THE EFFECT OF MARINE FOULING AND SEAWATER CORROSION ON DOPED TITANIUM NITRIDE ELECTRODE

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AUGUST 2022

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Dissertation submitted in partial fulfillment of the requirements for the degree of Bachelor of Engineering with Honours

(Materials Engineering)

Universiti Sains Malaysia

AUGUST 2022

DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled **"The Effect of Marine Fouling and Seawater Corrosion on Doped Titanium Nitride Electrode".** I also declared that it has not been previously submitted for the award for any degree or diploma or other similar title of this for any other examining body or council of university itself.

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ACKNOWLEDGEMENTS

Dear God, the Most Gracious and the Most Merciful, be praised. I would like to begin by humbly thanking Allah SWT for granting me the chance to finish my final year project on time while maintaining a steady mind and good physical health.

Besides, I truly want to convey my profound appreciation to my esteemed supervisor, Dr. Sheikh Abdul Rezan bin Sheikh Abdul Hamid, for his fantastic and unending support, guidance, and counsel throughout the entire project. I will always be in awe of his perseverance and drive for making this research possible and fully completed, since it would have been much more difficult to finish or complete without any of his guidance or help.

In addition, I want to thank Universiti Sains Malaysia for being ready to give me a chance to learn new things, broaden my horizons in terms of experience, discover my talents, and plan for the future over the previous four years. I appreciate the technicians at the Mechanical Engineering and School of Materials and Mineral Resources Engineering for their willingness to lend me their facilities, tools, and wise counsel so that I could finish my research or final year project.

Plus, I also deliver my profound gratitude for my mother, Noorazah binti Talib and my entire family's love, sacrifice, and dream for my future. Their unending help, tolerance, and understanding have let me finish this project without any problems. I will never forget how much my dear father, Muhammad Sabri bin Haron who has encouraged and supported me in shaping who I am today. I lack the words to express how grateful I am for their loyalty, encouragement, and belief in my capacity to realise my goals.

Additionally, I am very appreciative of all the support and guidance I had while doing my research, especially from my own lab mate and close friend, Amanda, who has been very helpful and supportive throughout my final year project. This endeavour will be challenging for me if

they don't assist and continuously support me. Finally, I also believe that it is a must for me to thank everyone who helped, directly or indirectly, with my final year project. I want to thank everyone for their feedback and recommendations, which were crucial to the effective completion of this study.

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LIST OF SYMBOLS

%	Percentage
M	Micro
Ag	Silver
$AgNO_3$	Silver Nitrate
Al	Aluminium
Au	Aurum
C	Carbon
Ca	Calcium
$CaCO_3$	Calcium Carbonate
Cl	Chloride
Cr	Chromium
Cu	Copper
E	Potential
Ecorr	Corrosion potential
e-	Electron
Fe	Iron
G	Grams
H	Hydrogen
I	Current
K	potassium
Li	Lithium
Mg	Magnesium

Mo	Molybdenum
Na	Sodium
NaCl	Sodium Chloride
Ni	Nickel
O	Oxygen
OH	Hydroxide
°C	Degree Celsius
SiC	Silicon Carbide
TiN	Titanium Nitride
wt%	Weight Percent
Z	Impedance
Zn	Zinc
ZrO_2	Zirconium Oxide (zirconia)

LIST OF ABBREVIATIONS

CE	Counter Electrode
DC	Direct Current
DOE	Design of experiment
EIS	Electrochemical Impedance Spectroscopy
Emf	Electromagnetic Field
FTIR	Fourier Transform Infrared Spectroscopy
ICCP	Impressed Current Cathodic Protection
mm	Millimeter
mm/y	Millimeter per year
OCP	Open Circuit Potential
OM	Optical Microscope
ppm	Parts per million
Rp	Polarization Resistance
Rs	Solution Resistance
RE	Reference Electrode
SACP	Sacrificial Anode Cathodic Protection
SEM	Scanning Electron Microscope
SHE	Standard Hydrogen Electrode
SCE	Standard Calomel Electrode
WE	Working Electrode
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

