Novel electrochemical method for monitoring and predicting localized corrosion

Naing Naing Aung

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Novel Electrochemical Method For Monitoring and Predicting Localized Corrosion

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School of Materials Science and Engineering

A thesis submitted to the Nanyang Technological University
in fulfilment of the requirement for the degree of
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LIST OF SYMBOLS AND ABBREVIATIONS

Symbol/Abbreviation	Explanation
ρ	Density of electrode material
α	Coefficients related to the potential drop through the electrochemical double layer
β_a, β_c	Anodic and cathodic Tafel slopes
β_{ak}	Tafel slope for anodic polarisation of wire k in a WBE
β_{ck}	Tafel slope for cathodic polarisation of wire k in a WBE
η	Overpotential
η_k	Overpotential of wire k in a WBE
σ_i	Standard deviation of the current
σ_v	Standard deviation of the voltage
$[Ox]$	Concentration of oxidized species
$[Ox]_k$	Local reactant concentration over WBE surface
$[Re]$	Concentration of reduced species
$[Re]_k$	Local product concentration over WBE surface
a, b	Characteristic constants of the electrode system
A	Constant (10^{-3} - 10^{-4}) that determines the width of the passivation peak
<i>AES</i>	Auger Electron Spectroscopy
<i>B</i>	Stern-Geary Constant
CR_k	Corrosion rate of wire k in a WBE
<i>CUI</i>	Corrosion Under Insulation

C_{dl}	Double layer capacitance
C_0	Concentration of oxidant at the electrode surface
C_0'	Concentration of oxidant in the bulk
C_R	Concentration of reductant at the electrode surface
C_R'	Concentration of reductant in the bulk
E	Actual reversible potential of an electrode
EIS	Electrochemical impedance spectroscopy
ENA	Electrochemical Noise Analysis
E_{br}	Break down potential
E^o	Standard reversible potential of the electrode couple
E_{corr}	Corrosion potential or open circuit potential
E_k	Corrosion potential of wire k in a WBE
E_{ka}	Equilibrium potential of the anodic reaction of wire k in a WBE
E_{kc}	Equilibrium potential of the cathodic reaction of wire k in a WBE
E_m	Maximum potential
E_o^k	Standard potential of wire k in a WBE
E_{pit}	Pitting potential
E_p	Repassivation potential
E_{sys}	Overall system potential of a WBE
E_w	Equivalent weight of the electrode
F	Faraday constant
i	Measured current density
i_{avg}	Average anodic current density
i_{corr}	Corrosion current density

i_{cp}	Critical passivation current
I_{gk}	Galvanic corrosion current of wire k in a WBE
I_k	Corrosion current of wire k in a WBE
I_{ka}	Anodic reaction current of wire k in a WBE
I_{kc}	Cathodic reaction current of wire k in a WBE
i_{max}	Maximum anodic current density
i_o	Exchange current density
i_{rms}	Root mean square (rms) of the current
i_{tot}	Total anodic current density
I_a	Anodic currents over the total surface
I_f	Anodic currents on the filmed areas
I_u	Anodic currents on the unfilmed areas
LI	Localization Index
LP	Localization Parameter
LPR	Linear Polarization Resistance
mA	Milliampere
mV	Millivolt
n, n'	Number of electrons transferred in the anodic and cathodic reactions
N_a	Number of anodes
p	Constant used to shape the passivation peak (two symmetrical; 2–3 asymmetrical)
R	Universal gas constant
R_n	Electrochemical noise resistance
R_n^k	Electrochemical noise resistance of wire k in a WBE
R_p	Polarization resistance

R_p^k	Polarization resistance of wire k in a WBE
R_s	Solution resistance
S	Fraction of the metal area which is unfilmed
$(1-S)$	Fraction of the metal area which is filmed
SCE	Saturated Calomel Electrode
SHE	Standard Hydrogen Electrode
$SKPFM$	Scanning Kelvin Probe Force Microscopy
$SRET$	Scanning Reference Electrode Technique
T	Absolute temperature
T_k	Local temperature over a steady-state WBE surface
WBE	Wire Beam Electrode
XPS	X-ray Photoelectron Spectroscopy
$XAFS$	X-ray Absorption Fine Structures
$XANES$	X-ray Absorption Near Edge Structures
Z_ω	Impedance
Z_{re}, jZ_{im}	Real and imaginary components of the impedance

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ABSTRACT

This PhD research project was conducted to develop new electrochemical methods for studying localized corrosion processes in various environments. An electrochemically integrated multi-electrode array, namely the wire beam electrode (WBE) and electrochemical noise analysis (ENA) was applied in novel combinations to study several typical localized corrosion systems in a creative manner.

It was found that the WBE-ENA method was able to identify characteristic electrochemical noise signatures and to correlate them with localized corrosion behaviour. Specifically, characteristic electrochemical noise signatures were found to correlate with characteristic changes in WBE current distribution maps which indicate corrosion rates distributions, corrosion patterns and the degree of localized corrosion. A new concept, namely localization parameter (*LP*) was proposed. *LP* is a parameter for quantifying the degree of localized corrosion based on maximum anodic current density, total anodic current density, and the number of anodes in WBE current distribution maps.

During pitting corrosion processes, three characteristic noise patterns were observed: (i) the characteristic *peak* of rapid potential transient, towards less negative direction, followed by recovery (termed *noise signature I*) was found to correlate with the sudden disappearance of one or a few unstable anodes (ii) the characteristic noise pattern of quick potential change towards less negative direction followed by no recovery (termed *noise signature II*) was found to correspond with the massive disappearance of minor anodes leading to the formation of highly localized major anodes and (iii) the characteristic noise pattern of quick potential change towards more negative direction with no recovery (termed *noise signature III*) was found to correspond with accelerated propagation of stable anodes. In the pit initiation stage, the *LP* was found to decrease significantly and it increased again in the stable pit formation and accelerated stable pit growth stages. Corrosion inhibitors such as potassium dichromate, cerium chloride and lanthanum chloride were found to affect the pitting corrosion process and noise signatures. For instance, potassium dichromate effectively inhibited the pitting corrosion process and the *LP* successively

decreased throughout the corrosion process. With the presence of lanthanum chloride (LaCl_3), rapid potential transient towards more negative direction followed by exponential recovery (termed *noise signature IV*) was found to correlate with the initiation of new anodes and increase in the *LP*.

Characteristic noise patterns were also observed during the crevice corrosion process: (i) the characteristic noise pattern of quick potential changes towards more negative direction with no recovery (*noise signature III*) was found to correspond with the initiation and stabilization of anode inside crevice and (ii) the characteristic noise pattern of the cyclic potential oscillation at a constant frequency (termed *noise signature V*) was found to correspond with the stable anodic dissolution in the occluded cavity site in WBE current distribution maps. The *LP* for crevice corrosion was found to be low compared to that for pitting corrosion.

Several novel experimental methods were developed in order to explore the ability of the WBE and ENA for studying localized corrosion under buried conditions, under deposits and under atmospheric exposure. For the first time the WBE has been applied to monitor the penetration of corrosive species under buried conditions and to monitor the effects of ion movement on corrosion processes under simulated atmospheric corrosion conditions. This method was found to be an effective tool of studying the effects of ion diffusion on electrochemical corrosion processes and patterns. Corrosion of carbon steel buried in dry, moist and chlorinated sand, and corrosion of aluminium buried under insulation materials such as rock wool, glass wool, cotton wool and industrial tissue paper were also successfully monitored.

CHAPTER 1

INTRODUCTION

1.1 Background

Corrosion is known as a materials cancer that causes pre-mature failure of industrial and civil structures. In industry, corrosion is not only an economic, but also a safety and reliability concern. For instance, in the petrochemical industry, corrosion, especially localized corrosion is a predominant factor in causing the failure of piping and equipment, resulting in a substantial increase in the operating and maintenance costs of petrochemical plants and in some cases, extremely expensive and unscheduled shutdowns.

The most dangerous form of corrosion is localized corrosion rather than uniform or general corrosion. Localized corrosion may be in the form of pits, cavities or crevice damages and it may develop under various conditions. It results in high rates of metal penetration at specific sites and leads to catastrophic failure despite the fact that the majority of the metal surface may not be corroded. The monitoring and detection technique which gives real-time indications of localized corrosion penetration rate could be a highly desirable tool in the optimization of the performance of engineering components in a localized corrosion environment. However, there are currently many unanswered questions/difficulties regarding localized corrosion and in particular, major difficulties in its monitoring. They are described below.

a. Determination of Instantaneous Localized Corrosion Rates and Patterns

Visual examination, weight loss measurement, optical and scanning electron microscope observation are traditionally used to determine localized corrosion rates and patterns. However, these techniques are unable to determine instantaneous

localized corrosion rates or patterns. The requirement of the specimen removal from the electrolyte may alter and/or stop corrosion processes under investigation.

To characterize a localized corrosion process electrochemically, electrochemical parameters at local areas of a working electrode surface such as local anodic reaction current have to be determined. However, conventional electrochemical techniques face major difficulties in this respect. This is mainly because conventional electrochemical techniques use a one-piece electrode, constructed by a single piece of metal of a chosen size. Normally when such a one-piece electrode is used, only mixed and averaged electrochemical parameters over the whole electrode surface are measurable. These measured electrochemical parameters are neither related specifically to the anodic zone nor to the cathodic zone of the heterogeneous electrode surface. Moreover, with a one-piece electrode, it is impossible to measure the galvanic currents that flow in the electrode body between localized anodic and cathodic sites since an ammeter cannot be inserted between anodic and cathodic sites which are located on a single piece of metal surface.

Furthermore, conventional electrochemical techniques have limitations in determining the kinetics of a localized corrosion process. The fundamental formulation describing the electrochemical kinetics over a metal surface, the Butler-Volmer equation, is based on a uniform electrochemical mechanism. Traditional electrochemical techniques which are based on the Butler-Volmer equation such as the Tafel polarization method, the linear polarization method, cyclic polarization method and the AC impedance, are in principle, only applicable to measure the electrochemical kinetics of a uniform electrode surface (Tan, 1998).

Relatively new electrochemical techniques such as the scanning reference electrode (SRET) (Isaacs, 1974; Isaacs & Vyas, 1981), the scanning Kelvin probe force microscopy (SKPFM) (Frankel & Leblanc, 2002) have been applied as *in situ* techniques to map potential differences over an electrode surface and thus to detect localized corrosion patterns. These techniques, however, may not be suitable for monitoring certain types of localized corrosion such as crevice corrosion.

Among the existing methods, the electrochemical noise method is the most promising technique for monitoring the stochastic nature of localized corrosion (Dawson & Hladky, 1982; Dawson & Searson, 1988; Pistorius, 1996; Pride *et al.*, 1996). Two major applications of electrochemical noise analysis have been developed: (i) the noise resistance method was developed to determine general corrosion rates (Mansfeld & Xiao, 1993; Tan *et al.*, 1996; Bertocci *et al.*, 1997) and (ii) the noise signature method that was proposed to detect localized corrosion by recognizing characteristic noise patterns in the time domain (Dawson & Hladky, 1981) or in the frequency domain (Dawson & Hladky, 1982). Usually, the researchers studying the application of noise signatures to the identification of localized corrosion have related certain characteristic noise features observed during certain periods of experiment to localized corrosion such as pits that were identified visually or microscopically after experiment was completed (Bertocci *et al.*, 1983; Gabrielli *et al.*, 1983; Williams *et al.*, 1983a; Bertocci & Ye, 1984; Pistorius, 1996; Ferreira & Simoes, 1987; Heusler & Nachstedt, 1988; Bertocci, 1989; Okada, 1990; Fukuda & Mizuno, 1996; Tan *et al.*, 1998; Cottis *et al.*, 1998; Cheng & Luo, 1999; Cottis, 2001; Aballe *et al.*, 2001b; Smulko *et al.*, 2002a). Attempts have also been made to correlate electrochemical noise with the corrosion processes using optical microscopy and computer visualization in combination with simultaneous measurements of electrochemical noise (Legat *et al.*, 1998; Legat, 2000).

Although noise signatures have attracted most interests due to the possibility of localized corrosion identification and quantification, their applications still remains a rather controversial issue. One problem is the lack of proper experimental methods that could be used to directly correlate noise signatures to localized corrosion activities occurring at a specific location of an electrode surface. Another problem is that the exact origination process of electrochemical noise has not yet been clearly identified, although electrochemical heterogeneity has been recognized to play a critical role in electrode noise origination (Wojtowicz, 1973; McClintock, 1999) and also partly due to various mathematical models that have been employed in understanding electrode potential and current fluctuations (Gabrielli *et al.*, 1991; Hashimoto *et al.*, 1992).

b. Insufficient Understanding of Localized Corrosion Mechanism

Many researchers have worked to improve the understanding of localized corrosion mechanism during the past three decades (Galvele, 1976; Bertocci & Ye, 1984; Ferreira & Simoes, 1987; Coudreuse & Magnin, 1987; Roberge *et al.*, 1989; Roberge, 1993; Okada, 1990; Frankel, 1998; Klassen *et al.*, 2001; Vera Cruz *et al.*, 2003). Various theoretical models have been developed to understand the processes that lead to the initiation of localized corrosion (Szklaarska-Smialowska, 1986; Sykes, 1997). For instance, the initiation of localized corrosion has been interpreted in terms of thermodynamic equilibrium between passive films and salts (Vetter, 1971), movement of point defects within a passive film (Macdonald & Urquidí-Macdonald, 1986, 1987) or local thinning of passive films (Okada, 1990; Schaepers & Strehblow, 1995). In some cases (e.g., in CO₂ corrosion), localized corrosion may also be initiated by fluid flow (Schmitt *et al.*, 1999, Halvorsen & Sontvedt 1999). The pitting and repassivation potentials have been proposed as *characteristic parameters* for the initiation of localized corrosion (Wilde & Williams, 1971; Kiourtsidis *et al.*, 1999). Pitting was also found to initiate when the corrosion potential of the metal exceeds the pitting potential whereas existing pits or crevices cease to grow at potentials below the repassivation potential (Duquette & Lu, 1990; Pride *et al.*, 1994; Dimitrov *et al.*, 2000; Frankel & Zhang, 2003). In particular, the repassivation potential has been shown to be a parameter for the long-term prediction of the occurrence of localized corrosion (Dunn & Sridhar, 1997). The factors influencing growth and repassivation of metastable pits have been reported to include alloy composition, potential, chloride concentration, inclusions, inhibitors, etc. (Galvele, 1976, 1981; Frankel, 1998).

Despite major achievements made in the field of localized corrosion, some key questions remain controversial. For instance, there is insufficient understanding of the processes that lead to the breakdown of the passive film which initiate the nucleation of a metastable pit and cause pits to grow, terminate (Natishan *et al.*, 1996; Kelly *et al.*, 1999; Frankel & Scully, 2001; Szklaarska-Smialowska, 2002a).

1.2 Objectives and Scope

The main objective of this research work is to address some of the unanswered questions regarding localized corrosion monitoring and, in particular, localized corrosion mechanism.

This research work also endeavours to-

- Develop a novel electrochemical method for monitoring and predicting localized corrosion using the wire beam electrode (WBE) and electrochemical noise analysis (ENA) methods, and their combination in a creative way. Since the ENA method has been reported to be useful for detecting the initiation stage of localized corrosion by detecting typical potential and current noise signatures and the WBE is uniquely able to measure the propagation and growth stages of localized corrosion by measuring the distribution maps of non-uniform corrosion potential and current over a WBE surface, combination of the two methods could enable the monitoring of the initiation, propagation, growth and repassivation processes of localized corrosion.

- Develop novel electrochemical experiments for monitoring and predicting corrosion of major engineering materials under critical corrosion environments. Specifically, focus is on the monitoring of localized corrosion of stainless steel and carbon steel under two important and typical localized corrosion conditions, submerged and buried corrosion.

It is expected that this research will lead to better knowledge of localized corrosion mechanism of major metallic materials in critical environments, and result in better understanding of the electrochemical phenomenon in corrosion systems.

CHAPTER 2

LITERATURE REVIEW: LOCALIZED CORROSION AND ITS MONITORING TECHNIQUES

This chapter presents a literature review on electrochemical principles of metal corrosion, localized corrosion and its affecting factors, and also on conventional and new electrochemical methods for studying localized corrosion.

2.1 Electrochemical Principles of Metal Corrosion

2.1.1 Electrochemical Corrosion Cells and Reactions

Aqueous metal corrosion occurs mainly through the action of the electrochemical cell. Electrochemical corrosion cell involves two half-cell reactions; an oxidation reaction at the anode and a reduction reaction at the cathode. An electrically conductive path must exist between cathodic and anodic sites via the metal and an ionically conductive path through the electrolyte. The mass transfer, chemical reaction and physical state change are the sequential steps of electrochemical processes occurring at the anode and cathode.

The anodic process in an electrochemical corrosion cell is usually the metal dissolution, although other oxidation reaction may also occur. In natural aqueous environment, hydrogen evolution and oxygen reduction are the most common cathodic processes. Hydrogen evolution ($2H^+ + 2e^- \rightarrow H_2$) predominates in acidic environments. Oxygen reduction ($O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$) predominates in neutral and alkaline conditions. The half-cell reactions occur at microscopic anodes and cathodes covering a corroding surface. Macroscopic anodes and cathodes can develop as corrosion damage progresses with time. The half-cell reactions can take place on one metal or on two dissimilar metals that are electrically connected. Examples of electrochemical cells include galvanic cells (cells made up of

electrodes of two different substances) and concentration cells (cells containing electrodes of the same substance under different conditions of concentration). Figure 2.1 shows the schematic representation of a typical iron electrochemical corrosion cell.

Figure 2.1 Schematic representation of electrochemical corrosion cell over an iron electrode under near neutral pH conditions (Source: Chamberlain & Trethewey, 1995)

2.1.2 Fundamental Theories for Electrochemical Corrosion

a. Electrochemical Corrosion Thermodynamics

Each half-cell reaction has a characteristic potential compared to a standard reference electrode. All other half-cell potentials are calculated with respect to the standard hydrogen reference electrode (SHE). It is universally accepted that a hydrogen-hydrogen ion half-cell potential is zero when the hydrogen ion activity is unity. For a simple reversible electrode reaction, $Re \rightleftharpoons Ox + ne^-$, the rate of the forward reaction is independent of $[Ox]$ whereas the rate of the reverse reaction is proportional to $[Ox]$. As a result of the exponential dependence of rate of reaction on potential, the reversible equilibrium potential of an electrode E , can be linked to the standard reversible potential of an electrode reaction E^0 , by the Nernst equation

[Kelly *et al.*, 2003]. The Nernst equation describes the electrode potential of a half-cell reaction as a function of ionic concentrations as shown in equation 2.1.

$$E = E^0 + \frac{RT}{nF} \ln \frac{[Ox]}{[Re]} \quad (2.1)$$

where R = Universal gas constant

T = Absolute temperature in degrees Kelvin

n = Charge number of the electrode reaction

F = Faraday constant ($96500 \text{ C mole}^{-1}$)

$[Ox]$ = Concentration of oxidized species

$[Re]$ = Concentration of reduced species

Through the use of the Nernst equation, the Pourbaix diagram (Pourbaix, 1966) can be constructed as a function of potential and pH. The Pourbaix E-pH diagram gives the electrochemical thermodynamic behaviour of a metal under specific conditions and thus, it is widely used to evaluate the thermodynamics of an electrochemical corrosion reaction. Figure 2.2 shows a typical version of the Pourbaix diagram for the iron-water system at ambient temperature. This Pourbaix diagram enables the determination by means of potential and pH measurements. It gives information about a metal surface whether it is in a region of immunity where the tendency for corrosion is nil, or in a region where the tendency for corrosion is high, or in a region where the tendency for corrosion may still exist but where there is also a tendency for a protective or passive film to exist.

However, the thermodynamically derived Pourbaix diagram only provides information on corrosion tendency. It cannot be used to evaluate the rate of a corrosion reaction.

Figure 2.2 Pourbaix diagrams showing the conditions of corrosion, immunity, and passivation for iron-water system at 25°C (Source: Verink, 2000)

b. Electrochemical Corrosion Kinetics

The electrochemical kinetics of the anodic and cathodic processes determines corrosion rates. The kinetics of corrosion depends on various factors such as overpotential, exchange current density and the availability of reactants. The amount by which a potential deviates away from equilibrium is called the overpotential. For a given overpotential, the magnitude of reaction current flow can depend on a number of factors; including the charge transfer rate between solution species and the electrode, and mass transfer by diffusion, convection, and migration. Positive overpotentials enhance oxidation reactions on the electrode whereas negative overpotentials enhance reduction reactions to occur.

If an electrochemical reaction is under active control i.e. the electrode kinetics limits the current flow, the Butler-Volmer equation (Butler, 1924a; Butler,

1924b; Erdey-Gruz & Volmer, 1930) can be used to describe the kinetics of anodic and cathodic half-cell reactions as follows:

$$i = i_0 \left[\exp \frac{\alpha \eta n F}{RT} - \exp \frac{(1 - \alpha) \eta n' F}{RT} \right] \quad (2.2)$$

where i = Measured current density

i_0 = Exchange current density

η = Overpotential ($E - E_{corr}$)

α = Coefficient related to the potential drop through the electrochemical double layer

n, n' = Number of electrons transferred in the anodic and cathodic reactions

F = Faraday's constant

R = Gas constant and

T = Absolute temperature

The Butler-Volmer equation is fundamentally important for predicting the electrode reaction kinetics as a function of potential and forms the basis of corrosion rate measurements.

Electrode kinetics data are typically presented in a graphical form called polarization diagrams or mixed potential diagrams (i.e. the Evans plot, Figure 2.3). Both the Evans diagram and polarization curves can be used to describe a metal corrosion system. They are related, but different. The Evans diagrams are simplified plots of anodic and cathodic reaction curves of an electrochemical system while the polarization curves describe the potential current density behavior obtained experimentally by applying an external potential or current (Beaudoin & Ramachandran, 2001).

In 1938 Wagner-Truad mixed potential theory was first time used to explain the concepts of local anodes and cathodes operating at a mixed potential. According to the mixed-potential theory, any electrochemical reaction can be algebraically divided into separate oxidation and reduction reactions with no net accumulation of electrical charge. In the absence of an externally applied potential, oxidation of the metal and reduction of some species in solution occur simultaneously at a metal/electrolyte interface. Under these circumstances, the net measurable current is

zero and the corroding metal is charge neutral, with no net accumulation of charge. Corrosion is a typical mixed electrode process and mixed potential diagrams can be constructed to model a corrosion electrochemical cell:

Figure 2.3 Mixed potential diagram for iron corrosion in deaerated neutral solution at 25°C (Source: Fontana & Greene, 1978)

Based on the mixed-potential theory, the original Butler-Volmer equation has been modified into a form for corrosion kinetic calculations as follows:

$$i = i_{corr} \left[\exp \frac{\alpha \eta n F}{RT} - \exp \frac{(1 - \alpha) \eta n' F}{RT} \right] \quad (2.3)$$

If $\beta_a = \frac{2.3RT}{\alpha n F}$ for anodic reaction and $\beta_c = \frac{2.3RT}{(1 - \alpha) n' F}$ for cathodic reaction, the

equation (2.3) can be rewritten as:

$$i = i_{corr} \left[\exp \frac{2.3\eta}{\beta_a} - \exp \frac{2.3\eta}{\beta_c} \right] \quad (2.4)$$

For large anodic overpotentials ($\eta/\beta_a \gg 1$) and large cathodic overpotentials ($\eta/\beta_c \gg -1$), the Butler-Volmer equation can be simplified to lead to the Tafel equation (Tafel, 1905). Tafel equation relates polarization, η , to the rate, i_{corr} , and the overpotential can be considered as logarithmically dependent on the current density as described by the following equation.

$$\eta = a \pm b \log|i| \quad (2.5)$$

a and b are characteristic constants of the electrode system; b is the Tafel slope that provides information about the mechanism of the reaction, and a provides information about the rate constant of the reaction. The Tafel equation holds only for relatively high overpotentials, approximately 0.1 volt or higher.

