ELECTROCHEMICAL CHARACTERIZATION OF TIN ELECTRODE IN SYNTHETIC SEAWATER

AMANDA KWOK SI EN

UNIVERSITI SAINS MALAYSIA

2022

SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

UNIVERSITI SAINS MALAYSIA

ELECTROCHEMICAL CHARACTERIZATION OF TIN ELECTRODE IN SYNTHETIC SEAWATER

By

AMANDA KWOK SI EN

Supervisor: Dr. Sheikh Abdul Rezan Sheikh Abdul Hamid

Dissertation submitted in partial fulfilment of the requirements for the degree of

Bachelor of Engineering with Honours

(Materials Engineering)

Universiti Sains Malaysia

August 2021

DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled “Electrochemical Characterization of Tin Electrode in Synthetic Seawater”. I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or university.

Name of Student : Amanda Kwok Si En

Signature :

....

Date : 19 August 2022

Witnessed by

Supervisor : Dr. Sheikh Abdul Rezan Sheikh Abdul Hamid

Signature :

....

Date :

ACKNOWLEDGEMENT

I would hereby like to take this opportunity to express my deepest gratitude towards

My thesis supervisor, Dr. Sheikh Abdul Rezan Sheikh Abdul Hamid for his guidance throughout the entire progress for this thesis paper. Without his assistance and dedicated involvement in every step throughout the process, this research thesis would not have been accomplished.

I would also like to thank Dr Nasri for improving my understanding on the electrochemical processes and provide advice on how to perform my experiment. I like to thank the lab technicians, Encik Azam, Encik Azrul, Encik Meor, Encik Sharul, and Encik Syafiq for providing me with the necessary facilities and equipment to complete this project.

I would also like to thank my friends, Tan Boey Wei, Lim Chow Peei and Chai Pei Ying for their support and understanding. Without their encouragement and help, I would not have had the mental and emotional adaptability to complete this paper.

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ABSTRAK

Tin adalah elemen biasa yang biasanya ditambah kepada banyak bahan untuk meningkatkan rintangan kakisan. Penyelidikan ini mengkaji tingkah laku elektrokimia elektrod timah dalam air laut sintetik menggunakan polarisasi linear, voltammetri kitaran dan EIS dan juga untuk menyiasat kesan interaksi tiga faktor, kemasinan, suhu dan masa rendaman pada kadar kakisan dan rintangan polarisasi. Polarisasi linear dilakukan untuk mengkaji kadar kakisan dan rintangan polarisasi yang diperolehi daripada plot Tafel. voltammetri kitaran dilakukan untuk mengukur arus yang dihasilkan oleh sel elektrokimia Sn di bawah parameter kemasinan, suhu dan masa rendaman yang berbeza. EIS digunakan untuk menganalisis proses kimia yang berlaku di tapak elektrod Sn selepas rendaman dalam air laut sintetik.

Reka bentuk eksperimen digunakan untuk meramalkan hasil percubaan oleh itu lebih mudah untuk keluar dengan kesimpulan. Untuk polarisasi linear, ujian dilakukan berdasarkan 3 faktor iaitu kemasinan, suhu dan masa rendaman. Kadar kakisan tertinggi untuk ujian ini ialah 1.6545 mm/tahun untuk sampel yang mempunyai tahap kemasinan 33ppt, suhu 25°C dan masa rendaman 4 hari manakala kadar kakisan terendah ialah 0.00026 mm/tahun yang mempunyai tahap kemasinan 38ppt, suhu 35°C dan masa rendaman 2 hari. Faktor saliniti dan suhu mempunyai hubungan songsang dengan kadar kakisan manakala masa rendaman adalah berkadar terus dengan kadar kakisan. Bagi EIS plot Nyquist memainkan peranan penting dalam menyediakan kadar kakisan, kerana plot kawasan separuh bulatan menjadi lebih besar, kadar kakisan akan meningkat. Dari ujian, model litar setara boleh didapati.

ABSTRACT

Tin is a common element generally added to many materials to improve the corrosion resistance. This research studies the electrochemical behaviour of tin electrode in synthetic seawater using linear polarization, cyclic voltammetry and EIS and also to investigate the interaction effect of three factors, salinity, temperature and immersion time on the corrosion rate and polarization resistance. Linear polarization is done to study the corrosion rate and polarisation resistance obtained from Tafel plot. Cyclic voltammetry is done to measure the resulting current produced by the Sn electrochemical cell under different parameters of salinity, temperature and immersion time. EIS is used to analyse the chemical processes occurring at the site of the Sn electrode after immersion in synthetic seawater.