KESAN MARIN FOLING DAN KAKISAN AIR LAUT KE ATAS

ELEKTROD TITANIUM NITRIDE YANG DIDOP

ABSTRAK

Kakisan air laut adalah sesuatu yang tidak lagi asing kehidupan harian, ia merupakan satu kejadian semula jadi yang menyebabkan masalah kegagalan dan marin foling ke atas semua bot dan kapal secara global termasuklah di Malaysia serta segala aplikasi peralatan marin dalam persekitaran air laut. Malah, ia turut merupakan salah satu daripada penyumbang terbesar kepada masalah ini. Penyelidikan ini mengkaji penggunaan elektrod dope Titanium nitride terhadap simulasi persekitara marin fouling. Menggunakan 3 jenis air laut, marin fouling dan pH, ujian rendaman, polarisasi selari dan ujian elektokimia impedan spektroskopi (EIS) adalah ujian yang dilaksanakan untuk mendapatkan data. Penggunaan elektrod dope Titanium nitride dengan rumpai laut menujukkan penambahan berat yang paling tinggi iaitu 1.66g bagi ujian rendaman. Menggunakan analisis regresi sebagai garis panduan eksperimen bagi kedua-dua polarisasi selari dan elektokimia impedan spektroskopi (EIS). Bagi polarisasi selari, kadar hakisan tertinggi ialah 2.715 mm/tahun hasil dari rendaman selama 9 hari, air laut Ban Pecah dan kerang di mana sudah dijangkakan akan memberi kesan paling ketara terhadap kadar hakisan. Dimana pula kadar hakisan terendah ialah 0.48041 mm/tahun didapati dari 3 hari rendaman, air laut Batu Ferringhi dan rumpai laut. Daripada EIS, dua parameter yang dititik beratkan ialah pH dan bilangan hari rendaman. Ia dapat diperhatikan dimana kapasitan pukal terendah ialah 0.9971µF didapati dari ph 6.5 dan sembilan hari rendaman. Dimana pula the kapasitan pukal tertinggi ialah 0.98969 µF untuk ph 7.5 dan enam hari rendaman.

THE EFFECT OF MARINE FOULING AND SEAWATER CORROSION ON DOPED TITANIUM NITRIDE ELECTRODE

ABSTRACT

Seawater corrosion is no longer common in daily living routine or life, as it is a natural process that cause severe failure problems as well as inducing marine fouling which has been affecting the worldwide including Malaysia naval ships, vassals and marine applications in seawater as one of the biggest contributors to this concern matters. Hence sacrificial anode cathodic protection is selected to overcome the problems. This research studies the effectiveness of doped titanium nitride electrode in simulating the marine application in the seawater environment. By using specific seawater, pH, immersion testing, linear polarization and electrochemical impedance spectroscopy (EIS) are the test conducted to obtain the data. The sintered doped titanium nitride electrode that is used with seaweed shows the highest weight gain, which is 1.66g for immersion testing. Using regression analysis to design experiment for both linear polarization and electrochemical impedance spectroscopy. For linear polarization, the 3 parameters chosen are immersion days, type of seawater and type of fouling. The highest corrosion rate is 2.715 mm/year which come from nine days of immersion, Ban Pecah seawater and cockles which was expected to give significant effect on corrosion rate. Whereas the lowest corrosion rate is 0.48041 mm/years come from 3 days of immersion, Batu Ferringhi seawater and seaweed. From EIS, two parameter that being considered are pH and immersion days. It can be observed that the lowest bulk capacitance is 0.9971µF which come from 6.5ph and nine days. Whereas the highest bulk resistance is 0.98969 µF for 7.5ph and six days of immersion.

CHAPTER 1

INTRODUCTION

1.1   Research Background

The aim of this study is for studying and determining the effect of marine fouling and seawater on the doped Titanium nitride, TiN electrode in the seawater application which is associated and related to the accumulate of aquatic organisms such as plants, algae, or animals on surfaces exposed to the aquatic environment is known as marine fouling or biological fouling. The attachment of aquatic creatures to the ship's surface/facility can cause a variety of issues, including the increase of hydrodynamic volume, drain-stopping, metal corrosion, and more. Chemical methods for biofouling control are becoming increasingly inadequate due to residual toxicity, which pollutes the marine environment, necessitating the development of alternative methods. In general, the biofouling on marine structures such as ship hulls or thermal power plant water-cooling pipelines is unfavourable and not required in naval ships.

Marine fouling or biofouling, for example, increases fluid frictional resistance and reduces heat transfer efficiency. Chemical inactivation reagents such as copper and organotin coatings, as well as the injection of chlorine at greater concentrations, have thus far been successful in preventing marine biofouling. However, because of the lingering toxicity that causes pollution of the marine environment, these technologies are becoming increasingly inadequate for biofouling prevention. (Austin B, 1988) Even though UV- disinfection is another well-established approach for this purpose; however, it has a disadvantage in that it does not address microbe repair mechanisms and consequent regrowth, which is particularly problematic in these types of waters. (Nakasono S.,1992) As a result, various tactics are required to inactivate

biofilm without causing toxicity in the aquatic environment and to prevent it from regrown. Electrochemical inactivation is also being investigated as another potential alternate approach for saltwater treatment and biofouling avoidance.