It should be noted that the Butler-Volmer equation describes only *idealized* active controlled electrode, it is not applicable to situations where corrosion kinetics are controlled by mass transport of oxygen or other reactant molecules/ions from the bulk electrolyte. Under such diffusion restrictions, the cathodic reaction is no longer under activation control and the Butler-Volmer equation has to be modified (Rothwell & Tullmin, 2000).

In order to determine the corrosion rate without significantly damaging the test electrode, the Stern-Geary equation has been developed as a simplified form of the Butler-Volmer equation (Geary & Stern, 1957). Stern and Geary simplified the kinetics expression to provide an approximation to the charge transfer controlled reaction kinetics given by equation (2.6). In the Stern-Geary equation the corrosion current density can be derived from the polarization resistance which is defined as the tangent of polarization curve at the corrosion potential, and Stern-Geary constant, B . This equation is widely used in electrochemical corrosion (e.g. Rothwell & Tullmin, 2000):

$$i_{corr} = \frac{\beta_a \beta_c}{2.3 (\beta_a + \beta_c) R_p} = \frac{B}{R_p} \quad (2.6)$$

where i_{corr} = Corrosion current density

β_a, β_c = Anodic and cathodic Tafel slopes

R_p = Polarization resistance

The β_a and β_c are normally determined by Tafel curve or they can also be estimated by linear polarization measurement (EG&G Princeton Applied Research, 1993). The polarization resistance R_p is the key to corrosion rate measurement.

2.2 Localized Corrosion and Its Affecting Factors

Electrochemical corrosion theory suggests that uniform corrosion occurs when localized anodic and cathodic sites are sufficiently small and randomly distributed over an electrode surface. Uniform corrosion occurs at predictable rates and thus it is the least dangerous form of corrosion. It is the only form of corrosion whereby metal weight loss data from corrosion coupons can be used to accurately and reliably estimate corrosion rates.

However, in most practical corrosion environments, as shown in Figure 2.4, usually the anodes and the cathodes of an electrochemical corrosion cell are not uniformly distributed over an electrode surface. A corroding electrode surface is often electrochemically heterogeneous.

Figure.2.4 Schematic diagram showing the electrochemical heterogeneity over an electrode surface (Source: Tan, 1998)

2.2.1 Electrochemical Heterogeneity and Localized Corrosion

Electrochemical heterogeneity is a natural phenomenon that plays a key role in many significant electrochemical processes such as localized corrosion, cathodic and anodic protection, electro-deposition and electro-machining. Electrochemical heterogeneity can initiate from microscopic and macroscopic heterogeneities of materials and environments, as described in the following paragraphs.

a. Microscopic Heterogeneity in Materials

Variations in the composition of the metal surface, due to the presence of inclusions, different phases, grain boundaries, disturbed metal, and other causes can lead to the establishment of microscopically separated anodic and cathodic sites (Fontana, 1986). This will lead to microscopic electrochemical heterogeneity over an electrode surface and initiate localized corrosion. For instance, pitting corrosion has been reported to preferentially initiate on non-metallic inclusions in stainless steels when exposed to chloride solutions (Baroux, 1988; Jung & Böhm, 2000).

Microscopic heterogeneity in materials can also be resulted from the disruption of a passive film that usually provides a protective barrier to metals and alloys such as stainless steel, aluminium, and titanium (Kruger, 1988). Passive films are sensitive to localized damage. Disruption of the passive film leads to the exposure of bare sites to an environment, causing major microscopic heterogeneity over an electrode surface. For instance, stress in materials has been reported to cause breakdown of the passive film, causing microscopic heterogeneity and localized corrosion (Murata, 1988; Li, 2002).

Microscopic heterogeneity can also be due to roughness of a metal surface. It has been found that a rough surface finish can lead to the nucleation of metastable pitting (Yu Zuo *et al.*, 2002).

b. Macroscopic Heterogeneity in Materials

Macroscopic heterogeneity is usually due to connections of two dissimilar materials. One metal becomes the anode and the other becomes the cathode; i.e. macroscopic electrochemical corrosion cell develops over the metal surface (Fontana, 1986).

There are many localized corrosion problems associated with macroscopic corrosion cell in the joining of dissimilar materials (Pan *et al.*, 1996; Li, & Congleton, 2000). This electrochemical heterogeneity leads to rapid localized corrosion to the less noble metal. It is well known that when two metal pieces are in

electrical contact with each other, a *galvanic cell* forms. A typical example is shown in Figure 2.5.

Figure 2.5 Schematic illustration of macroscopic heterogeneity in environments resulting galvanic corrosion (Source: Murata, 1988)

c. Microscopic Heterogeneity in Environments

The environmental conditions at reacting surfaces could be quite different from those in a bulk solution once reaction initiates, unless the mass transfer of the reacting chemical is extremely fast. For instance, as corrosion proceeds, corrosion products may deposit forming tiny crevices that provide additional environmental change (Murata, 1988). Figure 2.6 shows a schematic illustration of corrosion product deposition on the stainless steel resulting in additional environmental change.

Figure 2.6 Schematic illustration of microscopic heterogeneity in environments resulting tiny crevices corrosion (Source: Murata, 1988)

d. Macroscopic Heterogeneity in Environments

The environments surrounding a metal surface are not generally uniform. For instance, salt and dust deposition can create environmental heterogeneity over a metal surface and corrosion products can accumulate at certain locations. Macroscopic heterogeneity in environments also arises from temperature difference over a metal surface, stress concentration, fluid velocity, and erosion. Variations in the concentration of metal ions or other species and variations of oxygen concentration over a metal surface can result in the establishment of an anode at those sites exposed to the environment containing the lower metal ions or oxygen content (Fontana, 1986).

A typical example of localized corrosion due to macroscopic environmental heterogeneity is corrosion of steel lamp post. Serious corrosion of lamp post usually occurs at a location several centimetres below the soil surface. This is because this location has three most favourable corrosion conditions: high level of moisture, high oxygen content, and the existence of crevice between the lamp post and soil. Oxygen concentration cell effects and chemistry changes in the crevice area lead to rapid crevice corrosion at the location.

The various factors affecting electrochemical heterogeneity and localized corrosion may overlap with each other under given conditions. The transition from microscopic corrosion reactions to macroscopic ones is not yet fully understood.

2.2.2 Major Forms of Localized Corrosion

Electrochemical heterogeneity is the root cause of many forms of localized corrosion. Due to various forms of electrochemical heterogeneity, various forms of localized corrosion are encountered. The most important and common forms of localized corrosion include pitting and crevice corrosion.

a. Pitting Corrosion

Pitting is the most common form of localized corrosion and is also the root of many other forms of localized corrosion failures (Dabosi *et al.*, 1994). Pitting corrosion is due to major electrochemical heterogeneity, often as a result of a puncture in the passive film. During pitting corrosion, an anode is situated in the pit and a cathode on the surrounding surface. Because of the relatively small anode area, the anodic current density is high and thereby also the corrosion rate. Thus, the cathode/anode area is very unfavourable and pitting penetration can occur in a short period of time. Pitting initiation, repassivation and propagation are the main stages of pitting corrosion (Szkarska-Smialowska, 1986; Böhni, 2000, Frankel, 1998; Frankel & Scully, 2001). They are described below.

Passive Film Breakdown and Pit Initiation: Passive film breakdown is considered to be the first stage of pitting. There are four important conditions for the passive film breakdown that initiates pits are: Critical potential, damaging species, induction time and localized sites. Various models for pitting initiation have been developed that satisfy these four conditions (Uhlig, 1978; Osterwald, 1981; Okada, 1985; Sharland, 1987; Macdonald & Urquidi-Macdonald, 1986, 1987; Dawson & Ferreira, 1986; Okada, 1990; Kudo & Nishimura, 1990; Szkarska-

Smialowska, 2002b; Pagitsas *et al.*, 2003). These can be arranged in three main groups (Szkarska-Smialowska, 2002b).

- The first group of pitting models proposes that before pit nucleation, penetration of Cl^- occurs without destroying the passive film. Dissolution of the metal occurs when Cl^- reaches the metal (Uhlig, 1978; Szkarska-Smialowska, 2002b).
- The next group of models postulates that mechanical breakdown of the passive film precedes local dissolution of the metal initiating pit (Szkarska-Smialowska, 2002b).
- Another group of models assumes local thinning of the passive film until the bare metal is discovered (Osterwald, 1981; Szkarska-Smialowska, 2002b).

In addition, an electrical breakdown model of the passive film was proposed (Szkarska-Smialowska, 2002b) based on the semiconductive properties of passive film.

Metastable Pitting: Metastable pitting refers to a stage that pitting initiates and grows for a limited period before repassivating. At lower potentials pitting initiation is followed by rapid repassivation (Baroux, 1990; Böhm, 2000). Even above the pitting potential, repassivation may still occur, showing the stochastic character of localized corrosion processes.

Pit Growth: When the active state within pits is maintained over an extended period of time, rapid metal dissolution usually occurs. Once a pit starts to grow, major electrochemical heterogeneity is developed that further promotes pit growth. The local pit environment becomes depleted in cathodic reactant (e.g. oxygen), which shifts most of the cathodic reaction to the boldly-exposed surface where this reactant is more plentiful. The pit environment becomes enriched in metal cations and an anionic species such as chloride, which electromigrates into the pit to maintain charge neutrality. The pH in the pit is lower owing to cation hydrolysis:

and the absence of a local cathodic reaction (Frankel, 1998; Frankel & Scully, 2001). The acidic chloride environment generated in pits is aggressive to most metals and tends to propagate the pit growth as indicated in Figure 2.7.

Figure 2.7 Pitting corrosion mechanism in corrosive electrolyte under submerged condition (Source: Fontana, 1986)

b. Crevice Corrosion

A crevice is a narrow gap either between two pieces of metal or between a metal and a tightly adhering material like plastic. Crevice corrosion is a highly localized attack on areas of a metal surface where mass transfer is limited by the system geometry. Crevice corrosion is associated with induction (initiation) and propagation stages.

Crevice Initiation: Depletion of oxygen inside the crevice, increase in acidity and in Cl^- concentration inside the crevice and permanent breakdown of the passive film with local corrosion activation, are the first three steps that are usually considered to constitute the initiation stage (Fontana & Greene, 1967; Ferreira & Simões, 1989; Sharland, 1992; Vajo *et al.*, 2003). When oxygen cannot penetrate a crevice, a differential aeration cell is setup. The environment may change within the crevice, which lowers the equilibrium potential of the metal in the crevice, making it more anodic and the surrounding environment will then act as cathode. As a

consequence, an accumulation of positive metal ions occurs in the solution inside crevice, disturbing the equilibrium of electroneutrality. Anions migrate from the bulk of the solution into the crevice and then lead to acidification of the crevice solution according to the reaction below:

When acidity reaches a critical value, the passive film suffers breakdown leaving the metal exposed.

Crevice Propagation: At the crevice sites, metal dissolution is accelerated, which leads to an increase in the rate of anion migration towards the crevice, and therefore to further acidification, and thereby generating an autocatalytic process. This is the accepted mechanism for the progression stage, which leads to the extension of the areas of attack (Fontana & Greene, 1967; Ferreira & Simões, 1989; Sharland, 1992; Vajo *et al.*, 2003). The phenomenological aspects of crevice corrosion are shown in Figure 2.8. The highly corrosive micro-environment of crevices tends to be similar to the micro-environment established at the base of corrosion pits. The difference between pitting and crevice corrosion is mainly in the initiation phase. The occlusion associated with a crevice provides a ready barrier to transport, making initiation of crevice corrosion easier. Accelerated corrosion in a crevice can initiate at potentials well below the pitting potential, and after considerable periods of exposure no prior evidence of crevice attack is observed (Frankel & Scully, 2001).

Figure 2.8 Crevice corrosion mechanism in corrosive electrolyte under submerged condition (Source: Fontana,1986)

2.2.3 Inhibition of Localized Corrosion

There are many methods such as inhibitors addition, design and environmental changes, coatings, and cathodic and anodic protections being developed to prevent localized corrosion (Hurley & Scully, 2002). Inhibitors play an important role in preventing localized corrosion. The use of inhibitors to protect metals against localized corrosion is based on the ability of certain chemical compounds or mixtures to reduce or suppress the rate of corrosion process by introducing them in a small concentration into a corrosive medium.

Inhibitors often work by adsorbing themselves on the metallic surface, and thus protecting the metallic surface by forming a film. Some may act by reducing the migration of chloride ions into the pit, and some may act by adsorbing at active sites to reduce pit growth kinetics. The effectiveness of these inhibitors often depends on their concentrations and the concentrations of chloride in the solution. So far it has been considered that inhibitors protect a metal against corrosion mainly by retarding the kinetics of the anodic reaction. However, it has also been found that under certain conditions, a metal can be passivated by accelerating the cathodic reaction using passivating inhibitors, which cause a large anodic shift of the corrosion potential, forcing the metallic surface into the passivation range. Increasing potential is beneficial to the repassivation of metastable pits (Cheng & Luo, 1999). There are two types of passivating inhibitors: oxidizing anions, such as chromate, nitrate and nitrite, which can passivate metal in the absence of oxygen (Rozenfeld, 1981; Kawai *et al.*, 1996; Takeshi Kikuchi & Kunitsugu Aramaki, 2000), and non-oxidizing ions, such as phosphate, tungstate and molybdate that require the presence of oxygen to passivate metal (Rozenfeld, 1981).

Of all the chemicals, chromates/dichromates inhibitors are the most widely used for protecting both ferrous and nonferrous metals against localized corrosion, especially in near-neutral environments containing aggressive anions such as chloride (Akiyama & Frankel, 1999; Jeffcoate *et al.*, 2000; Rozenfeld, 1981). Chromate was found to act as both anodic and cathodic inhibitor (Sasaki & Isaacs 2001). A remarkable property of chromate inhibitor is *self healing* active corrosion inhibition, which involves reduction and irreversible adsorption of Cr III to the surface of the electrode to block sites of adsorption (William & Richard, 2002).

$\text{Cr}_2\text{O}_4^{2-}$ and $\text{Cr}_2\text{O}_7^{2-}$ anions as oxidants will promote formation of passive film (Rozenfeld, 1981; Fujioka *et al.*, 1996; Cheng *et al.*, 1998; Jeffcoate *et al.*, 2000; Yu Zuo, 2002; Zhao & Zuo, 2002) and the greater effectiveness of CrO_4^{2-} inhibitor is reducing the number of nucleations and metastable events (Burstein & Ilevbare, 2003).

Owing to the toxic and carcinogenic nature of the most common chromate inhibitor, considerable effort has been directed towards developing other environmentally acceptable inhibitors. Extensive research has shown that the soluble rare earth metal salts are effective inhibitors of the corrosion of aluminum alloys, steel, and zinc (Hinton, 1992; Bernal *et al.*, 1995; Aramaki, 2001; Aballe *et al.*, 2001b; Arenas *et al.*, 2002; Li & Zhang, 2003). It has been reported that CeCl_3 and LaCl_3 behave as cathodic inhibitors and they act by blocking the cathodic sites of stainless steel corrosion in NaCl solution (Ives & Lu, 1993; Aldykewicz *et al.*, 1995; Aramaki, 2001; Aballe *et al.*, 2001b; Arenas *et al.*, 2002). Thermodynamically, stable cerium oxide may be responsible for blocking the active sites for both cathodic and anodic reactions of stainless steel crevice corrosion in 10% FeCl_3 solution (Ives & Lu, 1993). However, Isaacs *et al.* (1991) measured the current density distribution over a corroding steel under corrosion inhibition by cerium salts by a vibrating probe technique and they proposed that cerium acts as an anodic inhibitor for steels. The composition of cerium films on galvanized steel consists of a mixture of Ce(III) and Ce(IV) compounds, being very rich in Ce(III) in the first instants of the deposition process and becoming gradually enriched in the more oxidized form, Ce(IV). The presence of this film on the steel surface reduces the rate of both the cathodic and the anodic reactions but thicker films have revealed lower resistance to corrosion initiation (Montemor *et al.*, 2001). It has been found that in the presence of La^{3+} and Ce^{3+} ions, the corrosion potential of stainless steel remained almost unchanged, but both cathodic and anodic current densities are distinctly decreased. This finding suggests that the local anodic metal dissolution and the cathodic reduction of oxygen are simultaneously suppressed (Li & Zhang 2003).

2.3 Methods for Studying and Monitoring Localized Corrosion

Corrosion monitoring techniques can be divided into two general categories according to their principles of measurements: Non-electrochemical techniques that are based on the measurements of weight or physical parameters of a corroding electrode, and electrochemical techniques that are based on the measurements of electrochemical parameters and their changes over an electrode surface. Each general method has its advantages and limitations.

2.3.1 Non-Electrochemical Methods for Studying and Monitoring Localized Corrosion

The most common non-electrochemical methods for corrosion studies are visual inspection, optical and scanning electron microscopic observation of metal surface, weight loss measurement, X-ray radiography, electrical resistance, and ultrasonic techniques. Visual inspection of metal surface can determine the sizes and shapes of corroded area such as pits, while a more detailed examination of a corroded surface can be carried out through an optical and scanning electron microscope. Weight loss measurements can be conducted in various environments such as gas, conducting or non-conducting liquid media or soils of different moisture levels (Gupta & Gupta, 1979). The limitations of the weight-loss method are that the method requires periodic removal of the specimen from the environment, which could interrupt corrosion processes, and that it is not suited for instantaneous corrosion monitoring.

In the electrical resistance method, the corrosion rate is measured as the increase in the resistance of an electrical coil as it corrodes. This method also requires that the probe is exposed to corrosion environment for a period of time so it has difficulties in measuring instant corrosion rates. This method has been used for corrosion detection in pipeline (Zivica, 2000; Todoroki *et al.*, 2004), but it is generally cumbersome and time consuming.

X-ray radiography techniques such as X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) have been used to obtain chemical information of corrosion sample with minimum radiation damage to the sample surface (Schöberl, 1999; Thornton, 2004). X-ray absorption and fluorescence measurements have become powerful methods for in situ study of chemical and physical changes during electrochemical and corrosion processes (Isaacs *et al.*, 1995). Recently, a new technique by XAFS (X-ray Absorption Fine Structures) and XANES (X-ray Absorption Near Edge Structures) has been developed for in situ observation of metal corrosion. XAFS and XANES spectra were obtained with a special electrochemical cell to elucidate pitting for stainless steel (Masao Kimura *et al.*, 2002). However, the characterization of the composition and structure of thin passive film and the study of their interaction with corrosive environments requires a combination of sophisticated experimental techniques.

The acoustic emission technique, based on the rapid release of energy within a material generating a transient elastic wave propagation, has been demonstrated to monitor and study microscopic mechanisms of pitting corrosion (Mazille *et al.*, 1995; Fregonese *et al.*, 2001a; 2001b) and crevice corrosion (Kim *et al.*, 2003). An acoustic pipe tracer locates buried plastic gas lines by introducing an acoustic signal to the pipe. The receiver detects the sound waves that radiate from the pipe into the surrounding soil. Low frequency long range guided wave ultrasonic technique (Baby *et al.*, 2003) has also been used for the rapid survey of internal and external corrosion of pipes buried in sand or soil. However, it often has difficulties in accessing certain locations of a buried system and in determining the instantaneous rates of corrosion.

The magnetic field detection (Li *et al.*, 1996) and the electric field mapping technique (Johnson, 2000) have been developed to evaluate the rate of corrosion. The magnetic field detection can only be used on ferromagnetic metals and cannot be used as a real-time monitor. The disadvantages of the electric field mapping technique include the requirement of special multichannel hardware and the installation of a large number of miniature electrodes to obtain the high resolution for localized corrosion monitoring.

2.3.2 Electrochemical Methods for Studying and Monitoring Localized Corrosion

The main objective of electrochemical method is to determine the corrosion rate by measuring the corrosion current, which is the current flowing between the microscopically adjacent anodic and cathodic sites on a corroding metal surface. However, direct measurement of the corrosion current is typically not possible and thus polarization techniques are used for in corrosion measurements. Generally, conventional electrochemical methods are classified into: (i) electrochemical methods for the study of uniform corrosion, such as Tafel extrapolation, linear polarization resistance, electrochemical impedance spectroscopy (EIS), and (ii) electrochemical methods for the study of the passivity and localized corrosion, including cyclic potentiodynamic polarization.

a. Tafel Extrapolation Method

Tafel extrapolation method is often used to determine important corrosion parameters by extrapolating the linear portions of the Tafel plot back to their intersection. The value of either the anodic or the cathodic current at the intersection is i_{corr} . When reaction mechanisms for the corrosion reaction are known, the corrosion current, i_{corr} , can be calculated using Tafel slope analysis as shown in Figure 2.9.

In the polarization curve, the measured current is the sum of the anodic and cathodic reaction currents at any given potential. At potentials below the free corrosion potential E_{corr} the response is mainly that of the cathodic process. At potentials above E_{corr} the reverse occurs. In an ideal situation both the contributions would be simple exponentials-straight lines on the plot. According to the modified Butler-Volmer equation (equation 2.4),

$$i = i_{corr} \left[\exp \frac{2.3\eta}{\beta_a} - \exp \frac{2.3\eta}{\beta_c} \right],$$

where β_a and β_c are the anodic and cathodic Tafel parameters given by the slopes of the polarization curve ($\frac{\partial E}{\partial \log i}$) in the anodic and cathodic Tafel regimes respectively.

Figure 2.9 Classic Tafel Analysis (Revie & Uhlig, 1985)

In practice the Tafel plot may have no linear zone due to mass transfer limitations, formation of oxide film etc. and thus the extrapolation analysis can be difficult to apply. On the other hand, this method applies a large polarization voltage that can cause irreversible damage to the electrode surface and hence is not recommended for on-line corrosion rate measurement.

b. Linear Polarization Resistance (LPR) Method

Linear polarization resistance (LPR) technique is the most frequently applied technique to determine the rate of corrosion continuously in real-time, from a probe permanently installed in the corrosive fluid (Mansfeld, 1986; Barnarrt, 1986; Macdonald *et al.*, 1991; Berke *et al.*, 1990; Gowers *et al.*, 1994). The

electrochemical principle behind the linear polarization technique is expressed by the Stern-Geary equation. LPR technique utilizes a measurement of the slope of the potential-current density curve ($\frac{\Delta E}{\Delta i}$) at the free corrosion potential, yielding the polarization resistance, R_p , that can be related to the corrosion current by the Stern-Geary equation (in equation 2.6 and 2.9) for reactions under activation control.

$$R_p = \frac{B}{i_{corr}} = \frac{(\Delta E)}{(\Delta i)_{\Delta E \rightarrow 0}}, \text{ where } (B = \frac{\beta_a \beta_c}{2.3 (\beta_a + \beta_c)}) \quad (2.9)$$

The Stern-Geary constant B is a function of the anodic and cathodic Tafel slopes, β_a and β_c . The knowledge of R_p , β_a and β_c enables direct determination of the corrosion rate at any point in time using equation 2.9. The corrosion rate is inversely proportional to the polarization resistance is clearly seen in Figure 2.10.

Figure 2.10 Current-overvoltage behavior of corroding systems (Source: Scully, 1995)

Both LPR and Tafel extrapolation techniques are based upon an application of either steady fixed levels of current, followed by a monitoring of the potential, (galvanostatic) or an application of specific potential followed by a monitoring of the current (potentiostatic). The main difference between these two methods is that

the change in potential must be kept to less than ± 25 mV for the LPR technique, while the change of potential can go up to ± 250 mV for the Tafel extrapolation technique.