Design of experiment was used to design the experiment hence the number of samples required prior to experiment can be known. Apart from that it can be used to predict the outcome of the experiment hence it's easier to come out with a conclusion. For linear polarization, the testing was done based on 3 factors which are salinity, temperature and immersion time. The highest corrosion rate for this testing is 1.6545 mm/year for the sample that has a salinity level of 33ppt, temperature of 25°C and immersion time of 4 days whereas the lowest corrosion rate is 0.00026 mm/year which has a salinity level of 38ppt, temperature of 35°C and immersion time of 2 days. Salinity and temperature factors have an inverse relation to corrosion rate while immersion time is directly proportional to the corrosion rate. For EIS the Nyquist plot play important roles in providing the corrosion rate, as the area plot of semicircle become larger, the corrosion rate will increase. From the testing, equivalent circuit model can be obtained.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Seawater is a naturally abundant corrosive electrolyte proven by the large amount of corrosive structural damage of seawater on metal and alloys. Seawater is characterized by the variety of its elements which are either chemical (water, ions, gases, etc.) or mineral (carbonates, silicates, etc.) or biological, interacting together to create a very complex and corrosive medium which can chemically and electrochemically react with the metal surface (Memet, 2007). The most common forms of corrosion caused by seawater are galvanic corrosion, pitting and crevice corrosion (Delhi and 1985, 1985). Galvanic corrosion is caused by coupling two dissimilar materials exposed to a corrosive medium. Pitting is usually caused by localized attack from ions, salt particles as well as impurities in seawater. Crevice corrosion may develop from design features such as rivets and gaskets, as well as surface fouling by local marine bacteria.

According to statistics from (Hou *et al.*, 2018), about 1/3 of the annual production of metal scrap in the world is ascribed to the corrosion of metal materials and equipment. The direct economical loss accounts for approximately 2% to 4% of each country’s gross domestic product (GDP). Therefor in order to use marine resources efficiently and respond to suitable development actively, the corrosion behaviour of metals need to be observed and controlled.

Most metal structures used in sea water (ships, oil platforms, piers, pipelines, etc.) are traditionally made of mild low-carbon and low alloy steels and are subject to corrosion, especially if unprotected. Tin is a material with antifouling properties used in marine applications such as tin electroplated copper marine electrical cables on ships. In damp conditions, the tinned wires prevent the copper from corrosion and increase the flexibility in the harsh marine environment. In recent years, the addition of tin into other elements or composites have been found to aid the improvement of the corrosion resistance. Based on (Li *et al.*, 2015)(Ahmed Adnan *et al.*, 2021), when tin is added into steel and copper the formation of Sn and SnO oxide films improves the impedance the corrosion resistance and enhances the original passivation layer. In the research done by (Wang, 1999) in the effect of tin addition on the microstructure development and corrosion resistance of sintered steels, pitting corrosion is found in areas with less tin, in which the addition of powdered tin has caused an anodic reaction of the sintered alloys in 1M H_2SO_4 solution which transferred the corrosion potential to a noble value and consequently reduced the corrosion rate.

1.2 Problem Statement

Based on previous research, tin is said to be added to many other elements or composites such as stainless steel, copper etc to reduce the corrosion rate in different electrolytic media. This is due to the ability of tin to form a passivation layer or oxide layer reduces the corrosion attack of on the metal (Wang, 1999).

However, what if we added factors such as salinity and temperature into the equation. Not enough research has been been made on the effects of salinity and temperature towards the corrosion rate and anodic behaviour of tin itself as the metal. Generally, in most materials, it is known that the increase in salinity and temperature is said to result in a proportional increase in the corrosion rate as well. However, since we are analysing surface seawater, the oxygen solubility which is higher at the surface layer may affect the corrosion rate. Based on (Weiss, 1970; Zakowski *et al.*, 2014) salinity levels higher than 3% can affect the O_2 solubility in which high salinity contributes to lower solubility which reduces the corrosion rate. Higher temperatures can decrease the oxygen solubility

In this paper, electrochemical characterization and design of experiment methods are applied in this work to understand and analyse the electrochemical corrosion behaviour of Sn under salinity, temperature and immersion time parameters. Testing of Sn will be done using different characterisation methods such as linear polarization from, cyclic voltammetry at and electrochemical impedance spectroscopy(EIS).

1.3 Research Objectives

The research objectives of this study are:

i. To determine the electrochemical behaviour of tin electrode in synthetic seawater using linear polarization, cyclic voltammetry and electrochemical impedance spectrometry

ii. to investigate the interaction effect of three factors, salinity, temperature and immersion time on the corrosion rate and polarization resistance using Response surface methodology (RSM)

1.4 Scope of study

In this research, three factors are chosen which are salinity temperature and immersion time to investigate the effects of these parameters on the corrosion rate and polarization resistance.

