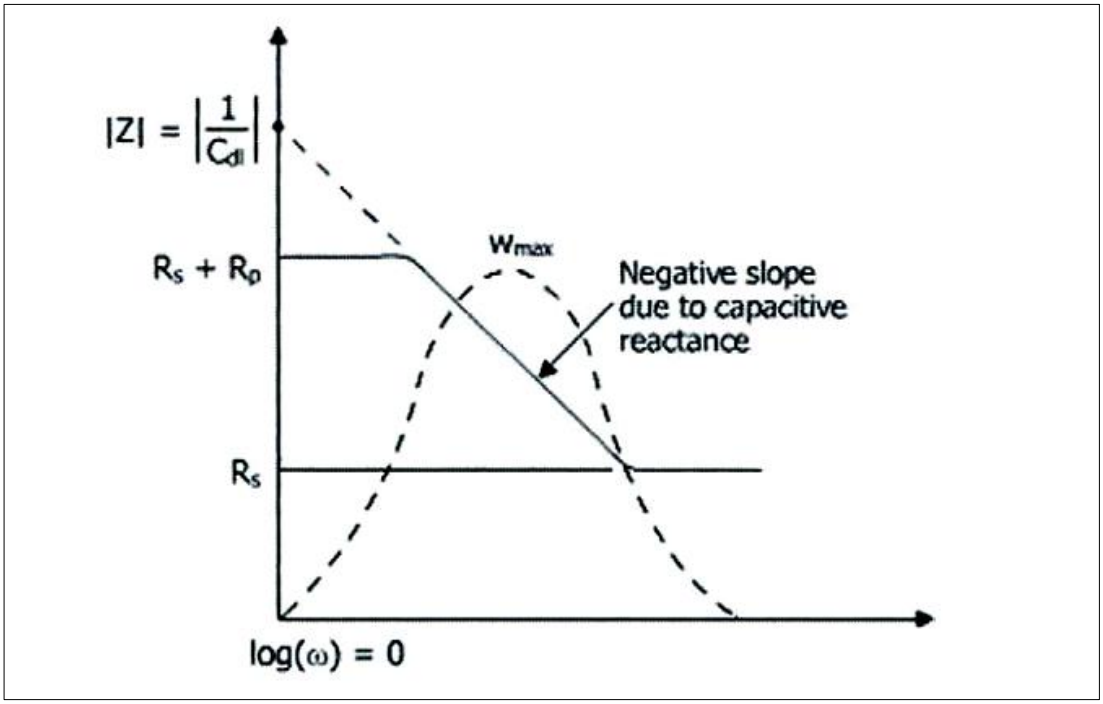

Figure 2.7 A typical Bode plot (Ahmad, 2006)

The response of an electrode to alternating potential signals of varying frequency is interpreted on the basis of circuit models of the electrode/electrolyte interface. Figure 2.8 shows two circuit models that can be used for analyzing EIS spectra. The simplest model for characterizing the metal–solution interface depicted in Figure

2.8(a), where the three essential parameters are R_s (the solution resistance), C_{dl} (the capacitance of the double layer), and R_p (the polarization resistance). The equivalent circuit of a metal with porous insulating coating is given in Figure 2.8(b) where C_c is coating capacitance, R_{po} is pore resistance and R_{ct} is charge transfer resistance, polarization is changed to charge transfer (Ahmad, 2006).