Researchers in many laboratories have found that large errors can occur in measuring uniform corrosion rates by D.C. linear polarization (Lorenz & Mansfeld, 1981; Mansfeld, 1986; Tan *et al.*, 1995). The reason for these errors is that the experiment R_p value contains contributions from ohmic resistances, such as the electrolyte layer resistance between the Luggin capillary and test electrode, surface scale resistance, and inhibitors film resistance etc. Hence, the linear polarization technique is generally not suitable for systems where there is high electrolyte resistance, surface scale resistance, etc.

c. Electrochemical Impedance Spectroscopy (EIS) Method

EIS is an *in-situ*, non-destructive technique that allows accurate and sensitive quantification of the corrosion rate of metal. EIS method has been applied to study corrosion, the behaviour and growth of passive films, coatings and buried structure corrosion (Silverman, 1986; Lemoine *et al.*, 1990; Jafar *et al.*, 1993; Haruyama & Sudo, 1993; Feng & Zdunek, 1994). Different electrode surface structures respond to different frequencies because they have different capacitances and resistances and so have different time constants. For instance, EIS is able to measure the solution resistance at high a frequency. EIS method replaces the DC excitation with AC signal of various frequencies and the solution resistance is estimated from impedance, Z_ω , measured in the high frequency range, while the sum of the polarization resistance, R_p , and the solution resistance, R_s , are estimated from the impedance in the low frequency range (Kelly *et al.*, 2003).

$$\text{At very low frequencies, } Z_\omega \rightarrow 0(\omega) = R_s + R_p \quad (2.10)$$

$$\text{At very high frequencies, } Z_\omega \rightarrow \infty(\omega) = R_s \quad (2.11)$$

EIS applies AC signal over a frequency spectrum usually in the range of 100 kHz to 50 μ Hz on electrode surface. At each frequency a sine wave is generated and fed into the potentiostat. This wave is then imposed on the cell and its potential and

current flow is measured. EIS data is commonly analyzed by fitting it to an equivalent electrical circuit model. Most of the circuit elements in the model are common electrical elements such as resistors, capacitors, and inductors. There are several ways commonly used for the graphical presentation of impedance data obtained over a wide frequency range. The two main methods which will be described in some detail are the Nyquist and Bode plots. The Nyquist complex plane plot graphs the resistive versus the reactive components of impedance, Z , and the Bode plot graphs the logarithms of the modulus of impedance and phase angle versus the logarithm of frequency.

Figure 2.11 illustrates the electrochemical double layer and surface dielectrical layers on a corroding metal, its equivalent circuit and the resulting impedance spectra (Barsoukov & Macdonald, 2005). The electrical double layer exists at the interface between an electrode and its surrounding electrolyte. This double layer is formed as ions from the solution *stick on* the electrode surface. Charges in the electrode are separated by an insulator, forming a capacitor, as shown in Figure 2.11. The value of the double layer capacitance, C_{dl} , depends on many variables including electrode potential, temperature, ionic concentrations, types of ions, oxide layers, electrode roughness, impurity adsorption, etc. The equivalent circuit includes a solution resistance, R_s , a double layer capacitance, C_{dl} , and a charge transfer or polarization resistance, R_p . The double layer capacitance is at a parallel with the charge transfer resistance. Impedance is commonly written in the form:

$$Z(j\omega) = Z_{re} - jZ_{im}, \quad \text{where } j = \sqrt{-1} \quad (2.12)$$

The general expression of the Butler-Volmer equation (equation 2.2) for the charge transfer reaction can be written as (Kelly *et al.*, 2003):

$$i = i_0 \left[\frac{C_0}{C_0'} \exp \frac{\alpha \eta n F}{RT} - \frac{C_R}{C_R'} \exp \frac{(1 - \alpha) \eta n' F}{RT} \right] \quad (2.13)$$

where C_0 = Concentration of oxidant at the electrode surface

C_0' = Concentration of oxidant in the bulk

C_R = Concentration of reductant at the electrode surface

C_R' = Concentration of reductant in the bulk

Figure 2.11 Network model for a corroding metal, its equivalent circuit and impedance spectra (Source: Silverman, 2000)

When the overpotential, η , is very small and the electrochemical system is at equilibrium, the Stern-Geary equation for the charge transfer or polarization resistance, R_p becomes:

$$R_p = \frac{RT}{nFi_0} \quad (2.14)$$

Figure 2.11 shows that the impedance is represented as a vector of length $|Z|$ on the Nyquist plot. Low frequency data are on the right side of the plot and higher frequencies are on the left. The value of the capacitance cannot be determined from the Nyquist plot. It can be determined by a curve fit or from an examination of the data points. The intercept of the curve with the real axis gives an estimate of the solution resistance (Kendig *et al.*, 1993). Determination of R_p can be achieved by subtracting the result of equation 2.11 from the results of equation 2.10 (Kelly *et al.*, 2003).

The advantage of EIS is its ability to identify the actual polarization resistance of the test subject from the various components of the system resistance, hence reducing errors in corrosion rate determinations, as in the case for Tafel extrapolation and LPR technique. However, since EIS technique is based on a uniform electrode, it is not usually used for localized corrosion monitoring.

d. Cyclic Polarization Method

Cyclic potentiodynamic polarization is the traditional electrochemical method for determining pitting corrosion tendencies of a specimen in a given metal-solution system. This is achieved by determining the pitting potential and the repassivation potential at discrete sites on an electrode surface under localized corrosion (Bastaweesy, 1995; Rao *et al.*, 2003). During a cyclic polarization experiment, as shown schematically in Figure 2.12, a new pit will initiate and existing pits will propagate at E_{pit} , the critical pitting potential. E_p is the repassivation potential below which there is no pitting. Between the E_{pit} and E_p , existing pits will propagate but no new pits will form. The existence of the

hysteresis is usually indicative of pitting and the size of the pitting loop is a rough indication of pitting tendency: the larger the loop, the greater the tendency to pit.

Figure 2.12 Typical graph representative cyclic potentiodynamic polarisation curve
(Source: Silverman, 2000)

In order to get the accuracy and reproducibility of experimental data, many approaches which permits quantitative analysis of more complex polarization curves in terms of theoretically based models has been developed (Hines, 1983; Otieno-Alego *et al.*, 1992; Flitt & Schweinsberg, 2005). Hines (1983) has assumed that the metal surface consists of two independent regions - one unfilmed and the other filmed. If S is the fraction of the metal area which is unfilmed then $(1-S)$ will be the

fraction filmed. The rate of the metal dissolution over the total surface, I_a , is the sum of the anodic currents on the unfilmed, I_u , and filmed areas, I_f .

$$I_a = I_u + I_f \quad (2.15)$$

In terms of current density,

$$i_a = i_u S + i_f (1-S) \quad (2.16)$$

In the presence of certain anions (e.g., Cl^-) the film is attacked and at points where the film is thin metal dissolution may proceed pitting corrosion. For the part of the anodic curve from the break down potential, E_{br} , to the maximum potential, E_m , the metal dissolution can be assumed by a linear logarithmic current density/potential relationship. The following empirical expression has been used for the dependence of the anodic current density, i_a , on the potential, E (Flitt & Schweinsberg, 2005):

$$i_a = i_{cp} \left[\frac{i_{cp} + \nu}{\nu} \right] \quad (2.17)$$

where i_{cp} = critical passivation current, $\nu = \exp \left[\ln i_{cp} + \left\{ \frac{E_m - (E + E_{br})}{\text{irontranspassiveslope}} \right\} \right]$.

The cyclic polarization can provide useful information about pitting sensitivity and thus it is widely used (Kiourtsidis *et al.*, 1999; Dimitrov *et al.*, 2000; Frankel & Zhang, 2003). However, this technique does not measure the rates of pitting corrosion or the distribution of pits. Such shortcomings of the polarization techniques limit their applications in localized corrosion study.

2.4 Relatively New Electrochemical Methods for Studying and Monitoring Localized Corrosion

To overcome some of the difficulties associated with conventional electrochemical methods, relatively new electrochemical methods such as scanning reference electrode technique (SRET) method, electrochemical noise analysis (ENA) and wire beam electrode (WBE) method have been developed.

2.4.1 The Scanning Reference Electrode Technique (SRET) Method

The SRET is an *in situ* technique for measuring micro-galvanic current flowing close to the surface of electrochemically heterogeneous specimen in an electrolyte (Isaacs *et al.*, 1991). It is considered to be a tool for examining electrochemical heterogeneity due to surface contamination, surface roughness, stress defects, filiform corrosion and paint/coating applications (Isaacs & Vyas, 1981).

The SRET technique relies on detecting extremely small potential variations, which exist on the surface of electrochemically nonuniform material surface exposed to an electrolyte. For instance, when a stainless steel surface is under pitting corrosion there exists a flow of metal ions in the solution above and around the pit site, as illustrated in Figure 2.13. This current movement leads to potential variations which SRET detects and quantifies.

The resolution of the SRET is dependent not only on the proximity of anodic and cathodic sites, but also on the magnitude of the corrosion current. Thus, if the flow of the current is large enough, the variation in potential could be detected. By scanning a *passive* reference probe with a fine capillary tip parallel and in close proximity to the metal surface, the potential distribution in the solution can be measured. The scanning probe arrangement utilized to measure these potential variations usually consists of two platinum tips having in the order of one to five micrometers in diameter configured as differential inputs to the measuring electronics in order to reduce the inherent noise occurring at any frequency other than the frequency of probe vibration (Figure 2.13). As the probe scans over the

metal surface, there will be an IR drop between the two tips of the probe (Isaacs & Vyas, 1981). The electrochemical cell is separately controlled by the use of a potentiostat and reference electrode system. Using the above system, the SRET data can be displayed as linescans or 2D area maps offering a spatially resolved representation of the electrochemical heterogeneity present at an electrode surface.

Figure 2.13 Schematic illustrations of the probe tips and the SRET measurement
(Source: Isaacs & Vyas, 1981)

The SRET has been applied in studying various forms of localized corrosion such as pitting initiation, surface film breakdown, (Isaacs, 1974; Isaacs & Vyas, 1981; Akid & Mills, 2001; Bellanger & Rameaua, 1995), stress corrosion cracking (SCC) (Allah-karam *et al.*, 2001; Isaacs & Vyas, 1981), galvanic corrosion (Akid & Mills, 2001; McMurry, 2001), as well as intergranular corrosion (Isaacs, 1974).

There are limitations for SRET in studying corrosion systems that only generate small corrosion currents or that have anodic and cathodic sites not well separated. The SRET only responds to potential variations in the solution, which are associated with the flow of current and does not relate directly to the potentials of the metal surface (Powell *et al.*, 1999; McMurry, 2001). The sensitivity of SRET is

highly dependent on corrosion current value, electrolyte conductivity and the probe proximity over corrosion sites. The movement of scanning tips can interfere with electrochemical processes occurring over an electrode surface, especially when a corrosion product forms over an electrode surface.

2.4.2 The Electrochemical Noise Analysis (ENA) Methods

Electrochemical noise has received considerable attention since Iverson's study (1968) on electrode potential fluctuations and corrosion processes and Tyagai's studies (1971, 1974) on electrode noise in electrochemical engineering. Iverson (1968) suggested the possibility of studying the corrosion processes and quantitatively measuring the rate of corrosion by analyzing electrode voltage fluctuations. Bertocci (1980, 1981) investigated EN using a specially constructed low noise potentiostat together with a Fourier spectrum analyser and linked EN to localized corrosion processes.

There are two related, but distinctly different approaches to measuring electrochemical potential and current noise. The potential noise of a single sample can be monitored relative to a low noise reference electrode. The current noise between a pair of identical electrodes can be measured using an ammeter. In real systems, the two current measuring electrodes are typically not similar, and the coefficient of variation is strongly dependent on the asymmetry between the two electrodes. A similar measurement can also be made on a single electrode by controlling its potential relative to a low-noise reference electrode. It is also possible to combine both of these techniques by measuring the current noise between two identical electrodes while at the same time monitoring the potential noise of the coupled electrodes relative to a low-noise reference electrode or to a third identical electrode. The typical experimental setup of an ENA method is based on the conventional three-electrode method as shown in Figure 2.14.

Figure 2.14 The typical experimental setup of an ENA method (Source: Tan *et al.*, 1998)

Since the early 1980s electrochemical noise analysis has been used to study corrosion related processes. Eden *et al.* (1986) discovered the relationship between electrochemical noise and corrosion rate. The electrochemical noise resistance, R_n , is comparable to the polarization resistance, R_p . The R_n is defined as the ratio of the standard deviations of potential noise and of the current noise ($R_n = \sigma_v/\sigma_i$) between two identical working electrodes which are linked by a zero resistance ammeter:

$$R_n \approx R_p \quad (2.18)$$

This relationship has received considerable interest and has been experimentally confirmed by various researchers (Mansfeld & Xiao, 1993; Tan *et al.*, 1996; Bertocci *et al.*, 1997). In order to explain this relationship theoretically, a concept called *statistical linear polarization* was developed. The basic idea of the statistical linear polarization is that the difference in random potential noise between two identical electrodes works as an internal polarization voltage signal, producing current noise (Tan *et al.*, 1996). The noise resistance, deduced from statistical analysis of potential and current noise signals, is reasonably equivalent to linear polarization resistance, which is measured using an externally applied potential signal. Later, this time domain relationship was extended into the frequency domain to produce noise impedance spectra (Mansfeld & Xiao, 1994). The concept of noise

impedance was further developed leading to a patent (Eden *et al.*, 1991) which describes a method and apparatus for producing electrochemical impedance spectra using the spontaneous electrochemical potential and current noise signals. Good experimental correlation between the spectral noise impedance and the magnitude of the electrode impedance has been observed (Cottis *et al.*, 1998). Recently, Lowe *et al.* (2003) proposed the correlation between the measured potential and current noise derived using an equivalent circuit.

Hladky and Dawson (1981, 1982) found that localized corrosion generates characteristic potential noise patterns. They advocated the use of ENA as an indicator of localized corrosion. Since fluctuations in the corrosion potential can indicate a change in the thermodynamic state of corrosion processes, the change in the current noise could be an indicator of the corrosion kinetics. Each type of corrosion could have a characteristic *fingerprint* or *signature* in the signal noise. This fingerprint can be used to predict the type and severity of corrosion (Pistorius, 1996). It is thus believed that electrochemical noise signatures can provide fundamental information about the incubation, propagation and repassivation process of localized corrosion. In the case of pitting corrosion, a noise event could indicate the breakdown of a passive film, leading to major electrochemical heterogeneity and pitting initiation. For this reason, there has been increased interest in the use of electrochemical noise signatures analysis to investigate various types of corrosion systems including uniform corrosion (Gabrielli *et al.*, 1985) and localized corrosions, and especially pitting and crevice corrosion (Dawson & Hladky, 1981, 1982; Bertocci *et al.*, 1983; Williams *et al.*, 1983a; Macdonald & Urquidi-Macdonald, 1986; Gabrielli, *et al.*, 1986; Dawson & Uruchurtu, 1987; Ferreira & Simoes, 1987; Heusler & Nachstedt, 1988; Bertocci, 1989; Dawson, 1996; Fukuda & Mizuno, 1996; Cheng *et al.*, 1999; Gonzalez-Rodriguez *et al.*, 2000; Aballe *et al.*, 2001b; Smulko *et al.*, 2002a; Smulko *et al.*, 2002b).

It is believed that general corrosion gives quite steady and flat corrosion potential, with the potential time graphs as shown in Figure 2.15 (Yang *et al.*, 1998). Different noise patterns were observed during the incubation and initiation periods of pitting. Bertocci (1980) measured the current noise of polarized aluminum electrodes undergoing pitting and observed a significant increase in electrochemical

noise activity when an electrode was polarized close to the pitting potential, particularly at lower frequencies. During the incubation of pits, the fluctuations of potential were in phase with the current fluctuations, indicating the major role the faradaic current plays in pit incubation (Cheng & Luo, 2000). The initiation of pitting was characterized by sharp fluctuations of potential and current. The slower recovery of potential always exceeded the time for the recovery of the current. This was attributed to the slow discharging of the capacitance on the electrode surface (Cheng & Luo, 2000). The typical potential and current fluctuation patterns of pitting initiation of carbon steel and stainless steel are shown in Figure 2.16 and Figure 2.17.

Figure 2.15 The typical potential and current fluctuation patterns of A516-70 carbon steel after immersion in NaHCO_3 solution containing 0.15 M Cl^- showing general corrosion (Source: Yang *et al.*, 1998)

Figure 2.16 The typical potential and current fluctuation patterns of CrNi 18-9 steel after immersion in a 0.6 M solution of $FeCl_3$ showing pitting corrosion (Source: Smulko *et al.*, 2000a)

Figure 2.17 The typical (a) potential and (b) current fluctuation patterns of A516-70 carbon steel after 4 hours immersion in chloride solution showing pitting corrosion (Source: Cheng & Luo, 2000)

The identification of signature electrochemical noise signals obtained as potential and current time record series may be undertaken by a variety of means. For example:

- Examination of the time record trace may give an indication of the types of processes occurring (Dawson & Hladky, 1981).
- Frequency domain transforms can provide insight into the fundamental mechanisms operative and give information about low frequency impedance of the interface, etc., as Hladky and Dawson (1982) first reported.
- Statistical analysis may be used to derive values of the low frequency root mean square (rms) values of the signals and indication of localization, etc.,
- Fractal analysis, chaos theory etc.

In a pioneer study, Hladky and Dawson (1981) analyzed electrochemical noise signals in the time domain in order to detect characteristic *noise signatures* for various forms of localized corrosion. Simoes and Ferreira (1987) observed that there were two transients in potential, characterized by a quick drop followed by a slow (exponential) recovery. These transients were ascribed to the nucleation of metastable corrosion sites, which did not develop, but repassivated. This interpretation was confirmed by current transients, which revealed an anodic current on the electrode (Bertocci & Ye, 1984; Simoes & Ferreira, 1987). Bertocci *et al.* (1983) and Williams *et al.* (1983b, 1985) observed two types of current transients for pitting initiation. The type I transient was distinguished by a slow growth which was followed by sudden repassivation of the pit. Gabrielli *et al.* (1986) and Osterwald (1981) proposed the characteristic noise signatures of iron and iron base alloys. The shape of the type I transient has been interpreted by a sudden decrease of the corrosion rate in the pit due to a commutation between a multiplicity of the possible states of dissolution of iron and iron base alloys (Gabrielli *et al.*, 1986; Osterwald, 1981). The type II transient was related to a sudden failure of the protective layer followed by repassivation processes (Gabrielli *et al.*, 1986). It appeared to be characteristic of aluminium and non chemical initiation of the corrosion. This suggests that the initiation phase might have different mechanisms on different metals.

Hladky and Dawson (1981) first observed electrochemical noise in crevice corrosion systems in the presence of pit. They observed that cyclic oscillations continued at a constant frequency over considerable periods of time. Many researchers have detected the existence of current and potential transients in the passive state, proceeding the onset of crevice attack (Dawson & Hladky, 1981; 1982; Bertocci & Ye, 1984; Ferreira & Simoes, 1987; Roberge *et al.*, 1989; 1993; Klassen *et al.*, 2001; Darowicki & Smulko, 2003). Once crevice attack is found, pit initiation ceases. Cottis (2001) also pointed out that the onset of crevice corrosion often has a large drop in potential as the active crevice polarizes the passive non-crevice surface. If this drop is permanent, then visual inspection of the potential-time record indicates crevice corrosion. If the passive surface is unable to sustain the current needed in the active crevice, then oscillations in the potential-time record can occur as the crevice activates and passivates.

Frequency domain analysis has also been used to identify noise signatures (Dawson & Searson, 1988; Lee & Mansfeld, 1998; Alawahdi & Cottis, 1999, 2001). However, there are uncertainties in the determination of noise signal characteristics such as *roll-off*. A characteristic roll-off slope can be determined from the log (potential PSD) verses log (frequency) plot at high frequencies, which depends on the double layer capacitance (Alawahdi & Cottis, 1999; Cottis, 2001). Searson and Dawson (1988) observed a roll-off of -20 dB/decade as an indicator of pitting attack and -40 dB/decade for general type corrosion. However, Mansfeld and Xiao (1993) found that a sharp peak at a single frequency indicates crevice attack. Mansfeld *et al.* (2001) also found that a roll-off of -20 dB/decade in PSD plots, proposed as a noise signature for localized corrosion, was not necessarily the characteristic of localized corrosion. Legat and Zevnik (1993) proposed that there was a correlation between potential and current noise PSD plots and corrosion system. However, Montesperelli and Gusmano (2004) did not find any clear correlation between the roll-off in PSD plots and corrosion behavior.

Another method of correlating electrochemical noise with localized corrosion is by determining the localization index, *LI*. *LI* is defined as the ratio of the standard deviation of current fluctuation, σ_i , and the root square mean of current

fluctuation determined in electrochemical noise measurements, i_{rms} (Mansfeld & Sun, 1999):

$$LI = \frac{\sigma_i}{i_{rms}} \quad (2.19)$$

As a general rule, if the LI has a value approaching 1, the corrosion process is unstable, and is therefore more likely to be stochastic. More uniform corrosion processes, on the other hand, have LI values which are typically of the order of 10^{-3} (Cottis, 2001). However, a slow drift in the current through zero may give an artificially high value of LI , and therefore indicate localized corrosion even though the corrosion process has a Gaussian distribution which is symptomatic of general corrosion. The LI must therefore be used with care (Cottis, 2001). Mansfeld and Sun (1999) concluded that the LI should be considered as a measure of the deviation from the assumed identical behavior of the test electrodes and not as an indicator of corrosion mechanisms.

Generally, although several important applications of ENA have been proposed, the nature, origin, and production mechanism of electrode voltage and current noise have not yet been clearly understood. The correlation between the noise signal features and an actual process of localized corrosion still remains controversial.

2.4.3 The Wire Beam Electrode (WBE) Method

Although conventional electrochemical method and theories, such as the fundamental Nernst equation, the Butler-Volmer equation and the Wagner-Truad mixed potential theory were all developed based upon a uniform electrode surface; they have major limitations in studying heterogeneous electrochemical processes. In order to overcome this problem, a multi-piece electrode, namely the wire beam electrode, has been developed (Tan, 1991; Tan & Yu, 1991; Tan, 1998; Tan *et al.*, 2000; Tan, 2000).

The WBE is an electrochemically integrated multi-piece electrode system usually fabricated from a metallic wire bundle embedded in insulating materials

with its surface shape simulating a practical work-piece. Each wire in a WBE behaves as an individual electrochemical sensor that measures electrochemical parameters from local electrode areas. The working surface of the WBE is electrochemically integrated by coupling all the terminals of the wires in the solid phase and by closely packing all the wires in the solid/electrolyte interface. The electrochemical integration minimizes the influence of the insulating layer on electron and ion movements and thus the working surface of a WBE effectively can simulate a conventional one-piece electrode. Similar corrosion patterns were experimentally observed over a WBE and a large area, one-piece electrode surface exposed to an identical localized corrosion environment. The typical experimental setup of a WBE is shown in Figure 2.18. This experimental result has also been explained theoretically (Tan, 1998).

The WBE concept is based upon the fundamental assumption that the surface of each individual wire in an integrated WBE is homogeneous even though the overall electrochemical reaction rates, patterns even and overall WBE surface is heterogeneous. Since the surface area of each individual wire is much smaller than that of an integrated WBE surface, it is reasonable to assume that each wire surface is homogeneous in electrochemical reaction rates and patterns (Tan, 1998, 2000). The WBE concept enabled the extension of conventional electrochemical theories and techniques to the studies of localized corrosion (Tan, 1998, 1999, 2000; Tan *et al.*, 2000) and other heterogeneous electrochemical processes (Tan & Yu, 1991, Tan, 2002).

The WBE method can be used to measure the potential of any selected wire k in an integrated WBE surface, E_k , by temporarily disconnecting from the WBE system and rapidly connecting it to a high impedance voltmeter using a computer controlled automatic switch device. This E_k could consist of components including a local equilibrium potential E_k^o where a mini-equilibrium is supposed to exist between an Ohmic drop and an overpotential η_k that polarizes the wire k from E_k^o to the overall potential of the integrated WBE system, E_{sys} . E_k^o characterizes the thermodynamics of location k and it can be determined by measuring E_k immediately after the rapid Ohmic drop and η_k but before the occurrence of major changes in surface mini-environment. E_k^o is determined by local reactant and

product concentration of $[O]_k$ and $[R]_k$ and local temperature T_k over a steady-state WBE surface by the fundamental Nernst equation. For a simple electrode reaction, $Ox + ne^- \rightarrow Re$ can be described as:

$$E_k^0 = E^0 + \frac{RT_k}{nF} \ln \frac{[Ox]_k}{[Re]_k} \quad (2.20)$$

Figure 2.18 A schematic diagram showing the conceptual design of a WBE and typical experimental setup of a WBE

In the practical case, electrochemical corrosion is usually more complicated and traditionally the Wagner-Traud mixed potential theory does not apply to a heterogeneous electrode where there is a distinct separation of electrode reactions. This limitation can be avoided if the WBE is applied. The mixed potential over each location of the WBE surface can be measured independently by the Wagner-Traud mixed potential theory. This way, the uniform mixed potential distribution over the entire WBE surface can be determined and mapped.