Linear polarization is used to study the corrosion rate and polarisation resistance obtained from Tafel plot. Then, design of experimentation technique is employed to understand the interaction between these factors. The observational change before and after corrosion is also determined using scanning electron microscopy (SEM). Cyclic voltammetry is done to measure the resulting current produced by the Sn electrochemical cell under different parameters of salinity, temperature and immersion time. Electrochemical impedance spectroscopy (EIS) is employed to analyse the chemical processes occurring at the site of the Sn electrode after immersion in synthetic seawater.

1.5 Outline of Chapters

This thesis contains a total of five chapters. In Chapter 1, the introduction, objectives and scope of work regarding the project was discussed. Whereas chapter two is on concept, theory and literature review related to the parameters for the electrochemical analysis of Sn and electrochemical characterization of Sn. Chapter three details on the experimental procedure and the characterization approaches for the project. Then, the results and discussion of the project was focused on chapter four. Finally, chapter five are for conclusion and recommendations for future work.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Corrosion could be classified as degradation of materials properties due to interactions with environments. It’s a natural phenomenon that occur on metal and wanted to be avoided. Research show that the annual costs which related to corrosion are high due to its important to ensure the safety use of the structure or component. There are several type of corrosion classification, the morphology of the attack, type of environment its exposed to, general corrosion, galvanic corrosion, pitting, and stress corrosion cracking (Shaw and Kelly, 2006). Corrosion also lead to reduce of lifetime for component, due to surface roughness, reduction of strength and lead to component failure. It is important to record accurate data of past corrosion to improve and to avoid the failure from reoccurring. Different function of component have different concern need to be considered during selection of materials and design (Saad-Eldeen *et al.*, 2016).

Corrosion reactions are generally oxidation and reduction reactions occurring at the anodic and cathodic areas. Like all reactions, corrosion reactions also involve the acceptance or donation of electrons, and the tendency for these reactions to occur is expressed by their reduction potential. The measurement of reduction potentials can be done by placing two separate electrodes in an electrolytic solution. The oxidation reaction will then occur at one electrode (anode) and the reduction reaction at the other (cathode). The resultant voltages between the two electrodes when no current is flowing is equal to the difference in reduction potentials of the oxidation and reduction reactions. The standard reduction potential of Sn from the reduction reaction of Sn is:

$$Sn^{2+} + 2e^{-} \rightarrow Sn \qquad E° = -0.136V$$

When a metal is placed in seawater, a large number of different oxidation and reduction processes occur on the metal surface. Consequently, the metal will obtain a potential which shows the combined rate and potential of all these reactions. This potential is considered a mixed electrode potential and in corrosion studies is referred to as the corrosion potential, E_{corr} (North and Objects, 1987).

2.2 Tin

Tin is allotropic, with the body-centered tetragonal normal, metallic (beta) form existing above the transformation temperature, which is located at approximately 13.2°C. The lower temperature allotrope, which is also commonly named as alpha or grey is cubic and develops with a large volume shift that frequently causes the material to disintegrate. Although it can be accelerated by mechanical deformation and postponed or completely repressed at lower temperatures by impurities like antimony, lead, and bismuth, transformation is kinetically slow. On the surface of the metallic form, grey tin typically shows as nodules of a friable material and resembles a corrosion product. As a result, corrosion and transformation processes are frequently difficult to tell apart. However, the transformation mechanism can only be differentiated using high electron microscopy in order to determine the relationship between the lattice orientations of the two different allotropes. Therefore, the [211] direction of grey tin is almost parallel to the [010] direction of white tin, and the [011) plane of grey tin is parallel to the [001] plane of white tin which correlates to a partially martensitic, partially diffusional model of the alpha to beta transformation.

Unalloyed tin's application is constrained by both its low melting point (232°C) and low tensile strength (15 MPa). While its softness and high ductility make it appropriate for cold working and beacring applications, its melting point and ability to "wet" other metals (typically through creation of intermetallic compounds) promote its usage as solder (for metal joining) and as a coating (for corrosion protection). Tin has a relatively low melting point and easily recrystallizes at room temperature; as a result, the effects of mechanical working are minimal and result from variations in grain size rather than from work hardening. It is also believed that the low melting point of tin contributes to the formation of tin whiskers, which under the right circumstances grow as fine threadlike structures up to millimetres in diameter per month.

2.3 Seawater

Table 2.3.1 shows the major elements or constituents found in seawater. Natural seawater slightly differs from synthetic seawater due to presence of living organisms which can affect corrosion. For this reason, natural seawater experiments are only suitable to be conducted in normal temperatures. At elevated temperatures, these living organisms can be destroyed by heat, therefore the effect of living organisms is not important at higher temperatures.