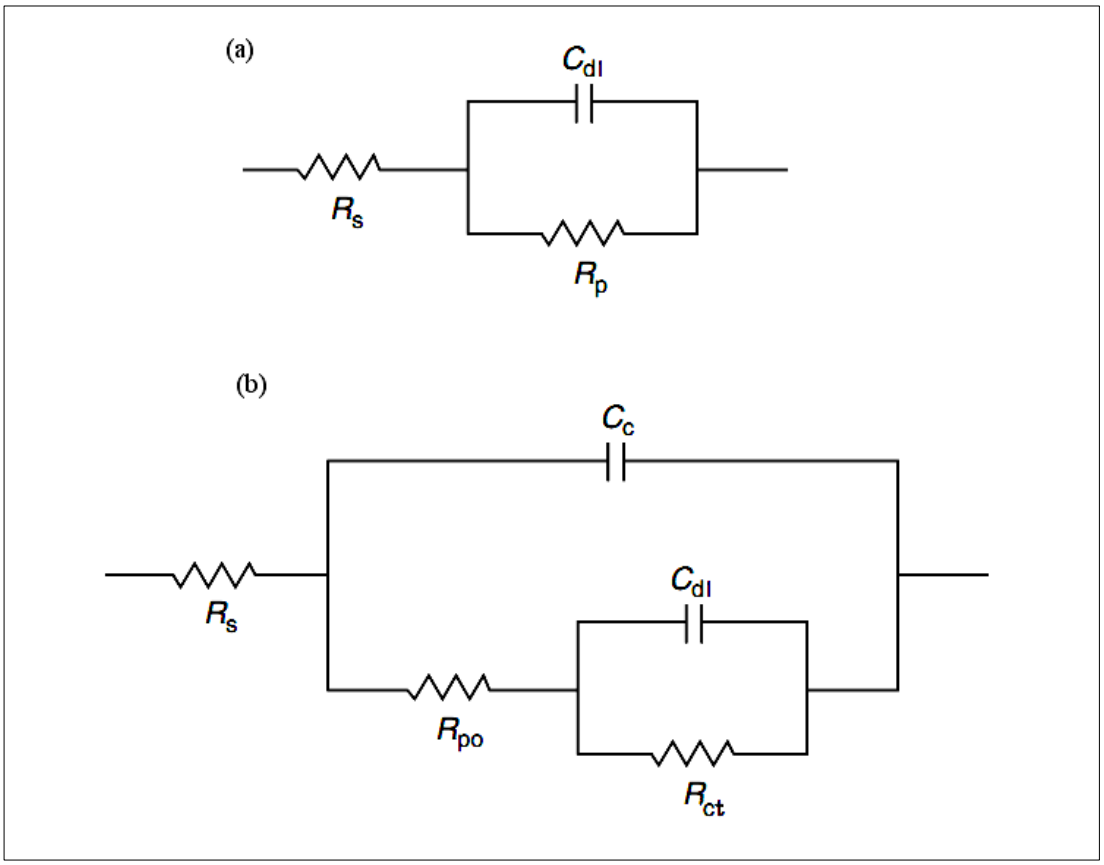

Figure 2.8 Equivalent circuit for (a) a bare metal and (b) a metal with porous insulating coating

Nyquist and Bode plots for the circuit in Figure 2.8(b) are given in Figure 2.9(a) and (b), respectively. On extrapolation to the log Z-axis, the value of C_c (coating capacitance) and C_{dl} (double layer capacitance) are obtained, as well as the values of R_s, R_{ct} and R_{po}, the pore resistance, which indicates the resistance of the insulating coating on any metallic surface.