The WBE concept also propagates an assumption that each wire surface is homogeneous in electrochemical kinetics. This permits the application of the fundamental electrochemical kinetics equation, the Butler-Volmer equation, to each wire surface. The approach effectively extends conventional electrochemical kinetic methods based on the Butler-Volmer equation, such as the Tafel polarization method and Stern-Geary linear polarization method, to the determination of heterogeneous electrochemical kinetics.

When wire k is connected to a multi-electrode system, it is polarized by other wires with a positive or negative overpotential, $\eta_k = E_{sys} - E_k$ depending on whether the polarization is anodic or cathodic. If the anodic and cathodic reactions on the wires are activation-controlled, corrosion on each wire is uniform. If the open-circuit potentials of the wires and the potential of the whole system are far away from the equilibrium potentials of wires, then the Butler-Volmer equation can be applied to wire k and also to the rest of the wires. E_k is the corrosion potential of wire k . It can be measured using a voltmeter via RE as shown in Figure 2.19 (a) when wire k is temporarily disconnected from the WBE system.

I_k is the corrosion current, which can be measured using a traditional electrochemical technique. E_{ka} is the equilibrium potential of the anodic reaction, and E_{kc} is that of the cathodic reaction. I_{ka} is the anodic reaction current, and I_{kc} is the cathodic reaction current. The difference between I_{ka} and I_{kc} is the galvanic current, I_{gk} , that flows into or out of the wire k , which is measurable using an ammeter, if all the wire terminals are connected together in a corrosive solution. It is shown in Figure 2.19 (b).

Figure 2.19 Schematic showing measurements of (a) corrosion potential and (b) galvanic corrosion currents of individual wires of the WBE

If corrosion occurs over a 100 wire WBE surface, some of the wires will behave as anodes and while others as cathodes. The overall current will then be equal to zero:

$$I_1 + I_2 + I_3 + \dots + I_k + \dots + I_{100} = 0 \quad (2.21)$$

The overall anodic corrosion current of wire k can be expressed as:

$$I_{ka} = I_{gk} + I_{kc} \quad (2.22)$$

At E_{sys} , on the basis of the Butler-Volmer equation, the anodic reaction current can be written as:

$$I_{ka} = I_k \exp \frac{\{2.303 (E_{sys} - E_k)\}}{\beta_{ak}} \quad (2.23)$$

where β_{ak} is the Tafel slope for anodic polarization of wire k .

The cathodic reaction current can be written as:

$$I_{kc} = I_k \exp \frac{\{-2.303 (E_{sys} - E_k)\}}{\beta_{ck}} \quad (2.24)$$

where β_{ck} is the Tafel slope for cathodic polarization of wire k .

Based on galvanic current, equation (2.23) becomes:

$$I_{ka} = \frac{I_{gk}}{1 - \exp\left[-\left(\frac{2.303}{\beta_{ak}} + \frac{2.303}{\beta_{ck}}\right)(E_{sys} - E_k)\right]} \quad (2.25)$$

If the open-circuit potentials of wires in a WBE are very different from the potential of the whole system (i.e., the wires are under large polarization), equation 2.23 can be simplified:

$$I_{ka} = I_{gk} \quad (2.26)$$

The criterion that permits the simplification of equation 2.25 and 2.26 could be that the difference between the open-circuit potential of a wire and the potential of the whole system is greater than 100 mV; an analogue to the validity condition of the Tafel equation (Tan, 1998). Localized corrosion current on all locations of the WBE can be estimated using equations 2.23, 2.25 or 2.26. In this way, the potential and galvanic current distribution maps over the WBE surface can be mapped. Typical maps of WBE measurement are shown in Figure 2.20 (Tan *et al.*, 2001b).

Figure 2.20 The typical results of (a) potential (V) and (b) galvanic distribution current maps (mAcm^{-2}) of WBE measurement (Source: Tan *et al.*, 2001b).

A further development in the WBE technique was made by combining WBE technique with electrochemical noise resistance measurements, R_n . The electrochemical data obtained was used to determine corrosion rates and their distribution and then to calculate accumulate corrosion depths (Tan *et al.*, 2000).

The WBE- R_n method has been successfully applied to simplify polarization resistance measurement (Tan *et al.*, 2000). The WBE- R_n method is a convenient technique for mapping the rates and patterns of uniform or localized corrosion (Tan *et al.*, 2000, 2001a, 2001b, 2001c). R_{nk} is calculated as the ratio of the standard deviation of the potential noise to that of the current noise between identical working electrodes (i.e. $R_{nk} = \sigma_v/\sigma_i$). Based on the assumption of uniformity of each wire surface, I_k from equation 2.22 can be expressed in Stern-Geary equation:

$$I_k = \frac{\beta_{ak} \cdot \beta_{ck}}{2.303(\beta_{ak} + \beta_{ck})} \cdot \frac{1}{R_{pk}} \quad (2.27)$$

where R_{pk} is the polarization resistance of wire k, which can be measured using traditional electrochemical techniques such as the linear polarization method. Theoretically as well as experimentally R_n has been found to be similar or equivalent to polarization resistance, R_p (Dawson & Hladky, 1982; Tan *et al.*, 1996, 1997).

$$I_k = \frac{\beta_{ak} \cdot \beta_{ck}}{2.303(\beta_{ak} + \beta_{ck})} \cdot \frac{1}{R_{nk}} \quad (2.28)$$

Combining equations 2.23 and 2.28;

$$I_{ka} = \frac{\beta_{ak} \cdot \beta_{ck}}{2.303(\beta_{ak} + \beta_{ck})} \cdot \frac{1}{R_{nk}} \cdot \exp \frac{\{2.303 (E_{sys} - E_k)\}}{\beta_{ak}} \quad (2.29)$$

According to Faraday's Law expression, whenever there is a large potential difference (e.g. > 100 mV) between anodic and cathodic zones (Tan, 1998) the galvanic current, I_{ka} , can be used to estimate instantaneous localized corrosion rates at the anodic zone.

$$CR_k(\text{mm/y}) = 10 \times 365 \times 24 \times 3600 \times \frac{E_w}{\rho F} \cdot \frac{\beta_{ak} \cdot \beta_{ck}}{2.303(\beta_{ak} + \beta_{ck})} \cdot \frac{1}{R_{nk}} \cdot \exp \frac{\{2.303 (E_{sys} - E_k)\}}{\beta_{ak}} \quad (2.30)$$

From equation 2.29, localized corrosion rates at all locations of the WBE can be calculated.

An instantaneous corrosion rate map was used to determine total corrosion depths over the whole experimental period. This was achieved by summing up the corrosion depths over various periods of exposure to give a cumulative result. The calculated total corrosion depths can be correlated quantitatively with the

microscopically observed corrosion depths and a photo of the corroded WBE. The result confirms the accuracy of the corrosion measurement method. The corrosion depth of wire k, Depth (i) during the specific period, i, is:

$$\text{Depth (i)} = CR_k \frac{1000 \cdot \text{period}}{24 \times 365 \times 3600} \quad (2.31)$$

Then, $\text{Total Depth}_k = \text{Depth (1)}_k + \text{Depth (2)}_k + \dots + \text{Depth (i)}_k$

where period is normally 24 hrs and the corrosion is assumed to be constant.

The WBE was initially developed and used to detect local defects in organic coating films (Tan, 1991; Tan & Yu, 1991; Wu *et al.*, 1995). The influence of film thickness and heterogeneity on organic coating was studied in 3% NaCl solution using the WBE. The WBE results showed good correlation with visual observation. The novel WBE method has been employed for studying localized corrosion and other heterogeneous electrochemical processes including water-drop corrosion, CO₂ corrosion, corrosion under non-uniform organic films, cathodic protection, crevice corrosion, and electroplating (Tan, 1991, 1998, 1999; Tan *et al.*, 2000, 2001a, 2001b; Kim & Tan, 2003). The WBE has also been successfully used to monitor the kinetics of long-term water-line corrosion of steel (Tan *et al.*, 2001c). Tan (1998) also studied heterogeneous electrochemical process occurring under a drop of water and under an organic protective film using WBE. The corrosion protective ability of rustroof oil films was evaluated. This technique can be used in designing effective cathodic protective systems for metal structure. The WBE-R_n technique has been used to measure CO₂ corrosion of steel in highly resistive multi-phase oil flowline conditions (Tan *et al.*, 2001a). This technique neither applies an externally imposed polarization nor a counter electrode. This work suggests that the combined WBE-R_n technique is capable of measuring CO₂ corrosion under multi-phase conditions and the WBE have certain advantages over conventional measurements for corrosion in highly resistive media.

Tan (1999) also employed the WBE for studying the processes of crevice corrosion and its kinetics. Comparisons between calculated corrosion depth map and corrosion appearance show a good correlation. Tan *et al.* (2001b) studied corrosion of stainless steel under CO₂ and O₂ environments in the presence of an

artificial crevice. The measured instantaneous kinetics of crevice corrosion was found to be quantitatively comparable with microscopic observation of corroded electrode surface. The work also showed that the combined WBE- R_n method has a limitation when applied to O_2 corrosion in a stagnant electrolyte. Figure 2.21 is an example of *observed* and *calculated* corrosion depth maps and photos over a WBE surface (Tan *et al.*, 2001b).

Figure 2.21 Examples of (a) Observed corrosion depth map (in μm), (b) Calculated corrosion depth map (in μm) (based on galvanic current), (c) Corroded WBE photo and (d) Calculated corrosion depth map (in μm) (based on noise resistance) (Source: Tan *et al.*, 2001b)

In general, the WBE has been successfully proven to be a convenient new tool in monitoring the patterns and kinetics of localized corrosion cells. However, in order to monitor and predict the detailed mechanism of localized corrosion processes, the WBE method needs to be combined with the other promising electrochemical method such as the electrochemical noise analysis.

2.5 Research Plan

The WBE method offers promise as a localized corrosion monitoring method. However, it is an emerging technology, and its performance as a localized corrosion sensor remains to be judged through future work. The key principle of this research will be to develop a new technique based on the wire beam electrode (WBE) method. In order to achieve highest sensitivity of detecting early sign of localized corrosion such as pitting and crevice corrosion the WBE is used in conjunction with noise signatures analysis.

In this research, several novel electrochemical experiments will be developed for monitoring and predicting corrosion under critical corrosion environments using the WBE-ENA technology. Main focuses of this research using the WBE-Noise Signatures method are:

- a. Monitoring localized corrosion - The initiation and propagation of pitting and crevice corrosion of major engineering materials such as SS316L and mild steel under typical localized corrosion conditions will be monitored by simultaneous measurements of potential noise and WBE current distribution maps.
- b. Evaluating localized corrosion inhibitors - Chemicals additives including CeCl_3 , LaCl_3 , Na_2CrO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ will be tested in various corrosive environments.
- c. Detecting corrosion under atmospheric and buried conditions - The WBE method will be applied to measure ions diffusion controlled atmospheric corrosion under simulated atmospheric corrosion of mild steel and SS316L; the penetration of corrosive species into sand and soil, and the occurrence of subsequent corrosion of carbon steel buried in dry, moist and chlorinated sand will be studied; and the susceptibility of different types of wetted fibrous thermal insulation to the ingress and penetration of contaminated moisture and water on aluminium will be monitored.

CHAPTER 3

EXPERIMENTAL METHODS AND PROCEDURES

3.1 Materials

In this research work stainless steel SS316L sheet of 1 mm thickness and wires with a diameter of about 1.5 mm, mild steel and aluminium AA1100wires with a diameter of 1.8 mm were used as electrode materials. The composition of SS316L, mild steel and AA1100 are listed in Table 3.1.

Table 3.1 *Composition of SS316L, mild steel and AA1100*

Stainless Steel SS316L						
Elements	C	Mn	P	S	Si	
Wt. %	<0.03	<2.00	<0.045	<0.03	<0.75	
Elements	Cr	Ni	Mo	Fe		
Wt. %	17.00-18.00	10.00-14.00	2.00-3.00	60.00-70.00		
Mild Steel (UNS no. G10350)						
Elements	C	Mn	P	S	Fe	
Wt. %	0.31 - 0.38	0.6 - 0.9	<0.04	<0.05	98.63 - 99.09	
Aluminium AA1100						
Elements	Si	Fe	Cu	Mn	Zn	Al
Wt. %	<1.0 (Si + Fe)		0.05-0.20	0.05	0.10	99.00

Chemi-Cast brand Epoxy and the hardener used for electrodes mounting and other purposes were provided by Chemicrete Enterprises Pte. Ltd., Singapore. The ratio of epoxy resin and hardener is 10:4. Chemicals used in various corrosion

experiments were reagent-grade, which are listed in Table 3.2. The chemicals were provided from Sino Chemical Co. Pte. Ltd., Singapore. Deionised water was used for the preparation of electrolyte solutions.

Table 3.2 *Specification of chemicals*

Chemicals	Specification
Ferric chloride	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ -min 96.0%, Free chlorine-max 0.005%, Iron (II)-max 0.03%
Sodium chloride	NaCl -min 99.9%, SO_4 -max 0.004%, Cu, Fe, Pb-max 0.0002%, I, Ca, Mg-max 0.002%, Br-max 0.01%, PO_4 & Heavy metals-max 0.0005%
Sodium carbonate	Na_2CO_3 -min 99.9%, Cl-max 0.002%, PO_4 -max 0.001%, SiO_2 -max-0.0025%, SO_4 -max 0.005%, N-max 0.001%, Pb- max 0.0005%, Al-max 0.0015%, Ca-max 0.005%, Fe-max 0.0005%, K-max 0.01%, Mg-max 0.0005%, Trocknungsverlust-max 1.0%
Potassium dichromate	$\text{K}_2\text{Cr}_2\text{O}_7$ -min 99.9%, Cl-mix 0.001%, SO_4 -max 0.005%, Ca- max 0.02%, Cu-max 0.001%, Fe-max 0.002%, Na-max 0.02%, Pb-max 0.005%, Niederschlag-max 0.005%
Sodium chromate	$\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$ -101.1%, Insoluble matter-max 0.001%, Cl- max 0.001%, SO_4 -max 0.005%, Al-max 0.001%, Ca-max 0.001%
Nickel sulphate	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ -rest, Ni+Co-min 20.6%, Insoluble in H_2SO_4 - max 0.05%, As-max 0.001%, Cd-max 0.005%, Co-max 0.5%, Cu-max 0.002%, Fe-max 0.005%, Pb-max 0.002%, Zn-max 0.005%
Cerium chloride	$\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ -99.9%
Lanthanum chloride	$\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ -min 99%, Ca-0.001%, Mg-0.0001%, Cu- 0.0001%, Fe-0.0001%, Pb-0.0001%, Zn-0.1%

For buried steel corrosion experiment, clean and dry sand was used. ASTM C136-01 Standard Test Method for Sieve Analysis of Fine and Coarse Aggregates was used to measure the particle size distribution of sand sample. This experiment began with the cleaning of the sieves through the use of an air gun and wire brush. After thorough cleaning, a 500 grams sample of sand of various particle sizes was weighed. The sieves were also individually weighed at this time. The sieves were then stacked on top of each other, with the finest mesh on the bottom, the largest mesh on the top, and a lid for the top to bottom. Then, the sand was poured into the sieves, and the sieves were placed in the mixer for 15 minutes. Afterwards, the sieves were separated and then weighed to find out the amount contained in each. The results of this experiment showed that in dry sieving the majority of the particles were left in the sieve of standard size 1 mm as shown in Table. 3.3. Based on the data collected from the experiment, the majority of particles in the sample of sand were larger than 0.5 mm but smaller than 1.18 mm. The particle size distribution of sand is shown in Figure 3.1.

Table 3.3 *Data collected from sieve analysis*

Sieve (mm)	Weight Retained (g)	% Cumulative Weight Retained	% Cumulative Weight Passing
1.4	0	0	100
1.18	134	26.8	73.2
1.00	159	58.6	41.4
0.825	72.4	73.08	26.92
0.710	62.9	85.66	14.34
0.600	46.5	94.96	5.04
0.500	11.5	97.26	2.74
0.425	0.6	97.38	2.62
<0.425	4.0	98.18	1.82

Figure 3.1 The particle distribution of sand used in the buried structure corrosion experiment

Four types of insulation material, rock wool, glass wool, cotton wool and industrial tissue paper were used for the corrosion under insulation experiment. Rock wool and glass wool are synthetic vitreous fibres made by collecting thin threads of wool fibres together and processed to form a rigid blanket of fibbers of varying thickness. In the fibre blanket, the wool fibres are not packed densely together but contain pores within the fibres, creating an interconnected network of pores. As a result, air or liquids can pass freely between the fibres laterally and vertically. Cotton wool is natural fibre with high absorbency for liquids, in contrast to the characteristics of rock wool and glass wool. However, similar to them, cotton wool fibres are also in blanket form, less rigid but with the fibres packed more densely together in comparison. An interconnected network of pores exists within the blanket of fibres as well. Industrial tissue paper is natural fibre and has high absorbency for liquids, similar to cotton wool. However, it comes in thin sheets and its bulk structural form exists as a continuous layer, in contrast to that of the other three fibrous insulations. This continuous layer form results in the insulation having high absorbent properties, exceeding that of cotton wool. Across the plane of the

layers, there are a few pores as well, which further increases its absorbency property. This is because pores trap air, which hinder absorption. Figure 3.2 shows micro-views of rock wool, glass wool, cotton wool, and industrial tissue paper.

Figure 3.2 (a) Micro-view of rock wool, (b) glass wool, (c) cotton wool and, (d) industrial tissue paper.

3.2 Electrode Preparation

3.2.1 The Wire Beam Electrode

During wire beam electrode preparation, one hundred metal wires coated with epoxy were mounted together in 10×10 array using epoxy resin and each wire acts both as a mili-electrode (sensor) and a corrosion substrate. The gap between neighbouring wires should be thin, about $20\ \mu\text{m}$ in thickness, providing insulation

(a)

The SS316L WBE (Figure 3.3a) uses wires of 0.15 cm in diameter. The working area (the area occupied by the wire beam) was approximately 2.25 cm² (1.5 cm × 1.5 cm) and the total metallic area was approximately 1.77 cm². The mild steel WBE (Figure 3.3b) was fabricated from 100 carbon steel wires (0.18 cm in diameter) by embedding wires in epoxy resin. Its working area was approximately 4.24 cm² (1.8 cm × 1.8 cm) and the total metallic area was approximately 2.54 cm². The aluminium wire (Figure 3.3c) had a surface area of about 0.01166 cm², the whole area of the work surface of WBE specimen was about 1.5 cm × 1.5 cm (total metallic area was about 1.166 cm²). The terminals of 100 wires were connected to the computer cables in order to measure potential and current distribution over the WBE surface using Auto-switch and AutoAC instruments.

3.2.2 One-piece Electrode

SS316L sheet was cut into 1.5 cm × 1.5 cm coupons for the preparation of one-piece electrodes. The coupons were connected to Cu wire using silver paste and were then mounted with epoxy, as shown in Figure 3.4.

Figure 3.4 Photograph of one-piece electrode

3.3 Experimental Setup and Instrumentation

3.3.1 WBE Measurement System Setup

Figure 3.5 shows a typical WBE measurement system setup for the corrosion potential and current distribution measurement. The WBE measurement system mainly consists of an Auto-switch v2 (custom made), a computer and an AutoAC, namely GillAC (ACM instruments, England). The photograph of the arrangement of WBE measurement setup is shown in Figure 3.6.

Figure 3.5 Schematic illustrations of the measurement of (a) potential and (b) galvanic current of each wire of a WBE specimen

Figure 3.6 The arrangement of WBE measurement

The Auto-switch is a multiplexing system designed for electrochemical measurements involving multiple electrodes. It is capable of arbitrarily connecting these electrodes to either of two lines, which may be used as two working electrode connections on an instrument-specifically, an AutoAC. A computer, via its parallel interface port, controls the Auto-switch. The Auto-switch system is required to facilitate taking of the measurements of selected electrodes with an AutoAC, consisting of two working electrode connections and a reference electrode connection, which effectively performs the calculations of the potential and current measurements. The analog switches can be programmed in an arbitrary fashion to select any electrode pair to allow any desired measurement configuration.

AutoAC can function as a voltmeter to record corrosion potential of each wire, as shown in Figure 3.5(a), as well as function as an auto zero resistance ammeter to measure current flowing between each wire and the remaining wires of the whole wire bundle, as shown in Figure 3.5(b). It enables current (from 325 mA to 10 pA) and voltage to be measured accurately and to be recorded automatically from a WBE surface through pre-programmed systematic measurements.

The corrosion potential distribution is obtained by sequentially measuring the open circuit potential of each wire against the reference electrode (SCE) using the AutoAC and AutoSwitch. The galvanic currents flowing between each individual wire and the wire beam system are measured by sequentially inserting the AutoAC between a chosen wire terminal and all other terminals shorted together using the AutoSwitch. Current or potential values measured from each wire of WBE (I_k and E_k , $k = 1 - 100$) are plotted using Mathcad environment (Mathcad Professional &, MathSoft, Inc., Massachusetts, USA) to produce a WBE galvanic current distribution or a WBE potential distribution map.

The maximum anodic current density (i_{max}), which has the largest positive current density value, the total anodic current density (i_{tot}), which is the sum of all the anodic current densities, and the number of anodes (N_a) can be obtained from the WBE current distribution map by registering in a data table for a WBE consisting of 100 wires, as shown in Table 3.4. For instance, i_{max} is 3.418 mAcm^{-2} , and N_a is 22. i_{tot} can be obtained by adding all the 22 positive anodic current values (bold font)

shown in Table 3.4. The measured anodic current density from an individual wire has a positive value. Thus, i_{tot} can be obtained by:

$$i_{tot} = 0.00003 + 3.198 + 0.142 + 0.122 + 0.122 + 0.497 + 0.684 + 0.214 + 0.39 + 0.835 + 0.039 + 3.418 + 0.313 + 0.221 + 0.104 + 2.067 + 0.634 + 0.368 + 0.257 + 0.017 + 0.153 + 0.872 = 14.6670 \text{ mAcm}^{-2}$$

Table 3.4 Data from WBE map of galvanic current (mAcm⁻²)

3E-05	-6E-6	-0.229	-0.229	0.39	0.039	-0.336	-0.17	0.368	-6E-05
-0.232	-0.136	-0.309	-0.038	-0.023	-0.32	-0.277	-0.237	-0.208	-0.162
-9E-03	-0.102	-0.021	-10E-4	-2E04	-0.933	-1.025	2.067	0.257	-0.287
-0.285	-0.262	-0.075	-0.229	-0.347	3.418	0.313	0.634	-0.193	-0.118
3.198	-2E-04	0.684	-0.046	-0.039	-0.215	0.221	-0.169	-0.165	-3E-04
-0.163	0.142	-0.348	-0.41	-0.042	-0.209	-3E-04	-0.168	-3E-04	-0.086
-0.398	-0.088	0.214	-3E-04	-0.008	-2E-04	-0.261	-3E-04	-0.114	-9E-04
-0.238	0.122	-3E-04	-0.888	-0.001	-3E-04	0.104	-0.19	0.017	-0.309
-0.138	0.122	-0.34	-0.199	-0.216	-0.024	-0.255	-0.319	-0.19	-0.241
-0.494	0.497	-3E-04	-3E04	0.835	-0.324	-3E-04	-0.164	0.153	0.872

Since i_{max} shows the rate of anodic dissolution of the most active anode, and i_{tot} describes overall corrosion of a WBE, the ratio of the maximum and total anodic current density can be used to describe the non-uniformity of anodic current distribution. The degree of localization of corrosion can also be expressed as a function of the number of anodes.