Table 2.3.1: The eleven major elements or constituents in seawater (Hovanec *et al.*, 2004)

The Eleven Major Elements or Constituents in Seawater (g/kg)			
Sodium (Na^+)	10.781	Chloride (Cl^-)	19.353
Magnesium (Mg^{2+})	1.284	Sulfate (SO_4^{2-})	2.712
Calcium (Ca^{2+})	0.4119	Bicarbonate (HCO_3^-)	0.126
Potassium (K^+)	0.399	Bromide (Br^-)	0.0673
Strontium (Sr^+)	0.00794	Boric Acid (H_3BO_3)	0.0257
		Fluoride (F^-)	0.00130

The presence of chloride and bicarbonate ions increase the corrosion attack of tin. Cl^- ions specifically are extremely corrosive in nature in which it can penetrate the passivation films SnO and directly attack the metal surface. Synthetic salts may minimise the corrosion of chloride attack as they have the blending capacity to eliminate chlorine or chloramides, as in the case of the salt used in this experiment (Crystal Sea® Marinemix Bioassay Laboratory Formula Aquarium salt).It should also be mentioned that the pH of seawater is usually in the range from 7.5 to 8.2, which indicated an excess of hydroxyl ions.

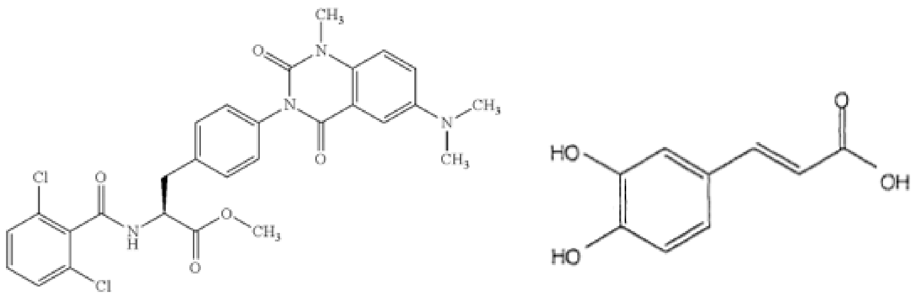

Figure 2.3.1: Different chemical formulas of seawater salt

Source: Left(Neak), Right (Mugeek Vidalondon)

Depending on the concentration of ions and surrounding environmental factors, the chemical formula of seawater salts can vary. Figure 2.3.1shows a few examples of the possible chemical formulas of seawater salts.

2.4 Corrosion patterns of seawater on tin

Since tin produces its own passivation film, pitting corrosion is highly likely to be expected, as the seawater contains ions which can attack the passivation layer and result in localised pitting corrosion. Many studies such as (Memet, 2007) (North and Objects, 1987), reported pitting corrosion from seawater in tin. Observational studies (Reinhart and Jenkins, 1972) reported localized pitting and crevice corrosion phenomena at depths of 5 feet (approximately 1.5m below sea surface) after immersion in seawater for a year. In synthetic seawater the corrosion behaviour is found to be similar to that of diluted seawater, except that the black tin oxide layers where crumbling and more flaky than the hard layer formed in diluted seawater (Lloyd and Wilson, 1968).

2.5 Equilibrium studies

Of the two usual oxidation states of tin the potentials of the Sn^{2+} /Sn and Sn^{4+}/ Sn^{2+} electrodes indicate that thermodynamically Sn^{2+} is more stable which will naturally form a more stable passivation layer SnO to protect the metal Sn. Some possible anodic reactions of elemental tin under experimental condition are as follows (Le *et al.*, 2008; Li *et al.*, 2015) :

$$Sn + 2OH^- - 2e^- \rightarrow Sn(OH)_2 Sn + 2OH^- - 2e^- \rightarrow SnO + H_2O$$

$$Sn(OH)_2 + 2OH^- - 2e^- \rightarrow Sn(OH)_4$$

$$SnO + H_2O + 2OH^- - 2e^- \rightarrow Sn(OH)_4$$

$Sn(OH)_2$ and $Sn(OH)_4$ compounds are not the final steady state of the Sn rust layer, in which most of them will further transform into more stable tin oxides (SnO and SnO_2) via the following actions below. The main corrosion product of elemental tin, SnO_2 also does not form its own passivation film, resulting in further oxidation into divalent products such as $SnO.H_2O$ and $SnCl_2.2H_2O$ (North and Objects, 1987)