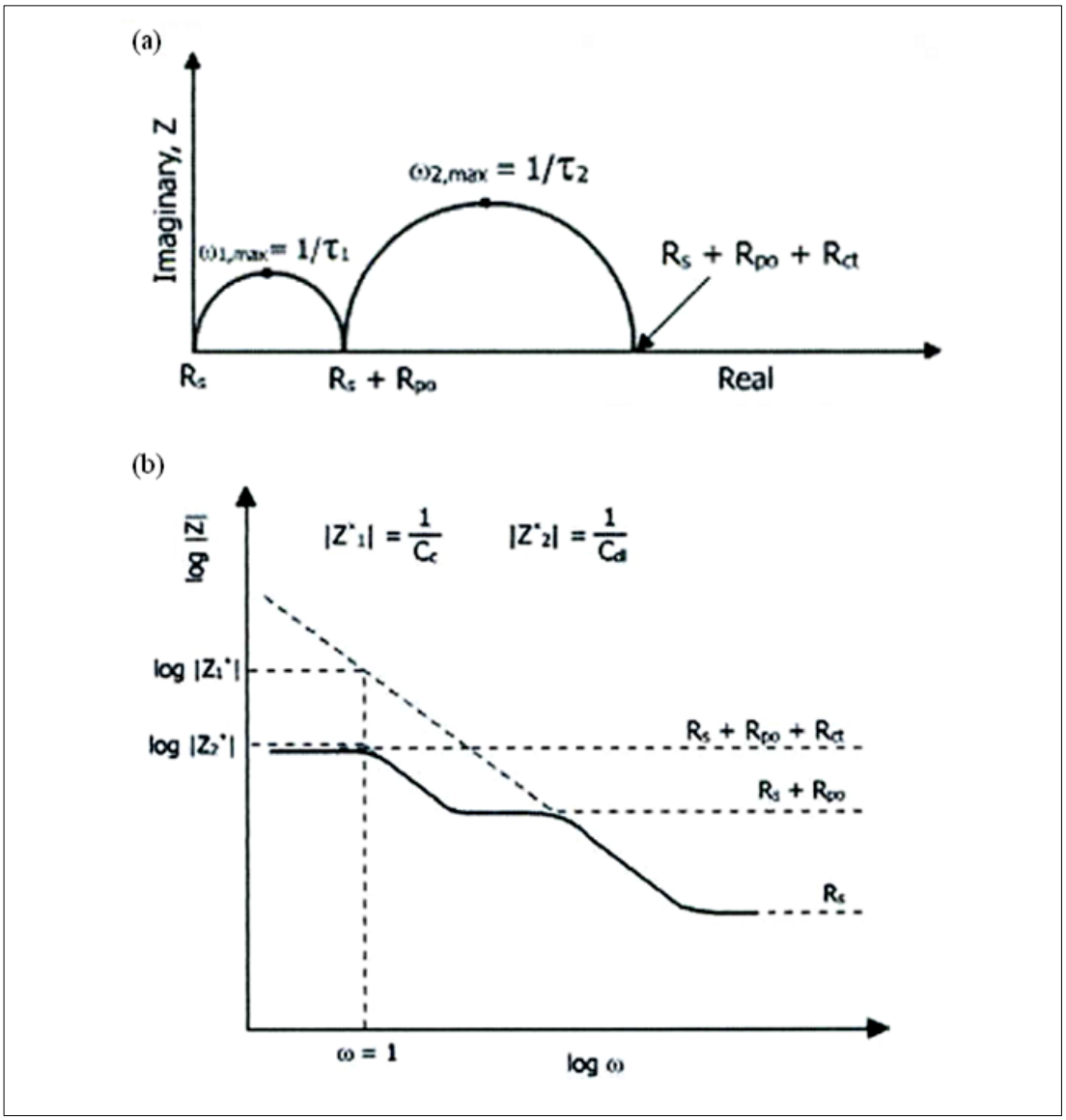

Figure 2.9 (a) Nyquist plot and (b) Bode plot for a metal with porous insulating coating (Ahmad, 2006)

2.4.2.2 Potentiodynamic polarization

Polarization curves can be recorded with the aim to investigate passivation properties of materials, to clarify environmental effects, and to determine corrosion rates in galvanic and crevice corrosion, critical potential for pitting corrosion, as well as potential ranges where the material is liable to stress corrosion cracking (Bardal, 2004). Two main parameters are defined from polarization curves; corrosion

potential, E_{corr} and corrosion current I_{corr} (corrosion rate). The slopes of polarization curves, called Tafel slopes, define the large or small difficulty of anodic and cathodic processes. A degree of polarization is a measure of how the rates of anodic and cathodic reactions are influenced by various environmental (concentrations of dissolved oxygen, cations, anions, pH, temperature, agitation in solution) and surface processes (electrochemical reactions, adsorption, film formation) factors (Groysman, 2010).