3.3.2 Setup for Polarization Measurement

Polarization measurements have been carried out to study inhibition effects on pitting corrosion using AutoAC. The setup of polarization experiment is

schematically illustrated in Figure 3.7. An electrochemical cell consists of a salt bridge, a platinum auxiliary electrode, a saturated calomel reference electrode (SCE) and a one-piece electrode. The experimental procedure was in accordance with the standard ASTM Designation G61. Specimens were immersed in the test solution and the polarization scan was carried out towards more noble values at a rate of 10 mV min^{-1} , after allowing a steady state potential to develop. The potential was scanned from below E_{corr} in the anodic direction until localized corrosion was initiated as indicated by a large increase in the applied current.

Figure 3.7 Schematic diagram showing the arrangement of polarization measurement

3.3.3 Setup for Measuring Potential and Current Noise from a Traditional One-Piece Electrode

In order to compare electrochemical noise from traditional electrode with that from the WBE system, conventional electrode noise measurements were carried out. The experimental setup is based on the conventional one-piece electrode method as shown in Figure 3.8. The stainless steel one-piece electrodes were mounted in epoxy and polished up to 1000-grit abrasive SiC paper. These one-piece electrodes were rinsed with deionised water, ethanol and dried in the air, and then exposed to a corrosive solution under static conditions at air-conditioned room

temperature (about 20 °C) to allow corrosion to occur. Potential noise was measured by recording the open circuit potential of the short-circuited two electrodes, against a saturated calomel electrode (SCE) using the AutoAC. In this experiment, the current noise between a pair of identical SS316L electrodes was measured while the potential noise was monitored by measuring the open circuit potential of a one-piece SS316L electrode, against SCE using AutoAC.

Figure 3.8 Schematic diagram showing experimental setup for electrochemical noise measurement using conventional one-piece electrodes

3.3.4 Setup of a New Experiment Based on the Combined Use of WBE and ENA for Studying Pitting Corrosion

The WBE was utilized in this work to study localized corrosion because it exhibits a feature that could be very valuable for such study. WBE can enable the direct correlation of noise activities to a specific location of the WBE surface, i.e. to relate electrode noise to its origin. This investigation can help the establishment of an unambiguous correlation between electrochemical noise patterns and localized electrochemical corrosion processes. Combination of WBE and noise signatures can directly correlate noise signatures to localized corrosion activities occurring at a specific location of an electrode surface.

The experimental method of applying WBE in conjunction with the ENA is a new technique. The experimental design is illustrated in Figure 3.9. The WBE employed in this work included a SS316L WBE and a carbon steel WBE. The working surfaces of the WBE were polished with 400, 800 and 1000 grit silicon carbide paper and cleaned with deionised water and ethanol. The freshly polished WBE was positioned horizontal facing-up position. The working surfaces were totally immersed in a corrosive solution [6% Ferric chloride solution for stainless steel and 0.017 M NaCl + 0.008 M Na₂CO₃ solution (*Evans solution*) for carbon steel] under static conditions at air-conditioned room temperature (about 20 °C) to allow corrosion to occur. During exposure, all the wire terminals of the WBEs were connected together and so electrons could move freely between wires. The solutions were prepared with de-ionized water and analytical grade reagents. The effect of inhibitors on pitting was also carried out using chromate, cerium chloride and lanthanum chloride inhibitors using the same experimental setup.

Figure 3.9 Schematic diagram showing an experimental setup for detecting potential noise over a WBE and for mapping galvanic currents flowing into/out of each wire in the WBE from pitting corrosion system

In order to measure potential noise and galvanic current distribution over a WBE concurrently, two AutoAC were used in the experimental setup. Electrode potential noise was recorded by measuring the open circuit potential of the wire beam, with all terminals of wires all connected, against the SCE. Potential noise recording was conducted immediately after a WBE was immersed in the test solution with a data sampling rate of two data/second, and the recording was continuous over the whole test period. The galvanic current distribution maps over the WBE surface was measured without interrupting the continuous electrode potential noise measurements. Galvanic currents flowing between each wire and the whole short-circuited WBE system were measured by connecting another AutoAC between each chosen individual wire terminal and all other terminals (shorted together) using the Auto-switch. Each map takes about 15 minutes to measure, by scanning from wire 1 to wire 100. Galvanic current measurements were performed intermittently, while potential noise measurement was carried out continuously over the whole experiment period. Galvanic current measurements must not interrupt the continuous potential noise measurements. Raw galvanic current data were transferred to analysis software written under Mathcad environment (Mathcad Professional &, MathSoft, Inc., Massachusetts, USA) for producing maps, namely, WBE galvanic current distribution maps, as described previously (Tan *et al.*, 2000).

3.3.5 Setup of a New Experiment Based on the Combined Use of WBE and ENA for Studying Crevice Corrosion

Figure 3.10 shows a typical experimental setup using the WBE-ENA method in the measurement of crevice corrosion with and without the presence of corrosion pits. A WBE made from 100 identical mild steel wires (0.18 cm in diameter) was totally immersed in a corrosive electrolyte containing 0.017 M sodium chloride and 0.008 M sodium carbonate (Evans solution) under static conditions at 20 °C to allow corrosion to occur. The working surface of the WBE was polished with 400, 800 and 1000 grit silicon carbide paper and cleaned with de-ionized water and ethanol. The freshly polished WBE was positioned in a horizontal position facing-up. In this research, the crevice area was created by a narrow gap between the wire beam electrode surface and an adhering plastic semi sphere. A diameter of about 2 cm

plastic semi sphere was placed on the WBE surface to create crevice area as shown in Figure 3.10. The geometry of the crevice in the experiment was determined by the diameter of the semi sphere. Potential noise measurement and the WBE galvanic current measurement were carried out using the same procedures described in (iv). The measurements were continued until the crevice corrosion system was stable.

Figure 3.10 Schematic diagram showing an experimental setup for detecting potential noise over a WBE and for mapping galvanic currents flowing into/out of each wire in the WBE from crevice corrosion

3.3.7 Setup of a New Experiment for Studying the Effects of Ions Movement on Simulated Atmospheric Corrosion

Figure 3.12 illustrates an experimental design which for the first time was used to measure electrochemical parameters from a corroding WBE surface under a simulated atmospheric corrosion environment. The WBEs employed in this work included a stainless steel (SS316L) WBE and a carbon steel WBE. The working surfaces of the WBEs were polished and cleaned using de-ionized water and ethanol before being positioned horizontally facing-up. The WBE surface was then covered by a piece of filter paper (42 MN grade) that was cut into a special shape, as shown in Figure 3.12, and was moistened in distilled water. In order to create a slow and gradual ion diffusion over the WBE surface, a pipette filled with solid chemicals such as FeCl_3 , NaCl or NiSO_4 (AR grade) was placed on the stick side of the filter paper, close to wire 1 of the WBE. In this case, solid chemical from the pipette would gradually dissolve and diffuse away from wire 1 location, creating concentration gradients over the WBE surface. To understand the effects of ions diffusion on corrosion behaviour, potential and current measurements were carried out using the same procedure described in (iv).

Figure 3.12 Schematic diagram showing the measurement of electrochemical parameters from a corroding WBE surface under a simulated diffusion-corrosion environment

3.3.8 Setup of a New Experiment for Studying Corrosion under Insulation (CUI)

The experiment setup for corrosion under insulation is shown in Figure 3.13. An aluminium AA1100 WBE was used in this experiment and enclosed in a container. A minimum size hole was made at the top of the container to accommodate the reference electrode and the funnel (for introducing liquid to the insulation). The insulation was held in place on the WBE by the use of a plastic frame of negligible weight. The insulations used in the experiment were as shown in Figure 3.14. The reason for using different types of insulation is that different insulations respond differently to moisture and water, thus varying the severity of CUI in each case. The reference electrode was rested on the damp insulation to prevent compression on the damp material. In addition, the container was filled with 500ml of de-ionized water to reduce loss of moisture from the damp insulation throughout the experiment.

Figure 3.13 Schematic diagram showing an experimental setup for detecting potential noise over a WBE as well as for mapping galvanic currents flowing into/out of each wire in the WBE from corrosion under insulation system

Figure 3.14 The insulation used in the CUI experiment (Left) Front-view and (Right) Plane-view of insulations; from left, rock wool, industrial tissue paper, cotton wool and glass wool

The diffusing speed / penetration rate of the corrosive agent (5.0% CuSO_4 in 100ml deionized water) through thermal insulations: rock wool, glass wool, cotton wool and industrial tissue paper wetted with a contaminated salt solution (0.5% detergent with 4.5% NaCl in 100ml deionized water) was carried out. At the start of the experiment, 8.0ml of the contaminated salt solution (0.5% detergent content) was dropped through the funnel onto insulation. At the same time, corrosion potential noise and galvanic current distribution over the WBE surface were measured over various periods for 24 hours. After 24 hours, 5.0 ml of corrosive agent was dropped through the funnel onto the wet insulation. The Cu^{2+} ions in the solution simulated corrosive species that penetrated the wet insulation and its penetration time through the wet insulation to reach the WBE surface would be determined. Corrosion potential noise and galvanic current distribution over the WBE surface were measured continuously for the next 24 hours to determine this diffusion time. Additionally, the corrosion rates and the corrosion patterns associated with the different insulations under wetted conditions on the WBE were studied.

3.4 Reliability of Experimental Results

In practice, corrosion systems are generally time-varying in practice, further complicating reproducibility. In order to gain maximum reliability of the experimental results, all experiments presented in this thesis were carried out at least three times. For all experiments, the characteristic features in electrochemical noise and WBE current distribution maps should be reproducible even though these results were not exactly the same.

CHAPTER 4

RESULTS AND DISCUSSIONS I: MONITORING AND PREDICTING LOCALIZED CORROSION USING WBE AND ENA

The WBE, in combination with noise signatures analysis, has been used to monitor and study localized corrosion such as pitting and crevice corrosion of SS316L and mild steel under typical localized corrosion and general corrosion conditions. The objective of this work is to identify parameters that could be used for monitoring and predicting localized corrosion, for studying the mechanisms of localized corrosion initiation and growth, and for evaluating the effects of corrosion inhibitors.

4.1 Pitting Corrosion of Stainless Steel 316L Submerged in FeCl_3 Solution

SS316L exposing to a solution containing FeCl_3 is a well-known corrosion system where localized corrosion such as pitting corrosion occurs (Dawson & Hladky, 1981; Fontana, 1987; Smulko *et al.*, 2002b; Punckt *et al.*, 2004). In this work, a series of experiments have been carried out to simultaneously measure electrode potential noise and the WBE current distribution maps over a SS316L WBE surface exposed to a 6% FeCl_3 solution using experimental setup shown in Figure 3.10.

Figure 4.1 shows typical electrode potential noise measured from the SS316L WBE surface during its 240 hours exposure to 6% FeCl_3 solution. For the purpose of comparison, Figure 4.2 shows typical electrode potential noise measured using a conventional dual electrode system shown in Figure 3.9. Similar characteristic noise signatures are observable in Figures 4.1 and 4.2, indicating that the SS316L WBE and the conventional SS316L electrodes have similar electrode

noise behaviour. Figure 4.3 shows WBE current distribution maps measured from the same WBE surface after being exposed to the testing solution for different periods of time. Four characteristic stages can be identified from the electrode potential records, as shown in Figures 4.1 and 4.3:

4.1.1 Four Characteristic Stages of Pitting Corrosion

1. The first stage of corrosion - The first stage was characterized by gradual potential shifting towards negative direction. As shown in Figure 4.1(a), during the first three hours of exposure, the potential of SS316L WBE shifted nearly -100 mV (from -10 mV to -106 mV vs. SCE). Legat *et al.* (1993) also observed the same noise signature after immediate immersion in stainless steel pitting system. Figures 4.3(a) – 4.3(f) show WBE galvanic current map measured simultaneously with potential recording over exposure periods of 5-20, 20-40 ... 160-180 minutes. It can be seen from Figure 4.3(a) that corrosion anodic sites existed at the very beginning of electrode exposure to the corrosion environment. This result suggests that the passive film on SS316L surface was non-uniform even at the very beginning of corrosion exposure since there were local *breakdown* sites distributing randomly over the WBE surface. The locations of these anodic sites remained almost unchanged during the first three hours of exposure, which is evident if galvanic current maps in Figures 4.3(b) – 4.3(f) are compared with that in Figure 4.3(a). The maximum anodic current density, however, increased significantly over the same period (from 0.94 to 2.166 mAcm⁻²). These results clearly show that the passive film on SS316L surface was not intact, but had *holes* that behaved as corrosion anodic sites. The continuous shifting of electrode potential towards negative direction shown in Figure 4.1(a) was obviously not due to an increase in anodic area, since the anodic area did not change much during the first 3 hours.

The electrode potential shifting was mostly likely due to a continued decrease in anodic potential. Since the major cathodic reaction in the corrosion system should have remained as oxygen reduction and the concentration of oxygen was controlled by diffusion from the air, the potential of the cathodic area should have remained stable. The major increase in galvanic currents between cathodic and

anodic zones must be due to decrease in potential in the anodic zone. This is most likely resulted from local thinning of anodic passive film, breakdown of the passive film and consequently the initiation of pits. It has been reported that the presence of aggressive ions, such as chloride ions, can attack preferentially some active points on the passive film, leading to the local thinning and breakdown of the passive film and consequently the initiation of pits (Heusler & Nachstedt, 1988). The initiation of the active points can also result from surface scratches and variations in the composition of the metal surface, due to the presence of inclusions, different phases, grain boundaries, disturbed metal, and other causes (Fontana, 1986). Our results suggested that within twenty minutes of exposure of SS316L WBE to FeCl_3 corrosive electrolytes, local thinning of the passive film occurred. These locally thinned or damaged spots on a passive film are considered to be *active points*. Local thinning of the passive film is a result of catalytically enhanced transfer of cations from the oxide film to the electrolyte (Strehblow, 1995). When local thinning of the passive film occurs because of local adsorbed species, the local electric field strength increases, which may eventually lead to complete breakdown of the passive film and pits initiation (Heusler & Nachstedt, 1988). Exposure of iron to chloride and other halides can cause local thinning of the passive film, even under conditions where a pit had not formed (Strehblow, 1995). Corrosion pattern was general in this pre-pitting stage of stainless steel corrosion since corrosion anodes appeared to be distributing randomly over the whole WBE surface.

2. The second stage of corrosion - As shown in Figures 4.1(b) and 4.1(c), the second stage of corrosion in this system featured a characteristic *peak* of rapid potential transient, towards less negative direction, followed by recovery. This noise behaviour occurred most frequently during 3-9 hours of exposure. We refer to this type of noise behaviour as *noise signature I*. This is a common electrode noise pattern reported in many pitting corrosion systems (Hladky *et al.*, 1981; Searson *et al.*, 1988; Tan *et al.*, 1998; Hashimoto *et al.*, 1992; Pistorius *et al.*, 1996) and is usually believed to result from metastable pit nucleation and repassivation processes (Hashimoto *et al.*, 1992). This typical pattern of sudden rise in potential and exponential recovery was also discovered by Smulko (2002) and Punckt *et al.* (2004). However this belief is mainly based on scientific reasoning, and has not been verified experimentally due to experimental difficulties. In this particular

experiment, as shown in Figures 4.1(b) and 4.1(c), this noise behaviour occurred most frequently during 3-9 hours of exposure. If the feature in *noise signature I* was indeed due to passive film rupture and subsequent repassivation of unstable pits, the WBE current distribution maps measured from the WBE surface should show anodic locations keep forming and disappearing with the extension of electrode immersion. However, as shown in Figures 4.3(g) – 4.3(t), the galvanic current distribution maps show no formation of major anodic sites during 3-8 hours of exposure. Instead, the original anodic locations remained almost unchanged with the extension of electrode immersion. An important observation can be made if the timing of *peak 1* in Figure 4.1(b) and *peak 2* in Figure 4.1(c) is compared with the current distribution maps in Figures 4.3(g) – 4.3(t). As shown in Figure 4.1(b), *peak 1* occurred over a 30 minute time window between 4 hours 10 minutes and 4 hours 40 minutes of exposure. This time window corresponds to the measurement of maps in Figures 4.3(j), 4.3(k) and 4.3(l). During this period, as shown in Figures 4.3(j) – 4.3(l), no new anode was formed; instead, one major anode disappeared. Similarly, *peak 2* in Figure 4.1(c), which occurred over a 30 minutes period between 6 hours 40 minutes and 7 hours 10 minutes of exposure, resulted in no anode formation; instead it correlated with the disappearance of a major anode, which can be seen by comparing maps in Figures 4.3(p), 4.3(q) and 4.3(r). This correlation clearly suggests that *noise signature I* was due to the disappearance of an unstable anode which leads to the reduction in anodic area and thus sudden potential shift to less negative direction. This result suggests that the origin of *noise signature I* in Figures 4.1(b) and 4.1(c) was not the conventionally believed passive film rupture process, but the anode disappearance process. The disappearance of a major anodic site leads to decrease in anodic area and thus caused a sudden shift of the electrode potential towards less negative direction. The corrosion pattern became localized during this stage after the disappearance of some minor anodes. However, the root cause of the sudden disappearance of anodes during the process is not clearly known. Although this requires further investigation, this phenomenon could be due to the major anodes cathodically polarized and protecting the unstable anodes, leading to the disappearance of unstable major anodes.

3. The third stage of corrosion - As shown in Figures 4.1(d), the third stage of corrosion featured the characteristic pattern of rapid potential transient, also

towards less negative direction, followed by no recovery. We refer to this type of noise behaviour as *noise signature II*. As shown in Figures 4.1(d) and 4.1(e), *noise signature II* became visible after approximately 87 hours of exposure. This noise pattern is usually assumed to result from pit nucleation and continuous growth processes (Hashimoto *et al.*, 1992; Pistorius *et al.*, 1996). If this assumption is true, the galvanic current distribution maps measured from the WBE surface should exhibit a typical feature that stable anodes are formed and lead to visible pits on the electrode surface. However, as shown in Figures 4.3(u) and 4.3(v), this stage of exposure corresponded to the massive disappearance of anodic sites, rather than the formation of new anodic sites. Since no other major change in corrosion anode or cathode was observable during this period, the appearance of *noise signature II* could reasonably be attributed to the massive disappearance of a corrosion anode. The galvanic current of the stable anode was further increased from about 3.05 mAcm^{-2} to over 10 mAcm^{-2} . This result suggests that the *noise signature II* corresponded with the stable pit formation. The increase in current density with time at the major anode of stainless steel shows a higher chance of forming the stable anode. It is generally agreed that the higher the current density at a metastable pit, the higher is the probability of its transition to a stable pit. This process, as shown in Figures 4.3(w) – 4.3(x), has lead to the formation of a major stable anode at location of wires 35 and two other smaller anodes. This behaviour was repeated in duplicate experiments. The corrosion pattern became more localized after the formation of stable pits. During this stage, as shown in Figures 4.1(e), the characteristic pattern of rapid potential transient towards more negative direction followed by no recovery was also observed. We refer this type of noise behaviour as *noise signature III*. This noise behaviour was observed after 216 hours of exposure. The *noise signature III* was corresponded with the rapid propagation of stable pit as shown in Figures 4.3(x) and 4.3(y). The corrosion pattern became more localized with deep pit at wire no. 35.

4. The fourth stage of corrosion - As shown in Figure 4.1(f), the fourth stage of corrosion featured the electrode potential fluctuating randomly in a narrow range. The electrode potential fluctuated within a narrow range of 2 mV over a 3-hour period. The major anode at location of wires 35, as shown in Figures 4.3(y) and 4.3(z), became stabilized and continued rapid anodic dissolution.

Fig. 4.1(a) Potential noise measured using a WBE, 15 mins-3 hours

Fig. 4.1(b) Potential noise measured using a WBE, 3-6 hours

Fig. 4.1(c) Potential noise measured using a WBE, 6-9 hours

Fig. 4.1(d) Potential noise measured using a WBE, 90-93 hours

Fig. 4.1(e) Potential noise measured using a WBE, 213-216 hours

Fig. 4.1(f) Potential noise measured using a WBE, after 240 hours

Figure 4.1 Time sequences of potential fluctuations obtained from a SS316L WBE system after exposure to 6% FeCl₃ solution for various periods of time

Figure 4.2 Time sequences of potential fluctuations obtained from a traditional SS316L electrode system after exposure to 6% FeCl_3 solution for the first 10 hours of exposure

Galvanic current distribution [3:3:20 hrs]

Fig.4.3(g)

Main anodes

Galvanic current distribution [3:20-3:40 hrs]

Fig.4.3(h)

Galvanic current distribution [3:40-4 hrs]

Fig.4.3(i)

Galvanic current distribution [4-4:20 hrs]

Fig.4.3(j)

Galvanic current distribution [4:20-4:40 hrs]

Fig.4.3(k)

Disappearance of unstable anode

Galvanic current distribution [4:40-5 hrs]

Fig.4.3(l)

Galvanic current distribution [5-5:20 hrs]

Fig.4.3(m)

Galvanic current distribution [5:20-5:40 hrs]

Fig.4.3(n)

Main anodes
remain stable

Galvanic current distribution [6:20-6:40 hrs]

Fig.4.3(o)

Galvanic current distribution [6-6:20 hrs]

Fig.4.3(p)

Galvanic current distribution [6:40-7 hrs]

Fig.4.3(q)

Galvanic current distribution [7-7:20 hrs]

Fig.4.3(r)

Disappearance of unstable anode

Galvanic current distribution [8:40-9 hrs]

Fig.4.3(s)

Galvanic current distribution [After 22 hrs]

Fig.4.3(t)

Disappearance of some minor anodes and the electrode surface becomes active

Galvanic current distribution [After 72 hrs]

Fig.4.3(u)

Galvanic current distribution [After 96 hrs]

Fig.4.3(v)

Massive disappearance of minor anodes

Galvanic current distribution [After 120 hrs]

Fig.4.3(w)

Galvanic current distribution [After 192 hrs]

Fig.4.3(x)

Figure 4.3 WBE current (mAcm^{-2}) distribution map obtained from a SS316L WBE showing the stable corrosion anodes after exposure to 6% FeCl_3 solution for various periods of time

The WBE current maps such as those shown in Figure 4.3 can be used to determine corrosion rate distribution maps, which give the instantaneous corrosion dissolution rate of the metal at the particular point in time (Tan *et al.*, 2000). Corrosion rate maps measured after different periods of the exposure were used to calculate total corrosion depths over the whole experimental period. This was achieved by summing up the calculated corrosion depths after various periods of exposure to give a cumulative result (Tan *et al.*, 2000), producing a calculated corrosion depth map. The calculated corrosion depth map and observed corrosion depth map are shown in Figures 4.4(a) and 4.4(b), together with a photo of the corroded WBE surfaces (Figure. 4.4 (c)). The observed corrosion depth map was obtained using an optical microscope (Nikon Epiphot 2000 and Nikon Epiphot 200) by plotting individual corrosion depth value of each wire verses their locations. The wire beam electrode was placed vertically downward on the sample stand of the optical microscope. The optical microscope was first focused on the bottom of a pit and then on the top of the pit. The corrosion depth can be obtained with the aid of the main scale and vernier scale attached in the optical microscope. It was found

that the accuracy of the calibrated corrosion depth was acceptable. If the corrosion scale were tens of microns thick then it would have introduced a serious uncertainty into the microscopic determinations of pit depth. However, the passive film usually only has a thickness of a few nanometres, and typically was 1–3 nm thick (Olsson & Landolt, 2003), so that the corrosion scale was much thinner. The maximum depth of corrosion pit on the SS316L WBE surface was approximately 2000–2500 μm . There is a clear correlation between the maps and the photograph.