$$Sn(OH)_2 \rightarrow SnO + H_2O$$

$$Sn(OH)_4 \rightarrow SnO_2 + 2H_2O$$

2.6 Description of seawater environment

2.6.1 Surface seawater

Surface seawater is a major component of the ocean ecosystem and has a profound impact on marine life. It provides food and habitat for marine life moderates the Earth’s climate by absorbing carbon dioxide from the atmosphere, and regulates the ocean’s salinity levels. The depth range of surface seawater can vary based on the measurement technique used, but it is usually between 1mm and 20m below sea level. Most biological and manufacturing activities occur near surface seawater, therefore the parameters of electrochemical tests of any material should be based on surface seawater as well. In the study done by (Reinhart and Jenkins, 1972), the alloys or metals submerged at 5 ft (~1.524m) all experienced higher corrosion rate compared to those submerged at 2370ft and 6780 ft, in which they concluded that the decreasing oxygen concentration relative to decreasing depth contributes to the increase in corrosion rate. It should also be noted that this applies to environments where marine life is sufficiently enough for gaseous exchange. However, further studies (Manasrah *et al.*, 2006; Bendtsen and Modelling, 2013) have found results that shows increasing oxygen content with decreasing depth, further indicating that the corrosion rate is higher at sea surface.

2.6.2 Factors affecting the corrosion mechanism

The prediction of the corrosion phenomenon on the metal surface requires understanding and knowledge of the range of parameters of the surrounding environment. These parameters influencing corrosion rates in seawater are interrelated and can mutually affect each other. For example, surface seawater can differ in salinity levels as compared to deep seawater due to the amount of dissolved oxygen as well as temperature differences that occur from the changes in water depth.

2.6.2.1 Dissolved Oxygen

Dissolved oxygen is one of the main influential factor in marine oxidation process and corrosion rate is determined by the cathodic process. (Macleod, Macleod and North, 2016) Oxygen is aggressive because of its depolarizing effect at cathodes and is protective because it leads to increased OH^- coating at the cathodes due to its ability to form insoluble compounds with most metals (Hackerman, 1952). Dissolved oxygen in seawater is caused by the air sea gas exchange or flux driven by the difference in the concentration of gas in the air and sea medium as well as gas transfer coefficient (Nightingale, 2013). The depth of the water body and the movement of water can affect the dissolved oxygen concentration. In general, the higher the concentration of dissolved oxygen, the higher the corrosion rate (Reinhart and Jenkins, 1972; North and Objects, 1987).

The solubility of dissolved oxygen in seawater can vary with salinity and temperature. As shown in studies done by (Weiss, 1970) expressing the relationship between gas solubility , temperature and salinity, increasing temperature and salinity levels resulted in an overall decreased oxygen solubility with experimentation data at a temperature range of -2 to 40°C and a salinity range of 0–40%. Further studies showed at high salinity values, the temperature effect on oxygen solubility is small (Debelius *et al.*, 2009).

From another point of view, the decrease of the dissolved dioxygen concentrations inside the corrosion products will provoke, as in the transition between the immersion and mud zones, an increase in the chloride concentration. This occurrence may be vital towards the modification of the composition of corrosion products (by inserting some chloride-containing corrosion products) (Memet, 2007).

2.6.2.2 Salinity

Salinity is the concentration of dissolved salts in a body of water, and is commonly measured in parts per thousand (ppt), parts per million(ppm) or g/kg. Different bodies of water have different salinity levels, for example fresh water has a salinity level of less than 1 ppt. The Dead Sea, which is the saltiest body of water in the world, has a salinity level of 276ppt. The salinities of different seawater environments are showed below in Table 2.6.1.

Table 2.6.1 Salinities of different seawater environments (Roberge, 2000)

Origin	Salinity
Rivers (mean world value)	0.1
Baltic Sea	<17

Black Sea	18-22
Altantic and Pacific Oceans	33-37
Mediterranean Sea	39-47
Red Sea	43-45
Dead Sea	276

Ocean water (normal open ocean ranges) generally have salinity levels approximately between 33ppt and 37ppt. The salinity of water on the surface layer of ocean can vary as they can depend on many factors such as the wind, temperature and movement of ocean currents from evaporation and precipitation processes (Nasreen, 2022).

Based on NASA's Soil Moisture Active Passive (SMAP) measurements of the global sea surface salinity data in January 2022 (NASA, 2022) in Figure 2.6.1, the ocean surface salinity levels ranged from 33ppt to 38ppt.