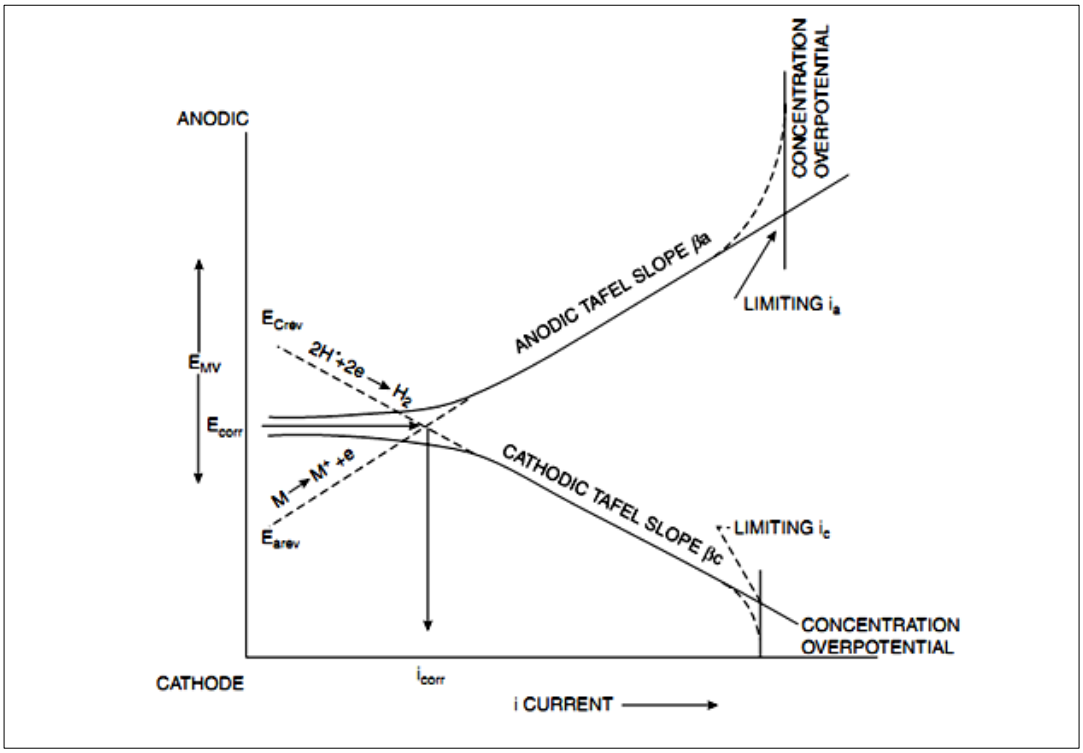

Figure 2.10 A hypothetical Tafel plot (Sastri *et al.*, 2007)

β_a and β_c are known as the anodic and cathodic Tafel constants. Tafel plots are useful in obtaining corrosion rates. Consider a sample of metal polarized 300 mV anodically and 300 mV cathodically from the corrosion potential E_{corr}. The potential scan rate may be 0.1–1.0 mV s^{-1}. The resulting current is plotted on a logarithmic scale. The plot is shown in Figure 2.10. The corrosion current i_{corr} is obtained from the plot by extrapolation of the linear portions of the anodic and cathodic branches of

the curve to the corrosion potential E_{corr}. The corrosion current may then be used to calculate the corrosion rate using the following equation (Sastri *et al.*, 2007):

$$\text{Corrosion rate (mpy)} = \frac{0.13\, i_{corr}\,(\text{EW})}{d} \tag{2.19}$$

Where i_{corr} is corrosion current density, (μA cm^{-2}), d, the density of the corroding metal (g cm^{-3}) and EW is the equivalent weight of the corroding metal (g). Additionally, the polarization resistance, R_p may also be calculated through the Stern-Geary equation (Ahmad, 2006):

$$R_p = \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)} \tag{2.20}$$

2.5 Uncaria gambir

Uncaria gambir is a member of the family *Rubiaceae* and genus *Uncaria* (Apea-Bah *et al.*, 2009). It is common in Malaysia, Singapore and Indonesia for its purpose in tanning and chewing with betel (Hayani, 2003). Gambir, the dried extract of young leaves of *Uncaria gambir*, is also used as an astringent medicine to treat diarrhoea and sore throat in Southeast Asia (Taniguchi *et al.*, 2007). Gambir plant can grow about eight feet high and has oval shaped leaves around 8 to 14 cm in length with 4 to 5 pairs or nerves. The leaves of the plant contain a kind of tannin called catechin which contains high value of pH, making it acidic (Suan, 2009). It has been reported that the main component in gambir is catechin and catechin anhydride (Taniguchi *et al.*, 2007; Muchtar *et al.*, 2008). The flowers and leaves of *Uncaria gambir* are shown in Figure 2.5.

Figure 2.11 *Uncaria gambir* plant (Raintree, 1996)

There are various techniques of extraction to produce gambir cube from its plant. Traditional gambir was prepared by boiling the young leaves and twigs of gambir. After the extract liquid was cooled, it was pressed mechanically to extract the juice. The juice was then dried into semi-solid paste, moulded and then dried (Hayani, 2003). There are different ways of moulding the final produce, in a block, cube or cake form.