Figure 4.4 (a) Observed pitting corrosion depth map, (b) Calculated pitting corrosion depth map values and (c) photograph showing a SS316L WBE surface after exposure to 6% FeCl_3 solution for 240 hrs

This experiment clearly demonstrated that the *noise signatures I* and *II* are indicators of minor anodes disappearance, leading to accelerated dissolution of major anodes. Obviously, recognition of such noise signatures can be applied as a means of early detection and prediction of localized corrosion. In many other practical corrosion systems, noise recordings can be more complex and can consist of the superimposition of the basic signatures described above.

4.1.2 Quantitative Data Analysis

In order to identify critical conditions for localized corrosion to initiate, and parameters for stable localized anodes to grow, further analysis of data shown in Figures 4.1-4.4 has been carried out, mainly based on the calculation of a new parameter, namely, the localization parameter (*LP*). *LP* is designed to describe the degree of localization of corrosion based on the maximum anodic current density (i_{max}); which has the largest positive current density value in a WBE current distribution map, the total anodic current density (i_{tot}), which is the sum of all the anodic current densities, and the number of anodes (N_a):

$$LP = \left(\frac{i_{max}}{i_{avg}} \right) \quad (4.1)$$

where the average current density, $i_{avg} = \frac{i_{tot}}{N_a}$

The values of i_{max} , i_{tot} and N_a can be obtained using methods described in Section 3.3 (i). For an uniform corrosion system, the deviation of the maximum current density of major anode from the average current density of the minor anode should be negligible:

$$\text{Uniform corrosion} \rightarrow LP = \frac{i_{max}}{i_{avg}} \text{ approaches to } 1 \quad (4.2)$$

For localized corrosion systems, the current distribution is highly non-uniform, and as a consequence, the maximum current density of the major anode becomes much higher than the average current density of all anodes:

$$\text{Localized corrosion} \rightarrow LP = \frac{i_{\max}}{i_{\text{avg}}} \gg 1 \quad (4.3)$$

Obviously, the larger the LP , the more localized is the corrosion. LP is an easy parameter obtained from WBE current distribution maps and it would be interesting to see localized corrosion initiation and growth stages, the effects of corrosion inhibitors in terms of the degree of localized corrosion. It is easy to present and compare the number of anodes, $i_{\max}$, i_{tot} and LP for different types of localized corrosion. It is also useful to study the trends of localized corrosion.

Figures 4.5 and 4.6 show the change of $i_{\max}$, i_{tot} , N_a and the localization parameter with immersion time of SS316L pitting system in 6% FeCl_3 solution. Four typical stages that can be identified from pitting corrosion in Figures 4.5 and 4.6 are as follows:

1. As shown in Figures 4.5 (a) – (d), during the first three hours, $i_{\max}$, i_{tot} , N_a and also LP values increased. This stage corresponds well with the first stage of corrosion shown in Figure 4.1(a) and Figures 4.3(a) – 4.3(f). This could be due to local thinning of the passive film, leading to an increase in number of anodes, anodic corrosion current, and LP values.
2. The second stage is characterized by the peaking of $i_{\max}$, i_{tot} , N_a and also LP values during 3-10 hours, as shown in Figure 4.5. The increase and decrease in the current during this stage could be due to increased pit initiation-passivation activities. This stage corresponds with the second stage of corrosion shown in Figures 4.1(b), 4.1(c) and Figures 4.3(g) – 4.3(r). However, this phenomenon requires further study.
3. The third stage shows that both values of $i_{\max}$, i_{tot} and LP were continuously increased leading to the stable pit formation. N_a values, however, decreased due to the massive disappearance of anodes. Fluctuation in N_a values was also observed during this period, as shown in Figure 4.5(c), indicating the formation of new minor anodes. It indicates that corrosion attack became more localized. This stage corresponds with the third stage of corrosion shown in Figures 4.1(d), 4.1(e) and Figures 4.3(u) – 4.3(x).

4. The fourth stage was the pit propagation stage, therefore the values of $i_{\max}$, i_{tot} and LP further increased which was observed after 216 hours while N_a values decreased again. The fourth stage corresponds with the fourth stage of corrosion shown in Figures 4.1(e) and Figures 4.3(y).

(a)

(b)

Figure 4.5 Changes of the (a) maximum anodic current density (b) total anodic current density, (c) the number of anodes and (d) localization parameter of SS316L in 6% FeCl₃ solution

In summary, this typical experiment suggests that the analysis and recognition of noise signatures can be used for the early detection and prediction of localized corrosion. The correlation between noise signatures and corrosion patterns change suggests that *noise signatures I, II and III* are indicators of unstable anodes disappearance and massive minor anodes disappearance, leading to accelerated dissolution of major anodes. The prediction of localized corrosion can be carried out by analyzing maximum anodic current ($i_{\max}$), total anodic current densities (i_{tot}), and the localization parameter, as a function of corrosion exposure time.

4.2 Corrosion of Stainless Steel 316L in the Presence of Rare Earth Chemicals

Rare earth chemicals such as cerium chloride have been reported to be localized corrosion inhibitors in some corrosion systems (Aramaki, 2001; Aballe *et al.*, 2001a; Arenas *et al.*, 2002). In the present work, a series of experiments have been conducted to evaluate their effectiveness for inhibiting pitting corrosion of SS316L in 6% FeCl_3 solution. The effect of cerium chloride inhibitor on SS316L pitting corrosion was studied in 6% FeCl_3 solution containing 2 wt.% CeCl_3 over an exposure period of 100 hours.

4.2.1 Three Characteristic Stages of Corrosion of Stainless Steel 316L in the Presence of CeCl_3

Experiments have been carried out to record electrode potential noise and to measure the WBE current distribution maps over a SS316L WBE surface in the 6% FeCl_3 solution using all experimental setup as shown in Figure 3.10. Figures 4.6 and 4.7 show potential noise data and WBE current distribution maps, those were measured simultaneously. The experiment was ended after finding the stable anodes. Three main characteristic stages of corrosion mechanism can be identified in stainless steel 316L corrosion with the presence of CeCl_3 :

1. The first stage of corrosion – This stage was characterized by gradual potential shifting towards negative direction. As shown in Figure 4.6(a), during the first one and half hours of exposure to 6% FeCl₃ solution containing 2 wt.% CeCl₃, the potential of SS316L WBE shifted nearly -55 mV (from -60 mV to -115 mV vs. SCE). In the WBE galvanic current distribution maps, as shown in Figures 4.7 (a), random distribution of anodes and cathodes was observed during the first one and half hours of exposure. Corrosion pattern was uniform in this stage of stainless steel corrosion.

2. The second stage of corrosion – The second stage featured a characteristic peak of rapid potential transient, towards less negative direction, followed by recovery (*noise signature I*) as shown in Figure 4.6(a) and 4.6(b). This noise signature was observed after one and half hours and 12 hours of exposure. WBE maps measured during this stage show that after one and half hours, some unstable anodes disappeared at the same time with increasing the maximum anodic current density from 1.025 mAcm⁻² to 1.711 mAcm⁻². After 12 hours, successive disappearance of unstable anode was observed again. The maximum anodic current density was further increased to 2.289 mAcm⁻², as shown in Figure 4.7(c) and 4.7(d). It was correlated with *noise signature I* in Figure 4.6 (a) and 4.6(b). The corrosion pattern became more localized during this stage after the disappearance of some minor anodes.

3. The third stage of corrosion – The third stage featured the characteristic pattern of rapid potential transient, also towards less negative direction, followed by no recovery (*noise signature II*). As shown in Figure 4.6(c), *noise signature II* was observed after 15 hours of exposure. In the WBE current distribution maps, *noise signature II* in Figure 4.6(c) was found to correspond with the massive disappearance of minor anodes, which leads to the stable anode formation at wire no. 29 after 15 hours. The maximum anodic current density value was further increased from 2.289 mAcm⁻² to 3.476 mAcm⁻² in Figure 4.7(e) and 4.7(f). The corrosion pattern became localized after the formation of stable pits.

Fig.4.6(a) Potential noise measured using a WBE, 15 mins-3 hours

Fig.4.6(b) Potential noise measured using a WBE, 12-15 hours

Fig.4.6(c) Potential noise measured using a WBE, 15-18 hours

Figure 4.6 Time sequences of potential fluctuations obtained from a SS316L WBE system after exposure to 6% FeCl_3 solution with 2 wt.% CeCl_3 for various periods of time

Figure 4.7 WBE current (mAcm^{-2}) distribution map obtained from a SS316L WBE after exposure to 6% FeCl_3 solution with 2 wt.% CeCl_3 for various periods of time

Summing up, the corrosion behaviour of SS316L in 6% FeCl₃ solution with the addition of 2% cerium chloride remained almost unchanged from that in a solution without cerium chloride, as is described in Section 4.1. The noise signatures and WBE current distribution maps also show similar characteristics to that in Section 4.1. This result suggests that cerium chloride did not behave as an effective inhibitor in this corrosion system. XPS results have shown that the cerium-rich film is formed by a mixture of oxides/hydroxides of Ce(III) and Ce(IV), (CeO₂, Ce(OH)₄, and Ce(OH)₃) (Ives & Lu, 1993). The oxidation state of the cerium is extremely sensitive to the quantity of dissolved oxygen, the pH of the solution, and exposure time. First the films were formed with a predominance of Ce(III) and then followed by an enrichment in Ce(IV) hydroxides. In this situation the film probably grows by precipitation on the cathodic sites. However, over-precipitation can allow the continuation of the anodic and cathodic processes (Arenas *et al.*, 2001). It is possible that lack of 2 wt% CeCl₃ inhibitor activity in SS316L corrosion in 6% FeCl₃ solution may be due to the effect of over-precipitation.

4.2.2 Four Characteristic Stages of Corrosion of Stainless Steel 316L in the Presence of LaCl₃

In another series of experiments, 2 wt.% LaCl₃ was added to 6% FeCl₃ solutions to evaluate lanthanum ions effectiveness as corrosion inhibitor for SS316L. Figures 4.8 shows typical electrode potential noise obtained from a SS316L WBE surface, while Figure 4.9 shows the concurrently measured WBE current distribution maps. Four main characteristic stages of corrosion mechanism can be identified in SS316L corrosion with the presence of LaCl₃:

1. **The first stage of corrosion** - The first stage was characterized by gradual potential shifting towards negative direction. As shown in Figure 4.8(a), during the first three hours of exposure the potential of SS316L WBE shifted nearly -60 mV (from -50 mV to -110 mV vs. SCE). WBE maps measured during the first stage, as shown in Figures 4.9(a) and 4.9(b), show that in FeCl₃ solution with LaCl₃, anodic and cathode sites are distributed in a random manner during three hours exposure. The maximum anodic current density increased from 1.229 mAcm⁻² to 1.56 mAcm⁻². Corrosion pattern was uniform in this pre-pitting stage. The noise

signatures and WBE current distribution maps also show similar characteristics to those in Section 4.1.

2. The second stage of corrosion - The second stage featured a characteristic peak of rapid potential transient, towards more negative direction, followed by recovery as shown in Figure 4.8(b). We refer this type of noise behaviour as *noise signature IV*. This noise behaviour occurred most frequently during 12-48 hours of exposure. The WBE current distribution maps in Figures 4.9(c) and 4.9(d) show that the *noise signature IV* corresponded with the initiation of new anodic sites at wire no.11 and 93. This is interesting behaviour that is different from the noise signatures observed previously. The corrosion pattern became less localized during this stage after formation of new anodes. On a corroding metal surface, there are always anodes and cathodes. In this experiment, it was possible that the La^{3+} cations stimulated the anodic process leading to unstable new anodes formation.

3. The third stage of corrosion - The third stage featured characteristic pattern of rapid potential transient, towards less negative direction, followed by no recovery (*noise signature II*). As shown in Figure 4.8(c) *noise signature II* was observed after 69 hours of exposure. WBE maps measured during the third stage, as shown in Figures 4.9(e) and 4.9(f), indicate that the *noise signature II* was correlated with a massive disappearance of anodes leading to stable anode formation. The stable anode was found at wire no.93 with the constant maximum anodic current density value about 15.029 mAcm^{-2} after 72 hours exposure.

4. The fourth stage of corrosion - The fourth stage featured the characteristic pattern of rapid potential transient towards more negative direction followed by no recovery (*noise signature III*). This signature was found after 80 hours of exposure in Figure 4.8(d). WBE current distribution maps measured during this stage, as shown in Figures 4.9(g) and 4.9(h), show that the stable anodes were under rapid dissolution. The maximum galvanic current of the stable anode at wire no. 93 was further increased to 24.881 mAcm^{-2} in this stage. The *noise signature III* in Figure 4.8(d) corresponded with the rapid propagation of stable pit. The corrosion pattern became more localized with serious pitting corrosion and deep pits were found.

Fig.4.8(a) Potential noise measured using a WBE, 15 mins-3 hours

Fig.4.8(b) Potential noise measured using a WBE, 12-15 hours

Fig.4.8(c) Potential noise measured using a WBE, 69-72 hours

Random distribution of anodes and cathodes

Galvanic current distribution [After 20 mins]

Fig.4.9(a)

Galvanic current distribution [After 3 hrs]

Fig.4.9(b)

Figure 4.9 WBE current (mAcm^{-2}) distribution map obtained from a SS316L WBE after exposure to 6% FeCl_3 solution with 2 wt.% LaCl_3 for various periods of time

In summary, although the soluble salts of rare earth metals such as Ce^{3+} , and La^{3+} have been reported to be effective for suppressing the corrosion of iron, steel and aluminum (Hinton, 1992; Bernal *et al.*, 1995; Aramaki, 2001; Aballe *et al.*, 2001a; Arenas *et al.*, 2002; Li & Zhang, 2003), the beneficial effect of rare earth chemicals such as CeCl_3 and LaCl_3 on SS316L corrosion in 6% FeCl_3 solutions was not observed in the above two series of experiments. In some earlier research work, it is reported that the inhibition mechanism of the rare earth elements is based on blocking the cathodic areas of the material, reducing the rate of the cathodic process and, as a consequence, that of the associated anodic process (Ives & Lu 1993). However, thicker rare earth oxide films or over-precipitation of rare earth particles due to a loss in the film coherence, when it reaches a critical thickness, cause a lower resistance to corrosion initiation and the continuation of the anodic and cathodic processes (Montemor *et al.*, 2001; Arenas *et al.*, 2001). The results suggest that the inhibition properties of the rare earth inhibitors may be extremely sensitive to a function of the inhibitor concentration, test environment such as the quantity of dissolved oxygen, the pH of the solution and the exposure time. In order to inhibit localized corrosion of SS316L, the key factor is repassivating the existing pits. Our results have brought focus to the ideas that 2 wt% concentration of CeCl_3 and LaCl_3 are not able to contribute to the repassivation of pits on stainless steel in 6% FeCl_3 solution.

4.3 Corrosion of Stainless Steel 316L in the Presence of Inhibitor Na_2CrO_4

In order to understand the effects of corrosion inhibitor on localized corrosion processes, a series of experiments have been carried out by exposing a SS316L WBE to 6% FeCl_3 solutions containing 2 wt.% Na_2CrO_4 .

4.3.1 Three Characteristic Stages of Corrosion of Stainless Steel 316L in the Presence of Inhibitor Na_2CrO_4

The experimental setup was the same as described in Figure 3.10. Figure 4.10 shows typical electrode potential noise obtained from the corrosion system. Figure 4.11 shows WBE current distribution maps measured simultaneously with potential noise recording over an exposure period of 240 hours. Three characteristic stages can be identified from Figures 4.10 and 4.11:

1. The first stage of corrosion - The first stage of corrosion in this system was also characterized by gradual potential shifting towards negative direction, similar to that shown in Figure 4.1(a). As shown in Figure 4.10(a), during the first three hours of exposure, the potential of SS316L WBE shifted nearly -125 mV (from -50 mV to -175 mV vs. SCE). The first stage lasted for 20 hours. The WBE current distribution maps measured during the first stage show only a few anodes on the WBE surface. Also their anodic current density values increased over the first 3 hours, as shown in Figures 4.11(a) and 4.11(b). However, the maximum anodic current density decreased from 0.328 mAcm^{-2} to 0.101 mAcm^{-2} . The continuous shifting of electrode potential towards negative direction could be due to the local thinning of the existing minor anodic sites caused by strong FeCl_3 electrolyte.

2. The second stage of corrosion - The second stage of corrosion featured a characteristic peak of rapid potential transient, towards less negative direction, followed by recovery. As shown in Figure 4.10 (b) and Figure 4.10 (c), it behaved similarly to *noise signature I* shown in Figures 4.1(b) and 4.1(c). This noise behaviour occurred most frequently during 20-80 hours of exposure. WBE maps measured during the second stage show that after 21 hours, one of anodic sites at wire no.16 became a major anode, while the maximum anodic current density decreased from 0.046 mAcm^{-2} to 0.043 mAcm^{-2} as shown in Figure 4.11(c) and 4.11(d). With the extension of corrosion exposure, as shown in Figures 4.11(e) and 4.11(f), the maximum galvanic current density further decreased to 0.033 mAcm^{-2} . The *noise signature I* appeared to correspond with a sudden decrease in the maximum anodic current density of the system due to the deposition of passive oxide layer on main anodes. It has been reported that $\text{Cr}_2\text{O}_4^{2-}$ and $\text{Cr}_2\text{O}_7^{2-}$ anions as

oxidants will promote formation of passive film on stainless steels (Yu Zuo *et al.*, 2002). The corrosion pattern became less localized during this stage after the repassivation of some anodes.

3. The third stage of corrosion - The third stage featured the characteristic pattern of rapid potential transient, also towards less negative direction, followed by no recovery (*noise signature II*). As shown in Figure 4.10 (d), *noise signature II* was observed after 80 hours of exposure. This *noise signature II* is similar to *noise signature II* shown in Figures 4.1(d) and 4.1(e). The characteristic noise patterns can be correlated with characteristic changes in WBE current distribution maps shown in Figure 4.11. After 123 hours, the disappearance of the anodes was observed with the decreasing maximum anodic current density value of about 0.025 mAcm^{-2} in the WBE current distribution maps as shown in Figures 4.11(g) and 4.11(h). It could be due to the repassivation effect of Na_2CrO_4 , leading to very low corrosion. However, a major difference in this effective inhibition system is that the potential change which occurred during the rapid potential transient was only about 1 mV, much smaller than that in Figures 4.1(d), 4.6(c) and 4.8(c), whereas the potential changes are greater than 2 mV. This result suggests that *noise signature II* has correlated with the repassivation of the existing major anodes. It is confirmed by reducing the value of the maximum anodic current density. These characteristics differentiate the behaviour in inhibition system from that of active localized corrosion system.

After 240 hours, almost all of the existing main anodes were repassivated, as shown in Figure 4.12(a). The maximum anodic current density of the system remained very low. There is a clear correlation between galvanic current distribution map (Figure 4.12a), and corroded WBE surfaces after 240 hours experiment, the enlarged photograph of corroded WBE surface is shown in Figure 4.12(b) and 4.12(c).

Fig.4.10(a) Potential noise measured using a WBE, 15 mins-3 hours

Fig.4.10(b) Potential noise measured using a WBE, 24-27 hours

Fig.4.10(c) Potential noise measured using a WBE, 69-72 hours

Fig.4.10(d) Potential noise measured using a WBE, 120-123 hours

Figure 4.10 Time sequences of potential fluctuations obtained from a SS316L WBE system after exposure to 6% FeCl₃ solution with 2 wt.% Na₂CrO₄ for various periods of time

Galvanic current distribution [After 240 hrs]

(a)

Corroded area

(b)

(c)

4.3.2 A Comparison between Non-inhibition and Inhibition of Stainless Steel Pitting Corrosion

The experiments described above have indicated that Na_2CrO_4 behaved as an effective inhibitor for SS316L pitting corrosion in solution containing 6% FeCl_3 , while CeCl_3 and LaCl_3 did not show inhibiting effects. This is confirmed by polarization curves shown in Figure 4.13. SS316L pitting corrosion in solution Na_2CrO_4 was found to be significantly cathodic compared to those in solution CeCl_3 , LaCl_3 and without inhibitor. The cathodic part of the SS316L pitting corrosion with Na_2CrO_4 curve reveals that the cathodic currents were much lower at all potentials. A comparison with the polarization curve without inhibitor, the Na_2CrO_4 polarization curve shifts left, indicating a smaller new i_{corr} which is the most important parameter in determining corrosion rate has reduced significantly.

Figure 4.13 Polarization curves of SS316L WBE in solution containing 6% FeCl_3 with and without inhibitor

CeCl₃ polarization curve clearly showed an anodic shift in E_{corr} , which is either symbolic of preferential suppression of the anodic half-reaction, or of preferential facilitation of the cathodic half-reaction. It has been proposed that the oxides/hydroxides of Ce³⁺ on the stainless steel surface are reduced quickly under applied cathodic current and expose the active metallic surface sites to the electrolyte where the cathodic reactions can take place (Bethencourt *et al.*, 1997, 1998; Powell *et al.*, 1999). Therefore, the anodic shift in E_{corr} in CeCl₃ polarization curve may be due to the preferential facilitation of the cathodic half-reaction.

SS316L pitting corrosion with CeCl₃ and LaCl₃ and without an inhibitor can be classified as active localized corrosion systems, while SS316L in 6% FeCl₃ with Na₂CrO₄, can be classified as an inhibited system. Further analysis of these corrosion or inhibition systems can be carried out based on the calculation of the localization parameter, LP . Figure 4.14 shows the change of i_{max} , i_{lot} , N_a and the LP with immersion time.

(a)

(b)

(c)

(d)

Figure 4.14 Changes in the (a) maximum anodic current density, (b) total anodic current density, (c) number of anodes, and (d) localization parameter of SS316L WBE in solution containing 6% FeCl_3 with and without inhibitor for 100 hours

Two major differences can be found if the behaviours of the active localized corrosion systems are compared with the inhibited system:

1. In order to obtain information about localization corrosion inhibition of the inhibitors, the inhibition degree must be evaluated in terms of both nucleation of pits and propagation of pre-existing pits. A valuable and remarkable property of chromate inhibitor is self healing active corrosion inhibition. Chromate inhibitor has shown repassivation ability of pits on stainless steel (Burstein & Ilevbare, 2003). In the inhibited system, i_{max} and i_{tot} values remained small and steady during all stages of corrosion. The localization parameter, LP, value was uniquely large during the first stage of corrosion due to the initial rapid anodic reaction required for passive film formation as shown in Figure 4.14(d). However, the LP value decreased continuously over the whole period of corrosion as a result of reducing i_{max} at the

anodic sites. The results suggest that Na_2CrO_4 inhibitor has been found to act as an effective inhibitor to repassivate pre-existing pits in localized corrosion of SS316L. The CrO_4^{2-} anion has a higher specific irreversible adsorption than the aggressive anion (Cl^-), meaning that the CrO_4^{2-} anion can displace the adsorbed Cl^- ions layer, leading to reduction in the number of nucleations and metastable pits (Refaey *et al.*, 2000; Burstein & Ilevbare, 2003). Once anodic sites are blocked by CrO_4^{2-} anion, O_2 chemisorption is prevented and O_2 becomes a much weaker oxidizing agent. It is suggested that chromate acts as both anodic and cathodic inhibitor (William *et al.*, 2002).

2. Conversely, the $i_{\max}$ and i_{tot} values as well as LP value for active localized corrosion systems, in particular, with LaCl_3 , increased over the corrosion exposure period. The results explain that the CeCl_3 and LaCl_3 inhibitors do not inhibit both pitting initiation and propagation stages at all. The rare earth oxide films does not have the self healing property and thicker rare earth oxide films can lower resistance to corrosion initiation and cause the continuation of the anodic and cathodic processes (Montemor *et al.*, 2001; Arenas *et al.*, 2001). It has also been found that higher inhibitor concentration can lead to a decrease in the inhibiting power of LaCl_3 (Bethencourt *et al.*, 1997, 1998). The beneficial effect of 2 wt% CeCl_3 and 2 wt% LaCl_3 on SS316L corrosion in 6% FeCl_3 solution has not been observed by any researcher. The results suggest that the inhibition efficiency of the rare earth inhibitors can change as a function of the inhibitor concentration, the test environment and the exposure time. It is possible that 2 wt% concentration of CeCl_3 and LaCl_3 are not able to contribute to the repassivation of pits on stainless steel in 6% FeCl_3 solution.