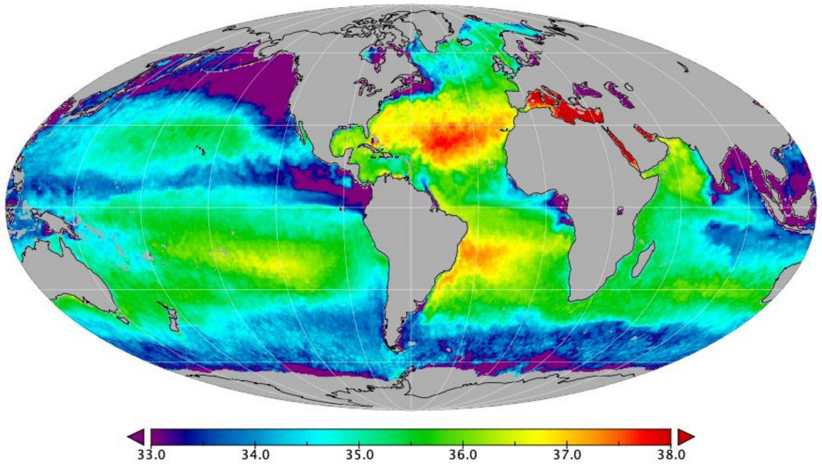

Figure 2.6.1: Global map of monthly sea surface salinity, January 2022

Source: (NASA, 2022)

Salinity can affect the corrosion rate in multiple ways. For example, the saline solution acts as an ionic conductor for ion transfer between the anodic and cathodic sites. It also cause the formation and destruction of different protective layers as well as alter the oxygen concentration (North and Objects, 1987). In general, increasing salinity raises the corrosion potential of natural water proportionately. However, water corrosivity also diminishes as salinity increases more than 3% due to lower oxygen solubility as salinity increases (Zakowski *et al.*, 2014) (Weiss, 1970). Corrosion rate also decreases with increasing depth and decreasing oxygen concentration; therefore, surface layer salinity is not equivalent to salinity in deep waters.

2.6.2.3 Temperature

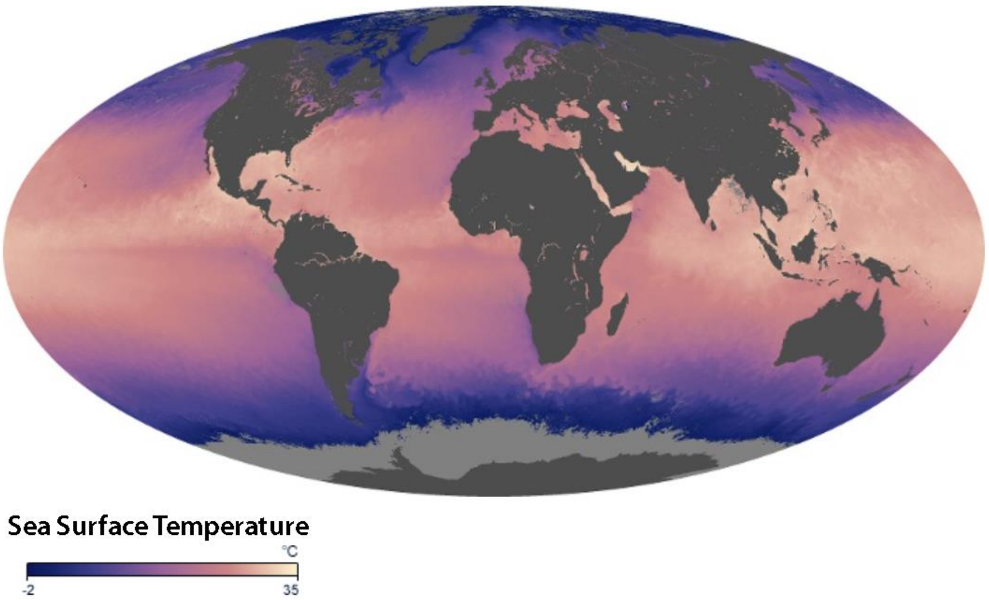

Figure 2.6.2: Global map of sea surface temperatures, March 2022

Source: (*Sea Surface Temperature*, 2022)

The sea surface temperature maps in Figure 2.6.2 (*Sea Surface Temperature*, 2022)are based on observations by the Moderate Resolution Imaging Spectroradiometer (MODIS) on NASA's Aqua satellite. Based on the map, global sea surface temperature can range from a minimum of -2°C to a maximum of 35°C.

In general corrosion theory, the corrosion rate will increase with increasing temperature, as heat is able to speed up chemical reactions. Studies including those from (Lee *et al.*, 1988; Narayanan *et al.*, 2008; Zhou *et al.*, 2017) have shown increase corrosion rate in relation to increasing temperature.The mechanism of the corrosivity spike from higher temperatures can be attributed to the increase in the number of molecules with enough energy to react in chemical and electrochemical reactions (Makhlouf, 2014). Since oxygen content and temperature are interrelated, the individual effect of each is difficult to differentiate. However, high temperatures can decrease the oxygen solubility rate of seawater, which in turn decreases the corrosion rate (Weiss, 1970).