2.5.1 The chemistry of gambir

In 1921, Thorpe and Whiteley had done a research to evaluate the chemical composition of gambir (Amos, 2010). Overall gambir consists of following chemicals; catechin 7-33%; catechin anhydride 20-55%; pyrocatechol 20-30%; gambir fluorescein 1-3%, red catechu 3-5%; quercetin 2-4%; fixed oil 1-2%; wax 1-2%; and a little trace of alkaloid. Hayani (2003) studied the catechin content in gambir from different methods of extraction using spectrophotometry. It was found that the percentage yield of catechin extracted is dependent on temperature while

Amos (2010) described that the composition of chemical contents of gambir depends heavily on the processing method or the handling method utilized on the gambir leaves. Every gambir central production region has specific and unique processing method hence each product has different chemical content. Risfaheri and Yanti (1993) reported younger leaves of gambir had produced higher yield and catechin content compared to older leaves.

Nonaka and Nishioka (1980) had isolated seven new biflavonoids from gambir which are gambiriin A1, A2, A3, B1, B2, B3 and C. Besides that, Taniguchi *et al.* (2007) also isolated four chalcane-flavan dimers, gambiriin A1, A2, B1, and B2, in addition to (+)-catechin, (+)-epicatechin, and dimeric proanthocyanidins, procyanidin B1, procyanidin B3, and gambiriin C. The characterization of these biflavanoids has been done using mass spectrometry, ^{1}H and ^{13}C NMR, reverse phase-high performance liquid chromatography (RP-HPLC) and gel permeation chromatography (GPC). The antioxidant activities of gambir has been evaluated by Anggraini *et al.* (2011) and Apea-Bah *et al.* (2009) using 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical scavenging assay. It was found that all the tested gambir extracts had high antioxidant content due to high catechin content in gambir.

The presence of catechin influences the antioxidant properties in gambir hence attracted researchers to study deeper into its application. Hussin (2010) revealed that gambir extract has the ability to inhibit corrosion of mild steel in acidic condition. The highest percentage of inhibition efficiency (IE) from all tests was found to be more than 90% at the concentration of 1000 ppm which concluded that gambir as a good corrosion inhibitor. Suan (2009) had performed a study on the transformation of rust by gambir. Based on the FTIR analysis, lepidocrocite (γ-FeOOH) was found to be the fastest to transform, followed by goethite (α-FeOOH) and finally magnetite

(Fe_3O_4). Other researchers, (Lucida *et al*., 2007) formulated gambir as one of the component in mouth antiseptic. However, further research needed to be done to improve the stability and solubility of catechin in the formulation. Achmad (2012) had modified the gambir extract to act as adsorbent to adsorb selected dyes. The adsorption capacities for Methylene Blue, Sunset Yellow FCF and Direct Red 23 were 149.3 mg g^{-1}, 6.4 mg g^{-1} and 26.3 mg g^{-1}, respectively and were well described by the Langmuir isotherm.

2.6 Catechin

Polyphenols are widely distributed in plants and are known to exhibit higher antioxidant activities. Flavonoids are the most common groups of polyphenols. Catechin belongs to the group flavonoid, which have a C6-C3-C6 skeletal and composed of two aromatic rings as shown in Figure 2.11. Catechin possesses four -OH phenolic groups which are located in two benzene rings connected via a non-aromatic ring. The non-aromatic ring consists of oxygen atom (C-O-C group) and one -OH group, hence makes catechin a non-planar molecule.

According to Friedman and Jurgens (2000), the meta-position of the phenolic groups in the first ring cannot form a quinone but the ortho-position of the phenolic groups in the second ring can react to form quinone. The spatial arrangement of polyphenol molecules is important for their stability against pH, because susceptibility to a chemical reaction will depend on –OH and π-electron system.

There are several compounds of the catechin family which include (-)-Gallocatechin, (-)-Epigallocatechin, (-)-Epigallocatechin gallate, (-)-Gallocatechin gallate, (-)-Epicatechin gallate and (-)-Catechin gallate (Kito *et al.*, 1968). Condensed tannins are polymers of flavan-3-ols (catechins) or flavan-3,4-diols or a combination of both.