4.4 Pitting and Crevice Corrosion of Mild Steel Submerged in Evans Solution

4.4.1 Pitting Corrosion of Mild Steel in Evans Solution

A mild steel WBE was exposed to a classical localized corrosion environment known as the Evans solution, to study its pitting corrosion. Figure 4.15

presents the typical electrode potential noise measured from a mild steel WBE surface after being exposed to the Evans solution. WBE current distribution maps over mild steel WBE surface, as shown in Figure 4.16, were measured simultaneously with potential recording over exposure periods of 9 hours. From the electrode potential noise record shown in Figure 4.15(a) – Figure 4.15(c) three characteristic stages were observed:

1. The first stage of corrosion – The first stage was characterized by gradual potential shifting towards negative direction. The potential of mild steel was observed, to be falling continuously from an initial potential of approximately –250 mV to –350 mV in three hours as shown in Fig. 4.15(a). WBE maps measured during the first three hours show that some active anodic locations changed to passive on the surface of the mild steel WBE in Figures 4.16(a) – 4.16(b). After this initial period, only two significant anodes remained at the location of wires no. 31 and no. 84. The maximum anodic current density of these anodes was gradually increased from 0.02 mAcm^{-2} to 0.046 mAcm^{-2} , as shown in Figure 4.16(f). The electrode potential shifting was mostly likely due to the continued decrease in anodic potential. Since the major cathodic reaction in the corrosion system should have remained steady as the oxygen reduced, and since the concentration of oxygen was controlled by diffusion from the air, the potential of cathodic area should have remained stable. The major increase in galvanic currents between anodic and anodic zones must be due to decrease in potential in the anodic zone. Even in this early stage of corrosion, corrosion pattern was localized.

2. The second stage of corrosion – The second stage of corrosion exposure featured the characteristic pattern of rapid potential transient towards less negative direction followed by recovery (*noise signature I*) as shown in Fig. 4.15(b). *Noise signature I* became visible after 3 hours 23 mins and 3 hours 46 mins of exposure. During this stage, the WBE current distribution maps measured from the WBE surface in Figures 4.16(g) and 4.16(h) show that the existing main anode at wire no.84 disappeared after 3 hours. At the same time, the growth of the main anode at wire no.31 was observed. The anodic area at wire no.31 was gradually expanded as shown in Figures 4.16(i) – 4.16(l), and then the main anode position was shifted to the nearest neighbouring wire no.32. The maximum galvanic current of the anode

was further increased to 0.098 mAcm^{-2} . The formation of a new anodic site at wire no.82 was observed at 3 hours 46 minutes and this unstable anode was repassivated within 20 minutes as shown in Figures 4.16(i) – 4.16(k). The *noise signature I* represents pit initiation and repassivation stage and this stage corresponded with the disappearance of the unstable anode as shown in Figure 4.16(i) - 4.16(k). During this stage, the corrosion pattern became more localized after some minor anodes disappeared.

The noise signatures from the first and second stages of mild steel pitting corrosion (Figure 4.15) are similar to those of stainless steel pitting corrosion (Figures 4.1). However, the *noise signature II* for massive disappearance of anodes was not observed in mild steel pitting corrosion. This could be due to the fact that the number of active anodes in this mild steel corrosion system was small, and thus massive disappearance was not necessary in this system.

3. The third stage of corrosion – The third stage of corrosion featured the electrode potential fluctuating randomly in a narrow range in Figure 4.15(c). The fluctuated electrode potential was 20 mV over a 3-hour period. WBE maps measured during this stage show further growth of the main anode at wire no. 31 and the formation of a new major anode at wire no. 32. The major anode at location of wire no. 32 became stabilized and continued rapid anodic dissolution with the galvanic current of 0.279 mAcm^{-2} , as shown in Figures 4.16(m) - 4.16(r). The pitting corrosion pattern became highly localized with the extension of the exposure time.

Fig.4.15(a) Potential noise measured using a WBE, 1-3 hours

Rapid potential changes towards less negative direction followed by recovery (Noise signature I)

Fig.4.15(b) Potential noise measured using a WBE, 3-6 hours

Fig.4.15(c) Potential noise measured using a WBE, 6-9 hours

Figure 4.15 Time sequences of potential fluctuations obtained from a mild steel WBE after exposure to Evans solution for various periods of time

Active area becomes passive leading to localized area

Galvanic current distribution [5-20 mins]

Fig. 4.16(a)

Galvanic current distribution [20-40 mins]

Fig. 4.16(b)

Two main anodes

Galvanic current distribution [40 mins-1 hr]

Fig. 4.16(c)

Galvanic current distribution [1-1:20 hr]

Fig. 4.16(d)

Two main anodes
still remained

Galvanic current distribution [1:20-1:40 hrs]

Fig. 4.16(e)

Two main anodes
still remained

Galvanic current distribution [2:40-3 hrs]

Fig. 4.16(f)

Figure 4.16 WBE current (mAcm^{-2}) distribution map obtained from a mild steel WBE showing the stable pitting after exposure to Evans solution for various periods of time

Figure 4.17 shows $i_{\max}$, i_{tot} , N_a and LP values characteristics of active localized corrosion system. The LP value, as well as $i_{\max}$ and i_{tot} values increased significantly after pitting initiation stage.

Figure 4.17 Changes of the (a) maximum anodic current density; (b) total anodic current density; (c) the number of anodes and (d) the localization parameter of mild steel WBE in Evans solution

4.4.2 Crevice Corrosion of Mild Steel in Evans Solution

By placing a semi plastic ball on the WBE to create a crevice, mild steel WBE exposed to an Evans solution experiment was further expanded into a crevice corrosion experiment is as described in Figure 3.10, section 3.3(v). The objective is to evaluate the effects of crevice on WBE map and noise signatures.

Figure 4.18 shows typical electrode potential noise measured from the mild steel WBE surface after being exposed to the Evans solution for 300 hours. The WBE current maps were measured concurrently with potential recording over the exposure period. The typical WBE maps showing the initiation, propagation and stable crevice corrosion are presented in Figure 4.19. WBE current distribution maps that were measured simultaneously are shown in Figure 4.19. Three characteristic stages can be identified from the electrode potential record shown in Figure 4.18(a) – Figure 4.18(c):

- 1. The first stage of corrosion** – The first stage was characterized by sharp drop in potential, shifting towards negative direction in Figure 4.18(a), without recovery (*noise signature III*). The major pattern has been changed from pitting to crevice after about one hour of exposure, which was demonstrated by WBE current distribution maps as shown in Figure 4.19(b). WBE maps measured during the first stage show the initiation of a major anode at wire no. 45 inside crevice area after one hour exposure, as shown in Figure 4.19(c). The maximum galvanic current of the corrosion system, however, decreased from 0.436 mAcm^{-2} to 0.385 mAcm^{-2} . Anodic potential within crevice decreased from -440 to -530 mV which could be due to continued potential decrease in the crevice area with decrease in oxygen concentration.

Hladky and Dawson [1981] first observed the change from pitting to crevice attack and they proposed that crevice corrosion is a preferred process compared to pitting attack and that once crevice attack begins, the then pit initiation ceases. It is generally believed that during the initiation of crevice corrosion, the environment in crevice has less oxygen and corrosion potential is low so the anodic and cathodic reactions take place preferentially in and outside of a crevice. As a result, there are other cathodically protected surfaces leading to stop pitting. Before the initiation of

crevice corrosion, anodic and cathodic reactions take place in and outside of a crevice. The *noise signature III* probably reveals the exact moment when massive anodic sites are initiated under the crevice area.

2. The second stage of corrosion – The second stage of corrosion exposure featured the characteristic potential noise pattern of the continuous cyclic oscillations at a constant frequency as shown in Figure 4.18(b) and 4.18(c). We refer to this type of noise behaviour as *noise signature V*. WBE maps measured during this stage indicate, that the propagation of crevice attack proceeded with the formation of new anodes in the crevice area. The first new stable anode became visible at wire no. 54 after 17 hours immersion time as shown in Figure 4.19 (d). The second stable anode was found at wire no. 76 with the maximum galvanic current of 0.171 mAcm^{-2} in Figure 4.19(e). The third stable anode was at wire no. 64 after 79 hours, as shown in Figure 4.19(g). After 107 exposure, there were four stable anodes inside crevice in Figure 4.19(h) and they combined each other leading to the significant crevice area as indicated in Figure 4.19(i). However, the maximum galvanic current was an increased to 0.211 mAcm^{-2} , and later further decreased to 0.114 mAcm^{-2} due to increase in anodic areas inside the crevice. As more and more anodes were formed inside the crevice, the average anodic current value became less resulting in maximum galvanic current value.

It is obvious that in this experiment, the *noise signature V* correlated with the successive and probably periodic formation of new stable anodes inside the crevice area as shown in Figures 4.19(d)-4.19(g). Apparently, the frequency of the cycle is changing with increased exposure of time because the rate of new stable anodes formation inside the crevice area is changing. The corrosion pattern became less localized with successive formation of anodes in the propagation stage. It has been proposed that the crevice progresses in well defined cycles; a rapid propagation stage followed by a longer interval of comparative inactivity (Dawson & Hladky 1981).

3. The third stage of corrosion – The third stage of corrosion exposure featured electrode potential fluctuating randomly in a narrow range. As shown in Figure 4.18(d), the electrode potential fluctuated within a narrow range of 15 mV over a three hours period. WBE maps measured during this stage indicate

continuous localized corrosion. During crevice propagation, no new pit appeared outside the crevice. On the other hand, the existing pit outside crevice ceased as shown in Figure 4.19(j). Corrosion proceeded in the whole occluded cavity site on the WBE by a combination of the stable anodes and the crevice system appeared to be very stable after 249 hours.

The WBE sample undergoing crevice corrosion was kept in the Evans solution for 300 hours. Instantaneous corrosion rate maps were used to determine total corrosion depths. This was achieved by summing up the corrosion depths over various periods of exposure to give a cumulative result (Tan *et al.*, 2000). Figure 4.20 shows a such calculated corrosion depth distribution map. The calculated total corrosion depths correlate quantitatively with the microscopically observed corrosion depths and the photo of the corroded WBE. This result confirms the accuracy of the corrosion measurement method.

Fig. 4.18 (a) Potential noise measured using a WBE, 15 mins-3 hours

Galvanic current distribution [After 15 mins]

Fig. 4.19(a)

Galvanic current distribution [After 30 mins]

Fig. 4.19(b)

Galvanic current distribution [After 1 hr]

Fig. 4.19(c)

Galvanic current distribution [After 17 hrs]

Fig. 4.19(d)

Galvanic current distribution [After 42 hrs]

Fig. 4.19(e)

Galvanic current distribution [After 63 hrs]

Fig. 4.19(f)

Galvanic current distribution [After 78 hrs]

Fig. 4.19(g)

Galvanic current distribution [After 105 hrs]

Fig. 4.19(h)

Galvanic current distribution [After 249 hrs]

Fig. 4.19(i)

Galvanic current distribution [After 300 hrs] Maximum anodic current

Fig. 4.19(j)

Figure 4.19 WBE current (mAcm⁻²) distribution map obtained from a mild steel WBE showing the initiation, propagation and stable crevice corrosion after exposure to Evans solution for various periods of time

Figure 4.20 (a) Observed pitting and crevice corrosion depth map, (b) Calculated pitting and crevice corrosion depth map values and (c) the photograph showing a mild steel WBE surface after exposure to Evans solution for 300 hrs

With the extension of the experiment, the maximum galvanic current value decreased six times (from 0.436 mAcm^{-2} to 0.071 mAcm^{-2}), indicating that the corrosion pattern became general after formation of large anodic area inside crevice in this stage. The changes in $i_{\max}$, i_{tot} , N_a and LP values of mild steel crevice corrosion, in the presence of stable pit with immersion time in Evans solution for 300 hours are shown in Figures 4.21.

In the first stage of crevice corrosion, $i_{\max}$, i_{tot} and N_a values increased (Figure 4.21) during 24-50 hours. This stage corresponds with the first stage of corrosion shown in Figure 4.18(a) and Figures 4.19(a)-4.19(d). A significant decrease in the localization parameter was observed as a result of more anode formation inside crevice in Figure 4.21. This is consistent with the fact that the corrosion became more general.

In the second stage, fluctuations in values of $i_{\max}$ and i_{tot} were found during 50-330 hours, as shown in Figure 4.21. The fluctuation of current during this stage could be due to increased initiation and repassivation activities inside crevice. Continuous decrease in the localization parameter was observed, as shown in Figure 4.21, during 50-330 hours period. This stage corresponds with the second stage of corrosion shown in Figures 4.18(b) and Figures 4.19(e) – 4.19(j). The change in localization parameter values shows that the degree of localization decreased when the system changed from a highly localized pitting corrosion to a less localized crevice corrosion.

In summary, this experiment suggests that the noise signatures from initiation and propagation stages of crevice corrosion are different from those of pitting corrosion. A comparison between N_a and LP values for pitting versus crevice was shown in Figure 4.22. The graph suggests that only a small number of stable anodes are formed in pitting corrosion and that results in the higher degree of localized corrosion. Conversely, in crevice corrosion the degree of localized corrosion is low due to the formation of many anodes inside the crevice under local corrosion current.

(a)

(b)

(c)

(d)

Figure 4.21 Changes of the (a) maximum anodic current density, (b) total anodic current density, (c) number of anodes and (d) the localization parameter of mild steel crevice corrosion in the presence of stable pit with immersion time in Evans solution

Figure 4.22 Comparison between the number of anodes and the localization parameter values for pitting versus crevice

CHAPTER 5

RESULTS AND DISCUSSIONS II: DEVELOPMENT OF NOVEL EXPERIMENTAL METHODS FOR MONITORING AND PREDICTING CORROSION UNDER VARIOUS ENVIRONMENTS

The WBE method and noise signatures analysis have been applied in several novel experimental methods for detecting, monitoring and predicting localized corrosion under various corrosion environments. The objective of this work is to develop practical experimental techniques for monitoring corrosion in *difficult-to-test* conditions such as buried steel corrosion, corrosion under insulation, and atmospheric corrosion. Traditional electrochemical techniques such as linear polarization measurement are often difficult to perform under these conditions because these corrosion environments usually have high electrical resistance, thin electrolyte layer, and have difficulty in setting up a three-electrode corrosion testing cell.

5.1 New Method for Monitoring Buried Steel Corrosion

Buried pipes or reinforcement steels can suffer localized corrosion in the presence of inhomogeneous soil, uneven aeration, stray current and aggressive chemical species such as chloride ions, sulphates as well as various types of bacteria. Although electrochemical measurements are useful in understanding buried metal corrosion (Broomfield *et al.*, 2002; Ergun & Yalçyn, 1996; Haruyama & Sudo, 1993; Cigna *et al.*, 1993; Polder, 2001), they are often difficult to perform due to high electrical resistance of soil or concrete. They also have limitations in terms of determining the pattern of corrosion.

5.1.1 Monitoring Mild Steel Corrosion Buried in Sand

Figure 3.11 has shown a novel experimental setup for monitoring metal corrosion buried in sand, based on the WBE method and noise signatures analysis. A series of experiments have been carried out to test the method in simulated corrosion environments; firstly in dry sand, then dampened sand and lastly, chlorinated sand. The experimental design used to measure electrochemical parameters from a corroding WBE surface under buried corrosion has been described in Figure 3.11 and Section 3.3(vi).

In dry sand, the galvanic current values measured using the WBE technique were as low as $6.245 \times 10^{-5} \text{ mAcm}^{-2}$, which agrees with the fact that corrosion rates in a dry sand environment are very slow. To simulate a practical corrosion environment that usually consists of damp sand and soil, 100 ml of distilled water was added slowly to 200 ml of dry sand. Figure 5.1 shows typical WBE current distribution maps measured after various periods of exposure to the damp sand environment. During the first three hours, as shown in WBE galvanic current maps of Figure 5.1(a) and 5.1(b), the anodic sites were mainly located at the bottom part of the WBE and the number of anodic sites increased with time. During this period, the electrode potential of the mild steel WBE shifted gradually towards negative direction (From -500 mV to -650 mV vs. SCE). The increase in anodic areas and decrease in cathodic areas, as shown in Figure 5.1a and 5.1b, could be responsible for this negative potential shifting. According to the mixed-potential concept, anodic and cathodic reactions changes contribute to the potential shift. Since anodic sites have active potential values the more anodic areas, the more active corrosion system becomes. As a consequence, this corrosion pattern could be responsible for the negative potential shifting from potential noise measurements. Obviously, mild steel corrosion in this damp sand environment was slow since anodic currents in Figures 5.1(a) – 5.1(e) are very low. During the 87 hours of exposure, the maximum anodic current had a very low value of 0.029 mAcm^{-2} (in Figure 5.1c).

Galvanic current distribution [After 15 mins]

Fig.5.1(a)

Galvanic current distribution [3 hours]

Fig.5.1(b)

Galvanic current distribution [72 hours]

Fig.5.1(c)

Galvanic current distribution [84 hours]

Fig.5.1(d)

Galvanic current distribution [87 hours]

Fig.5.1(e)

Figure 5.1 WBE current (mA/cm^2) distribution maps obtained from a buried mild steel WBE exposed to damp sand for various periods of time

Since practical sand environments are often contaminated with chloride ions; after the 87 hours exposure to the damp sand environment, 200 ml of 3.5% of NaCl solution was introduced to the test cell to simulate the corrosion of steel buried in NaCl contaminated damp sand. Simultaneously, WBE galvanic current and potential noise measurements were carried out. Figure 5.2 shows the potential noise data from the WBE surface after 200 hours exposure to the NaCl contaminated damp sand. The corresponding typical WBE current distribution maps are shown in Figure 5.3.

Four characteristic stages can be identified from the electrode potential record shown in Figure 5.2(a) – Figure 5.2(d):

1. The first stage of corrosion - The first stage was characterized by gradual potential shifting towards negative direction, as shown in Figure 5.2(a). WBE maps measured during this stage, as shown in Figures 5.3(a) – 5.3(e), show the expansion of anodic areas from the bottom to the top of the WBE surface. The continuous shifting of electrode potential towards negative direction shown in Figure 5.2(a) could be due to increase in anodic area and also due to possible decrease in anodic potential due to limited oxygen supply. In general, this corrosion behaviour is similar to phenomena described in Chapter 4, as in Figure 4.1(a). The corrosion pattern was general in this stage of buried steel corrosion.

2. The second stage of corrosion - As shown in Figures 5.2 (b), the second stage of corrosion in this system featured a characteristic peak of rapid potential transient, towards less negative direction, followed by recovery. This noise behaviour was found during 45-48 hours of exposure. WBE maps measured during this stage show that anodic area propagated to the WBE surface. After 45 hours of exposure, the anodic area propagated to almost all the WBE surface, as shown in Figure 5.3(f). However, the anodic current recorded was small, for instance, the maximum current in Figure 5.3(f) is only $7.334 \times 10^{-4} \text{ mAcm}^{-2}$. A phenomenon clearly observed in this stage is the formation of new cathodes, such as in Figure 5.3(e), which should be the origin of the *noise signature I* shown in Figure 5.2(b).

The root cause of the new major cathodes formation could be related to critical processes such as bacteria activities which promote cathodic reactions.

Bacteria are single-celled organisms, and are the most numerous denizens of the soil. Bacteria corrosion occurs as either a direct or an indirect result of the metabolic activity of certain minute bacteria, particularly, in water or soil environments. Bacteria can produce aggressive metabolites, such as organic or inorganic acids. For example, *Thiobacillus thiooxidans* produces sulfuric acid and *Clostridium aceticum* produces acetic acid. Acids produced by bacteria accelerate corrosion by dissolving oxides (the passive film) from the metal surface and thereby accelerating the cathodic reaction rate (Borenstein, 1994). This phenomenon is very interesting and requires further investigation.

3. The third stage of corrosion - As shown in Figures 5.2(c), the third stage of corrosion featured the characteristic pattern of rapid potential transient to less negative direction followed by no recovery. This noise behaviour became visible after approximately 57 hours of exposure. WBE maps measured during this stage show significant changes in galvanic current values and distributions. As shown in Figure 5.3(g), a galvanic current map measured after 63 hours show a massive and sudden disappearance of anodic sites, resulting in accelerated dissolution at a small number of remaining five main anodic sites with a high anodic current of 0.299 mAcm^{-2} . This phenomenon was repeated in our experiments. Obviously, the *noise signature II* correlated to a massive disappearance of anodic sites, resulting in stable anodes. This noise behaviour is similar to the phenomena described in Chapter 4, such as in Figure 4.1(d). The corrosion pattern became localized since most of anodes disappeared during this stage.

4. The fourth stage of corrosion - The fourth stage of corrosion exposure featured the electrode potential fluctuating randomly in a narrow range. As shown in Figure 5.2(e), the electrode potential fluctuated within a narrow range of 0.2 mV over a 3 hour period. WBE maps shows that this stage was the stabilization stage of buried steel corrosion. As shown in Figure 5.3(j), the galvanic current map indicates that the corrosion system has become stabilized and highly localized, with only five stable anodes and a large galvanic current values of 0.335 mAcm^{-2} .

Fig. 5.2 (a) Potential measured using buried mild steel WBE in NaCl contaminated damp sand, 15 mins-3 hours

Fig. 5.2 (b) Potential noise of buried mild steel WBE in NaCl contaminated damp sand, 45-48 hours

Fig. 5.2 (c) Potential noise of buried mild steel WE in NaCl contaminated damp sand, 57-60 hours

Fig. 5.2 (d) Potential noise of buried mild steel WBE in NaCl contaminated damp sand, 195-198 hours

Figure 5.2 Time sequence of potential fluctuations obtained from a buried mild steel WBE NaCl contaminated damp sand after exposure to for various periods of time

Galvanic current distribution [After 15 mins]

Fig.5.3(a)

Galvanic current distribution [After 3 hrs]

Fig.5.3(b)

Galvanic current distribution [After 6 hrs]

Fig.5.3(c)

Galvanic current distribution [After 30 hrs]

Fig.5.3(d)

Galvanic current distribution [After 45 hrs]

Fig.5.3(e)

Galvanic current distribution [After 50 hrs]

Fig.5.3(f)

Galvanic current distribution [After 63 hrs]

Fig.5.3(g)

Galvanic current distribution [After 84 hrs]

Fig.5.3(h)

Galvanic current distribution [After 130 hrs]

Fig.5.3(i)

Galvanic current distribution [After 199 hrs]

Fig.5.3(j)

Figure 5.3 Galvanic current (mA/cm^2) distribution map obtained from a buried mild steel WBE after exposure to NaCl contaminated damp sand for various periods of time

5.1.2 Effects of Dichromate Inhibitors on Buried Steel Corrosion

After the locally corroded electrode was exposed to NaCl contaminated damp sand for 200 hours, 100 ml of 3 wt.% $K_2Cr_2O_7$ inhibitor was added to the NaCl contaminated damp sand in order to investigate the effects of inhibition on buried steel corrosion. The effectiveness of inhibition has been evaluated by observing changes in noise signature patterns and WBE current distribution maps. In this experiment, as shown in Figures 5.4 and 5.5, three characteristic stages can be identified after the addition of chromate to the sand environment:

1. The first stage of corrosion - The first stage was characterized by gradual potential shifting towards negative direction from three hours to over 15 hours (Figure 5.4a). The WBE galvanic current distribution changed immediately after the addition of potassium dichromate into the sand environment. As shown in Figure 5.5(a), most of the electrode surface has become anode from the map in Figure 5.3(j) to map. Although the maximum current density decreased from 0.335 in Figure 5.3(j) to 0.174 $mAcm^{-2}$ in Figure 5.5(a), the total anodic current has increased significantly. For instance, the total anodic current density measured before the addition was only 1.895 $mAcm^{-2}$, as shown in Figure 5.3(j), and jumped to 2.36 $mAcm^{-2}$ immediately after the inhibitor addition in Figure 5.5(a). This result suggests that the dissolution of the buried steel WBE was accelerated by the addition of inhibitor. This sharp increase in initial total anodic current densities is an interesting phenomenon that has been observed repeatedly. The sharp increase in the number of anodes and the large initial anodic currents caused by the addition of dichromate should be due to the anodic reaction of the metal surface by dichromates, which is required for the formation of passive oxide layer on steel surface, leading to passivation. Indeed, the total anodic current decreased to 1.07 $mAcm^{-2}$ after extended exposure to the inhibitor added environment, as shown in Figure 5.5(b). The corrosion pattern was still localized in first stage of buried steel corrosion with inhibitor.