2.6.2.4 Immersion time

It is commonly known that corrosive rate is relative to time. The longer the immersion time, the longer the time taken for the interaction of Sn and electrolyte seawater to occur. Studies such as (Nik *et al.*, 2011; Al-Moubaraki *et al.*, 2014; Asadi *et al.*, 2015) saw an increase in the percentage of weight loss in correspondence to immersion time.

2.7 X-ray Diffraction (XRD)

Determination of phase compositions, in contrast to elemental compositions, is vital for understanding and investigating the corrosion process. X-ray Diffraction is a preferred method to identify and observe the change in chemical phases which can be used to explain corrosion processes. XRD measures the average spacing between rows and layers of atoms as well as detect the crystal structure of unknown materials. Additionally, this test is capable of measuring the shape, size as well as the internal stress of minute crystalline regions.

2.8 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) is an analytical technique used to identify organic and inorganic materials. This technique measures the absorption of infrared radiation by the sample material versus wavelength. The infrared absorption bands can identify various molecular components and structures. This technique is useful for analysing the chemical composition of smaller particles (typically 10 -50 microns) as well as larger areas on the surface.

2.9 Scanning Electron Microscopy (SEM)

Scanning electron microscopy uses a focused beam of high-energy electrons to produce a diversity of signals at the surface of solid specimens. The signals that derive from electron-sample interactions provides information about the sample. In corrosion studies, SEM is the perfect tool to observe close up images of the surface of the material, which provides an idea about behaviour of corrosion on the surface of the material. The black and white images obtained from SEM reveals the surface morphology, chemical composition, crystal structure and orientation of the material.

2.10 Three Electrode set up

Working, counter, and reference electrodes are all positioned in the same electrolyte solution in a conventional three-electrode cell as shown in Figure 2.10.1 . In three-electrode studies, the working electrode's potential is evaluated in relation to the reference electrode

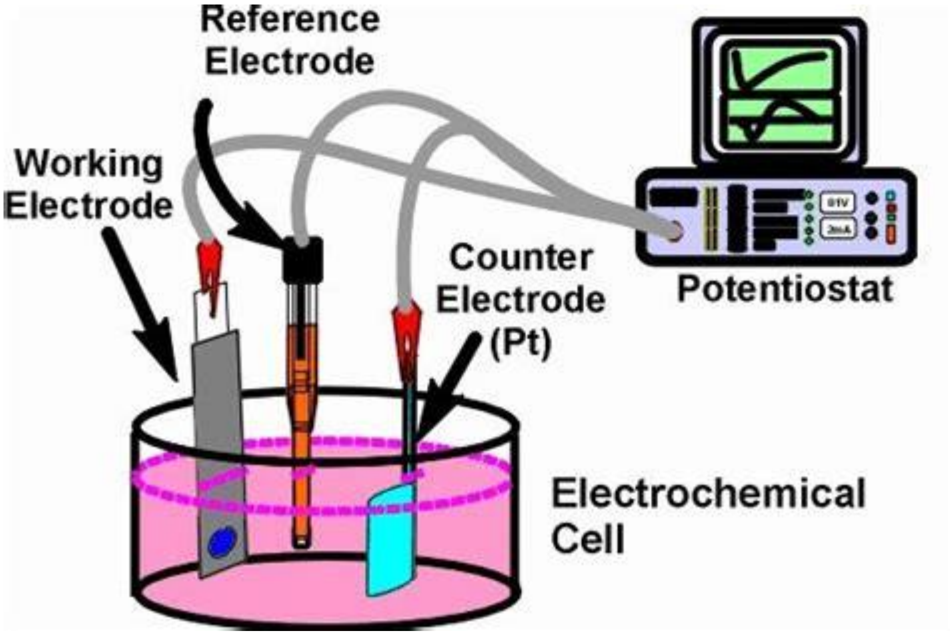

Figure 2.10.1: A three electrode configuration of the electrochemical cell

whereas charge flow (current) largely occurs between the working electrode and the counter electrode.

2.10.1 Working Electrode

The working electrode is an indicator electrode where the behavior of an electrochemical reaction is showcased. The working electrode is used to analyze the properties of the electrolytic medium. The working electrode may exhibit anodic or cathodic behavior based on the reduction or oxidation reaction. Depending on the size, shape and form of the material, the working electrode may appear in different forms such as in the form of an inlaid disk or plate, sheets, wires, sphere or cylinder.(Bond *et al.*, 2009) When choosing a suitable working electrode, a favourable redox reaction between the working electrode and the electrolyte without fouling of the electrode should be taken into consideration as well as the potential window from the resulting electrochemical behaviour of the working electrode should be wide for better analyte characterization range.