2. The second stage of corrosion - The second stage of corrosion featured a characteristic peak of rapid potential transient, towards less negative direction, followed by recovery (*noise signature I*) as shown in Figure 5.4(b). The number of

corrosion anodic sites and the value of galvanic current decreased significantly with continued exposure. As shown in Figures 5.5(c) and 5.5(d), low current area (or called passive area) was found to propagate to almost half of the WBE surface and the maximum anodic current density significantly reduced from 0.098 mAcm^{-2} to 0.045 mAcm^{-2} . This correlation clearly suggests that *noise signature I* was due to the reduction in anodic area and increase in cathodic area, leading to sudden potential shift to less negative direction. The root cause of the sudden disappearance of anodes during the process could be the passivation of unstable anodes.

3. The third stage of corrosion - The third stage of inhibition featured the characteristic pattern of rapid potential transient towards less negative direction, followed by no recovery (*noise signature II*) in Figure 5.4(c). In this stage, a massive disappearance of anodes was observed in WBE current maps shown in Figures 5.5(e) and 5.5(f), and at the same time the maximum anodic current density reduced to 0.029 mAcm^{-2} after 57 hours exposure, as shown in Figure 5.5(f). Chromate must have worked to passivate the steel surface. Usually, at the anode, ferrous hydroxide which is slightly soluble, is formed from the hydration of the ferrous ions. In the presence of dissolved oxygen, $\text{K}_2\text{Cr}_2\text{O}_7$ inhibitor may function by oxidizing ferrous hydroxide to a protective gamma Fe_2O_3 film. At the same time, the reduced chromate, $\text{Cr}_2\text{O}_3^{2-}$ is incorporated into the protective film (Rozenfeld, 1981; Fujioka *et al.*, 1996; Cheng *et al.*, 1998; Jeffcoate *et al.*, 2000; Yu Zuo *et al.*, 2002; Zhao & Zuo, 2002). The corrosion pattern was general due to the repassivation of localized corrosion areas.

Figure 5.6(a) and Figure 5.6(b) show total corrosion depth maps calculated by accumulating anodic dissolution after a total 346 hours of exposure in dry, damped, chlorinated and inhibited sand environments. Also a photo of final corroded WBE is shown in Figure 5.6(c). There is a clear correlation between the maps and the corroded WBE surface. The similar corrosion depths in Figures 5.6(a) and 5.6(b) suggest that corrosion was effectively inhibited by the addition of dichromate inhibitor.

ig. 5.4 (a) Potential measured using buried mild steel WBE in inhibited chlorinated sand environment, 15 mins-3 hours

Fig. 5.4 (b) Potential measured using buried mild steel WBE in inhibited chlorinated sand environment, 15-18 hours

Fig. 5.4(c) Potential measured using buried mild steel WBE in inhibited chlorinated sand environment, 54-57 hours

Figure 5.4 Time sequence of potential fluctuations obtained from a buried mild steel WBE after exposure to chlorinated sand with 3% $K_2Cr_2O_7$ inhibitor for various periods of time

Figure 5.5 WBE current (mAcm^{-2}) distribution map obtained from a buried mild steel WBE after exposure to chlorinated sand with 3% $\text{K}_2\text{Cr}_2\text{O}_7$ inhibitor for various periods of time

Figure 5.6 Calculated corrosion depth maps (a) before and (b) after exposure to 3% $\text{K}_2\text{Cr}_2\text{O}_7$ inhibitor and (c) the photograph showing corroded mild steel WBE after 346 hours of exposure to dry, damped, chlorinated and inhibited sand

5.1.3 A Comparison between Buried Steel Corrosion with and without Inhibitor

As described in the above experiments, buried steel corrosion in damp sand with NaCl was an active localized corrosion system. The degree of localization was significantly reduced by the addition of inhibitor Na_2CrO_4 . Further analysis can be carried out based on the calculation of the localization parameter, LP . Figure 5.7 shows the change in $i_{\max}$, i_{tot} , N_a and the LP values with immersion time. Two major differences can be found if the behaviours of the active localized corrosion systems are compared with an inhibited system:

1. In the inhibited system, $i_{\max}$ and i_{tot} values significantly decreased although there was a temporary increase in i_{tot} and N_a immediately after inhibitor addition. As described above, this phenomenon must be due to the anodic reaction required for the formation of passive oxide layer on steel surface.

2. With the addition of inhibitor, the LP value decreased significantly, as well as $i_{\max}$ and i_{tot} values.

This result confirms that the prediction of localized corrosion could be carried out by analyzing maximum anodic current ($i_{\max}$), total anodic current densities (i_{tot}), and the localization parameter, as a function of corrosion exposure time.

(a)

(b)

(c)

(d)

Figure 5.7 Changes in the (a) maximum anodic current density, (b) total anodic current density, (c) number of anodes and (d) localization parameter of a buried mild steel WBE after exposure to NaCl contaminated damp sand before and after addition of inhibitor for 346 hours

5.2 A New Method for Studying Localized Atmospheric Corrosion under Simulated Deposits

Localized atmospheric corrosion often occurs over a metal surface when it is covered by leaves from the tree, from airborne contaminants, from snow, from bird droppings, and from abrasive windblown sand, etc. Deposits over the metal surface form crevices and thus crevice corrosion could occur. Traditional electrochemical techniques such as linear polarization resistance measurement are often difficult to perform in atmospheric corrosion studies because it is too difficult to set up a three-electrode corrosion testing cell over a metal surface that is covered by deposits or by a very thin water layer. The objective of the work is to design a novel experimental method that can be used to measure electrochemical parameters from a corroding WBE surface under a simulated diffusion-corrosion environment for studying localized corrosion. The experimental design has already described in Figure 3.12. A series of tests have been carried out to test the applicability of this new method in monitoring simulated atmospheric corrosion of mild steel and SS316L.

The first test was carried out to measure *base* corrosion of mild steel and SS316L WBE surfaces that were placed under a filter paper wetted with pure de-ionized water. Figure 5.8 shows a typical WBE corrosion potential and galvanic current distribution maps. Common features that can be observed from these maps include:

- In this base corrosion system, the electrode surfaces were electrochemically non-uniform, as shown in Figures 5.8a-5.8d, distinctive anodes and cathodes are observable and the potential differences between anodes and cathodes were large (maximum differences were 34 mV over the mild steel WBE surface and 100 mV over SS316L WBE surface). The potential distribution maps (Figures 5.8a-5.8d) correlate well with the galvanic current maps (Figures 5.8b and 5.8d).
- The distribution of cathodic and anodic sites appeared to be random, and the anodic and cathodic locations changed frequently with the extension of experiments.

- The galvanic currents for both mild steel and stainless electrodes were very small (in the order of 0.001 mAcm^{-2}). These observations suggest that atmospheric corrosion of mild steel and SS316L under a wet filter paper was slow and the corrosion site distribution appeared to be random.

Figure 5.8 Typical Corrosion potential (in V) and galvanic current (in mAcm^{-2}) distribution maps measured from mild steel (Fig. 5.8a and Fig. 5.8b) and SS316L (Fig. 5.8c and Fig. 5.8d) WBE surfaces that were exposed under a filter paper (wetted with distilled water), before corrosive species diffusion

Significant changes in electrode potential and galvanic current maps occurred after a pipette filled with solid chemicals (FeCl_3 , NiSO_4 or NaCl) was placed on the filter paper close to wire 1 of the WBE (experimental setup in Figure 3.12). This was obviously due to the dissolution of solid chemicals in the pipette, and the diffusion of ions in the filter paper from wire 1 location where the pipette was located to regions further away, creating concentration gradients over the WBE surface. The purpose of this experiment is to simulate atmospheric corrosion with airborne chemical contaminants that transport from the environment to metal surface. Several typical corrosion patterns have been observed and their characteristics were found to be highly dependent upon electrode material and corrosion ions.

5.2.1 NiSO_4 Diffusion on Mild Steel Surface

Figure 5.9 shows the corrosion potential and WBE current distribution maps from mild steel WBE exposed to a simulated atmospheric corrosion condition with NiSO_4 diffusion for one, three and five hours. An interesting pattern observable in Figure 5.9 is that the cathodic area has started from wire one location and has propagated along the diffusion direction. Since NiSO_4 diffusion would lead to a Ni^{2+} ion concentration gradient over the WBE surface, and also to an electrochemical potential gradient, this behaviour is understandable according to the Nernst equation,

$$E = E^0 + \frac{RT}{nF} \ln \frac{[\text{Ni}^{2+}]}{[\text{Ni}]},$$

which describes the electrode potential of a half-cell reaction, E , as a function of ionic concentrations. Indeed, as shown in Figure 5.9(c), a potential distribution pattern appeared to emulate diffusion pattern with a maximum potential difference of 80 mV across the WBE surface. The distinct separation of anodes and cathodes caused galvanic currents to flow from the cathodic sites to the anodic sites. The current distribution, as shown in Figure 5.9, also appeared to emulate the diffusion pattern. These potential and current characteristics suggest that Ni^{2+} reduction ($\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}$, standard reduction potential: $-0.257 \text{ V}_{\text{SHE}}$) was the main cathodic reaction that controlled the corrosion process. The oxygen reduction

reaction ($O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$, standard reduction potential: $0.401 V_{SHE}$) appeared to be a minor cathodic reaction due to relative low oxygen concentration.

5.2.2 $FeCl_3$ Diffusion on Mild Steel Surface

Figure 5.10 shows corrosion potential and WBE current distribution maps measured when mild steel WBE exposed to $FeCl_3$ diffusion-corrosion condition for one, three and five hours. The general feature in Figure 5.10 is similar to that in Figure 5.9, i.e. potential and current distribution patterns appeared to emulate ion diffusion pattern. However, potential differences between cathode and anode in this system were much larger than those in the $NiSO_4$ system. As shown in the potential distributions of Figure 5.10, there was a maximum potential difference of 250 mV across the WBE surface. Such large potential difference has driven significant galvanic currents to flow among wires in the WBE. As shown in the current distribution maps in Figure 5.10, the maximum anodic current (0.57 mAcm^{-2}) was 50 times higher than that in Figure 5.9, and 100 times higher than that in Figure 5.1. This galvanic current distribution pattern suggests that ferric ion reduction reaction ($Fe^{3+} + e^- \rightarrow Fe^{2+}$, standard reduction potential: $0.771 V_{SHE}$) was the dominant cathodic reaction. Its high standard reduction potential and high concentration at locations near wire 1 lead to significant and distinct separation of anodes and cathodes. However, it is unclear why the diffusion of $FeCl_3$ propagated mainly along the edges of the WBE and why the diffusion appeared to be slower than that of $NiSO_4$ diffusion (Figure 5.9).

Figure 5.9 Corrosion potential (in V), galvanic current (in mA/cm²) distribution maps from mild steel WBE exposed to the NiSO₄ diffusion in distilled water after (a) one hour, (b) three hours, and (c) five hours

Figure 5.10 Corrosion potential (in V), galvanic current (in mA/cm²) distribution maps from mild steel WBE exposed to the FeCl₃ diffusion in distilled water after (a) one hour, (b) three hours, and (c) five hours

5.1.3 NaCl Diffusion on Mild Steel Surface

Figure 5.11 shows the corrosion potential and WBE current distribution maps measured when mild steel WBE exposed to NaCl diffusion-corrosion condition for one, three and five hours. The features in Figure 5.11 are very different from that in Figures 5.9 and 5.10. At the early stage of exposure, as shown in Figure 5.11(a), the distribution of cathodic and anodic sites appeared to be random and kept changing with time. With the extension of exposure, as shown in Figures 5.11(b) and 5.11(c), higher cathodic currents was found to concentrate along the corners and edges of the WBE surface with the magnitude decreasing in a contour-like manner towards the centre of the WBE surface. This characteristic pattern appeared to be due to higher oxygen concentrations at these locations where oxygen supply was more sufficient through two or three-dimensional diffusion. Higher oxygen concentrations along the edges and at the corners led to a higher potential at these locations (see Figure 5.11) and supported higher rate of oxygen reduction reaction ($O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$). In this case, oxygen concentration distribution was a dominant factor in determining the corrosion pattern. The main effect of NaCl on corrosion was that NaCl diffusion led to reduction in resistance of the filter paper and thus resulted in continued increase in galvanic currents, which is clearly observable in the current distribution maps of Figure 5.11.

Main Anodes

Main Cathodic Areas

Figure 5.11 Corrosion potential (in V), galvanic current (in mAcm^{-2}) distribution maps from mild steel WBE exposed to the NaCl diffusion in distilled water after (a) one hour, (b) three hours, and (c) five hours

5.2.4 NiSO₄ and NaCl Diffusion on Stainless Steel Surface

Significantly different features were observed from the corrosion potential and WBE current distribution maps measured when SS316L WBEs exposed to NiSO₄ and NaCl diffusion-corrosion conditions. As shown in Figures 5.12 and 5.13, corrosion cathodes and anodes appeared to be distributed randomly and, more importantly, these sites remained almost unchanged with the extension of diffusion-corrosion experiments. The characteristic concentration-controlled corrosion patterns shown in Figures 5.9 – 5.11 are totally absent in Figures 5.12 and 5.13. The most probable explanation to this phenomenon is that SS316L corrosion was controlled by the non-uniformity of the passive film on SS316L. It is well known that the corrosion resistance of stainless steel depends on the integrity and durability of its passive film. If passivity is not maintained and the passive film has localized weak sites or damages, these locations would become anodes where highly localized corrosion attacks could occur. With the extension of the diffusion-corrosion experiment, as shown in Figures 5.12 and 5.13, potential at anodic locations shifted towards more negative direction, which could be due to the continued deterioration of the passive film at anodic sites. Corrosion of mild steel was found to be determined by the electrochemical potential values according to the Nernst equation. For a mild steel WBE surface with varying NiSO₄ and FeCl₃ concentration, the electrochemical potential values were found to be related to Ni²⁺ and Fe³⁺ concentration, which were under ion concentration control. The locations with higher reduction potential values behaved as cathodes. For a mild steel WBE surface with NaCl diffusion condition, the electrochemical potential values were determined by oxygen concentration, and thus corrosion behaviour was controlled by oxygen concentration over the WBE surface. It is well known that the corrosion resistance of stainless steel depends on the integrity and durability of its passive film. If passivity is destroyed by corrosive ions, the breakdown of the passive at localized weak sites leads to the formation of passive-active cells. For a SS316L WBE surface with varying NiSO₄ and NaCl concentration, the corrosion processes were controlled by the random distribution of weak sites in passive film and ion concentration appeared to have only minor effects on corrosion patterns.

Figure 5.12 Corrosion potential (in V), galvanic current (in mAcm⁻²) distribution maps from SS316L WBE exposed to the NiSO₄ diffusion in distilled water after (a) one hour, (b) three hours, and (c) five hours

Figure 5.13 Corrosion potential (in V), galvanic current (in mAcm⁻²) distribution maps from SS316L WBE exposed to the NaCl diffusion in distilled water after (a) one hour, (b) three hours, and (c) five hours

5.2.5 FeCl₃ Diffusion on Stainless Steel Surface

Figure 5.14 shows the corrosion potential and WBE current distribution maps measured when SS316L WBE exposed to FeCl₃ diffusion-corrosion condition for one, three and five hours. It is observed that the diffusion of FeCl₃ results in a major cathodic reaction at wire one location ($\text{Fe}^{3+} + \text{e}^{-} \rightarrow \text{Fe}^{2+}$). The cathodic area was found to expand with the extension of exposure, probably due to diffusion of FeCl₃ over the WBE surface. Corrosion anodes appeared to distribute randomly. Their locations remained almost unchanged with the extension of the experiment, although some of the minor ones ceased growing during the exposure period. These anodic locations are believed to be due to the local damages in the passive film. Although there were many anodes, as shown in the potential distribution map of Figure 5.14(c), only a few of them were effective anodes that recorded high anodic current in the current distribution map of Figure 5.14(c). These effective anodes were in the proximity of the cathodic area and the galvanic current values at these sites increased significantly with the extension of experiment, indicating the propagation of localized corrosion. In general, maps in Figure 5.14 show the characteristics of both the ion diffusion-controlled corrosion patterns in Figures 5.9 and 5.10 (for cathodic process) and the passive film integrity-controlled corrosion features in Figures 5.12 and 5.13 (for anodic process).

The preliminary study of the corrosive ions diffusion on corrosion processes using WBE suggests that the WBE method can apply early detection of ion diffusion in localized corrosion. Different effects were observed by identifying characteristic changes in potential and current distribution maps and such effects were found to be highly dependent upon the type of electrode materials and the type of corrosive species. When corrosive ions reach an electrode surface, it should lead to significant electrode noise activities and potential changes. It will also lead to the initiation of localized corrosion. It is expected that the WBE-ENA technique can be applied to measure localized corrosion of stainless steel and mild steel under buried conditions by detecting ions penetration and further corrosion activities.

Figure 5.14 Corrosion potential (in V), galvanic current (in mAcm^{-2}) distribution maps from SS316L WBE exposed to the FeCl_3 diffusion in distilled water after (a) one hour, (b) three hours, and (c) five hours

(a)

(b)

Galvanic current distribution before jump in Potential

Galvanic current distribution after jump in Potential

Galvanic current distribution [After 3 hours]

Corroded area [After 3 hours]

Corroded area

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

6.1 Conclusions

A novel electrochemical corrosion sensor technology has been developed based on an electrochemically integrated multi-electrode array, namely the wire beam electrode (WBE) and electrochemical noise analysis (ENA). This novel method is based on a synergetic combination between potential noise signatures and WBE galvanic current map. Scientifically, this WBE-ENA technology has overcome some major limitations associated with existing corrosion monitoring techniques in measuring non-uniform electrochemical processes such as localized corrosion. The key developments of this work include a novel localized corrosion monitoring method based on the combined use of the WBE and noise signatures. Several novel experiments have been developed for monitoring and predicting corrosion under various corrosion conditions. From this research work, the following major findings and conclusions can be drawn:

- a. The characteristic noise signatures have been found to be indicators of localized corrosion initiation and propagation. Five typical characteristic noise signatures were observed from different types of localized corrosion processes:
  - The *noise signature I* (the characteristic peak of rapid potential transient towards less negative direction followed by recovery) featured the disappearance of unstable major anodic sites in pitting corrosion (or) the formation of cathodic sites in buried structure corrosion (or) the deposition of passive oxide layer on main anodes in inhibited localized corrosion
  - The *noise signature II* (the characteristic quick potential changes towards less negative direction followed by no recovery) corresponded with the massive disappearance of anodic sites leading to the accelerated dissolution of anodes in

localized corrosion (or) repassivation of major anodes in inhibited localized corrosion

- The *noise signature III* (the characteristic quick potential changes towards more negative direction with no recovery) correlated with the rapid propagation of the existing stable anodes,
- The *noise signature IV* (the characteristic quick potential changes towards more negative direction with recovery) featured the initiation of new anodes,
- The *noise signature V* (the characteristic cyclic oscillations at a constant frequency) corresponded with successive formation of stable anodes inside crevice area.
- The characteristic noise signatures can further distinguish the mechanism between different localized corrosion processes. For instance, the indicator for pitting corrosion was found to be three characteristic noise patterns: the *noise signature I*, the *noise signature II* and the *noise signature III*. The results suggested that local thinning of passive film or protective surface layer occurs when the environmental conditions become aggressive and many major anodic sites initiate. At pitting initiation stage, the unstable major anodic site suddenly disappeared that could be due to the major anodes cathodically polarized and protected the unstable anodes, leading to the sudden disappearance of unstable major anodes. The higher the current density at major anodes, the higher is the probability of its transition to a stable pit. As a result, most of metastable anodes are cathodically protected and leading the massive disappearance of anodic sites. The electrolyte inside the stable anodes may become very aggressive which will further accelerate corrosion. The indicator for crevice corrosion was found to be two characteristic noise patterns: the *noise signature III* and the *noise signature V*. It is suggested that during the initiation of crevice corrosion, the environment in crevice has less oxygen and corrosion potential is low so that anodic and cathodic reactions take place preferentially in and outside of a crevice. Crevice corrosion progresses in well defined cycles and a rapid propagation stage. The rate of new stable anodes formation inside crevice area was changing. The results showed that crevice corrosion is a *preferred* process and there will be

cathodically protected other surfaces leading to stop pitting. The indicator for localized corrosion inhibition and buried steel corrosion was found to be two characteristic noise patterns: the *noise signature I* and the *noise signature II*. The *noise signature IV* can be observed when electrolyte ions such as La^{3+} cations stimulated the anodic process leading to unstable new anodes formation.

- b. A new parameter, namely the localization parameter, LP , has been proposed as an indicator for the degree of localization in localized corrosion. LP is easy to present and that is useful for quantitative comparison of the degree of localized corrosion especially for the study of trends in localized corrosion initiation and growth. Continuous increase in the localization parameter indicates accelerated stable pit dissolution, while decrease in the localization parameter indicates more uniform corrosion or repassivation. The changes in localization parameter can be used to identify the stages of localized corrosion processes or the effects of inhibition.
- c. The WBE method has been proven to be effective for detecting atmospheric corrosion under real and simulated atmospheric conditions. In particular, the method is sensitive in measuring ions diffusion controlled atmospheric corrosion. The penetration of corrosive species into sand and soil, and the occurrence of subsequent corrosion of carbon steel buried in dry, moist and chlorinated sand have been selected to study. The susceptibility of different types of wetted fibrous thermal insulation to the ingress and penetration of contaminated moisture and water has been successfully monitored.

6.2 Recommendations for Future Work

The WBE-ENA method has been proven to be effective and capable of monitoring and predicting the localized corrosion under simulated submerged and buried conditions. This work should be further extended to other types of serious localized corrosion such as corrosion in concrete, stress corrosion cracking and also should be applied in the testing of electroplating process and the protective ability of electroplated coatings. Further research tasks could be developed the WBE sensors

on the concept of a new WBE-ENA technology and could be used as in situ monitors for *real world application* of non-uniform corrosion, especially localized corrosion. For instance, underground localized corrosion monitoring utilizing WBE sensor in a real system could be conducted as shown Figure 6.1.

In the system, it is demonstrated that the WBE sensor (in Figure 6.2a) is a quantitative and real-time tool for predicting localized corrosion patterns, corrosion rates and the degree of localization. The WBE sensor can have various designs for convenient installation on various industrial structures. Materials including alloys, high temperature resistant epoxy and ceramics could be used to manufacture such a sensor. In order to better simulate practical corrosion conditions, experimental conditions should be further improved. The more metal electrode wires in the wire beam electrode array, the better spatial resolution for the beam electrode technique. However, the multiplexing system (Auto-switch) involving multiple electrodes is required to be designed to be capable of connecting the wire beam electrode for the electrochemical parameters measurements. This is also a good idea to study pitting initiation for future work. The present WBE system is only able to monitor relatively slow electrode processes, since the system takes approximately 15 minutes to map a WBE. It needs to be modified for improving its capability of measuring rapid electrode processes. A permanent embeddable reference electrode (in Figure 6.2b) could be used for corrosion monitoring in underground corrosion monitoring. In order to measure potential noise and galvanic current distribution over a WBE sensor concurrently, data could be taken via telephone line and data analysis could be carried out using software.

(a)

(b)

Figure 6.2 (a) Wire beam electrode sensor and (b) Reference electrode for underground localized corrosion monitoring utilizing WBE sensor in a real system

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