2.10.2 Reference Electrode

The reference electrode is used to provide a stable potential which acts as a singular point of reference or control point for the measurement and comparison of unknown potentials. Examples of commonly used reference electrodes are Ag/AgCl in KCl solution and Hg/Hg_2Cl_2 in saturated KCl solution (SCE). Distance of reference electrode should be not more than 5mm from the working electrode to ensure uniform potential distribution and avoid the increase in ohmic resistance contributed by the solution in cyclic voltammetry tests as shown in the study done by Zhang et al., 2014.

2.10.3 Counter Electrode

The counter or auxiliary electrode is used to provide an input potential to the working electrode by allowing the flow charge flow through the electrochemical cell. It functions by producing a current flowing in the opposite direction to balance the current produced at the working electrode. Counter electrodes are usually made from inert materials with a few exceptions such as platinum, gold and carbon to prevent polarization interference from occurring electrochemically within the cell. The surface area of the counter electrode should be larger than the working electrode to reduce the polarization effect on the counter electrode as a larger surface area will result in reduced current density (Lefrou *et al.*, 2010).

2.11 Theory of corrosion kinetics

Corrosion reaction involves two independent cathodic and anodic half-cell reactions. According to Faraday’s law, there is a linear relation between the corrosion or metal dissolution rate and the charge transferred during the corrosion process.

A corrosion potential, E_{corr} is the potential where both cathodic and anodic reactions occur at the same rate In the condition where uniform corrosion occurs,

2.12 Corrosion Measurements

The easiest method to determine the corrosion rate of a targeted material is to allow the sample to be exposed to a corrosive medium and then measure the weight loss as a function of time. However, this method may be inaccurate as the extrapolation of weight loss results is required to predict the lifetime of the corrosion system. Certain types of corrosion processes (e.g. localized corrosion) will result in insignificant gravimetric changes therefore reducing the creditability of gravimetric measurements as a viable method for measuring corrosion rates. Instead, electrochemical techniques such as linear sweep measurements and linear polarization resistance are more suitable for the quantitative characterization and prediction of corrosion rates.

2.12.1 Immersion test

Immersion test is one of the easiest methods to determine the corrosion rate of a target material by allowing the sample to be exposed to a corrosive medium and then measure the weight loss as a function of time. The ASTM G31 test method normalizes corrosion rates to units of time in mm/yr or mils per year (mpy). As stated above, this technique may be inaccurate as short experimental interval cannot represent the overall reaction mechanism and is better represented by quantitative characterization measurements such as LS and LPR. To reduce experimental error, corroded or oxidized surface should be completely removed via grinding and polishing before starting the immersion test. (McCafferty,2010)

Immersion tests can be categorized into two categories, simple immersion tests and alternate immersion tests. Simple immersion tests are done by exposing the sample to the liquid medium and measuring the weight loss after a set period of time. Alternate immersion tests can be done by exposing the sample to the liquid medium for a specific time period and taking it out to dry. This process is consistently repeated for multiple cycles throughout the testing course.

The corrosion rate in mm/years from immersion testing can be calculated from the equation below:

$$CR = \frac{w}{D \times A \times t} \times k$$

Where:

w= weight loss in milligrams (mg)

k = constant (87.6)

D = metal density in grams per centimeter cube (g/cm^3)

A = area of testing sample in centimeter square (cm^2)

t = exposure time in hours

2.12.2 Linear polarization resistance

Linear polarization resistance is a non-destructive method used to determine the corrosion rates of a target material. As the material is polarized relative to the OCP potential (order of +10mV), the change in the potential will result in an induced current between the working and counter electrodes. The polarization resistance, R_ρ is obtained from the slope of the potential-current density curve over a small potential window. R_ρ is subsequently used to determine the corrosion rate of the material.

2.12.2.1 Tafel plots

A Tafel plot is a logarithmic plot expressing the relationship between the current and the electrode potential of the working electrode in an electrochemical cell which depends on the specific material analysed. Tafel plots can provide an estimate of the polarization resistance and corrosion rate using Tafel slope analysis of the resulting currents.

Corrosion rate can be calculated using the equation:

$$Corrosion\ rate, r = \frac{Mi}{nF\rho}$$

Where; Faraday constant, F is 96.485 C/Mol, i is the current, atomic mass M: 118.71g.mol-1, n is the number of e involved and ρ:7.31 g/cm^3 for tin (Sn)