The electrochemical inactivation approach relies on direct electron transfer between the microbial cell and the electrode, with no harmful chemicals produced in the process. The procedure begins with a constant voltage applied to the electrode, followed by an electrochemical reaction that allows the electrode to manufacture biocides (ROS: peroxides, hydroxyl radical & etc). The biocides that have been created will target bacteria and cause cell harm as the biofilm is removed. Besides, it is also important to note that the process of reducing a molecule or substance, commonly metal oxides, using powder metallurgy or powder sintering method which is applied in a high temperature furnace in this study for the synthesizing of Titanium nitride, TiN electrode and is considered to be the most suitable and closest synthesis technique to be utilized in order to obtain the required TiN electrodes. The obtained TiN electrode is already had been doped together with selected dopants of $AgNO_3$, ZrO_2 and Ni powders for determining the effectiveness of those applied doped-TiN electrodes in electrochemical activity inactivation on marine bacteria progress.

From reported statement of Nakayama et al. in 1998, the Titanium nitride, TiN can be utilized as an effective material for electrochemical biofouling prevention since it has a low electrical conductivity and does not degrade after usage, in a wide range of technical applications. Plus, due to its thermal stability and low electrical resistivity, a TiN layer is an essential and crucial material in the integrated circuit (IC) industry and is applied as a diffusion barrier between metal and silicon. TiN is also a biocompatible material that does not emit hazardous chemicals. Titanium nitride can

also be made without the use of titanium metal by carbothermic reduction of titanium oxides in a nitrogen atmosphere. It's a high-tech ceramic with the hardness and abrasion resistance to be used in engineering applications, particularly as thin hard coatings on metal cutting tools. Other uses include decorative coatings on jewellery and as an electrical conducting ceramic component in self-heating crucibles.

1.2 Problem statement

In general, the most important problem or the major issue found in this research is actually to investigate and learn the effect of marine fouling and seawater corrosion that are applied on the doped Titanium nitride electrodes ($AgNO_3$-TiN, ZrO_2-TiN and Ni-TiN) in terms of the obtainable corrosion rate and linear polarization measurement values for those doped TiN electrodes. This is due to the importance of assessing the detrimental effect or huge influence of existed marine fouling and seawater corrosion towards the implementation of marine applications in the targeted sea environment. Therefore, the use of doped titanium nitride is truly needed as the main representative for other seawater or marine applications like naval ships, marine pipes, oil and gas platform, research electrodes and so on.

Besides, the harsh chemical reaction induced by seawater corrosion is a huge problem to be solved along with the presence of marine fouling have affected many structural surfaces that is caused by the attachment of microbial cells to the substratum, the creation of biofilms, and the subsequent attraction of other microbes. As a result, inactivating microbial cells connected at the start of the process could be a good way to avoid biofouling caused by biofilm formation. Moreover, the treatment of seawater has gained popularity as a result of increased interest in industrial processes that use large amounts of seawater, such as aquaculture or shipping. It means that there are

dangers related with pathogen control or unwanted biofouling that must be avoided. The build-up of aquatic organisms such as plants, algae, or animals on surfaces exposed to the aquatic environment is known as biofouling or biological fouling. (Nakasono S.,1992)

Microfouling and macrofouling are both included in biofouling. The attachment of aquatic organisms to the hulls of ships is a major issue, as it increases the ship's hydrodynamic volume. This leads in a ten percent loss in speed, necessitating a 40 percent rise in fuel consumption to compensate. (Lakshmi E. et al., 2021) Furthermore, biofilms are collections of microorganisms made up of cells that connect to one another as well as to a surface. These biofilms of microorganisms are generated in drain pipes, water-cooled sides of metal surfaces in heat exchangers, and valves for oil pipelines, among other places and cause a variety of issues such as drain-stopping, metal corrosion impediments for valve-handling, and more. Biomass growth on marine infrastructures, in particular, generates higher fluid frictional resistance in ship hulls. Therefore, an efficient method of producing effective electrochemical electrode in inhibiting and inactivating the marine fouling growth is truly significant and highly required for the marine related industries.

1.3   Selected dopants to synthesize doped TiN electrodes

Titanium Nitride powder

The titanium nitride is generally described and known as the extremely hard ceramic material and refractory compound that possesses high microhardness and also great chemical as well as thermal stability that is often being applied as the coating material on the titanium alloys, carbides as well as some aluminium components in

order of enhancing and increasing the targeted surface properties of the substrate or product to be produced. Besides, titanium nitride also is known and considered as the best alternative nanomaterial and plasmonic to the gold, Au which known to have very unique physiochemical properties that is highly notable in various plasmonic devices. It also has been used in various types of applications as the important component in any special refractories and cermet, utilized in the anoxic metal casting as the base material for the crucible as well as the precursor element for many wear resistant and authentic decorative gold-like coating. In the purpose of synthesizing the doped TiN electrodes, titanium nitride is nominated to be a highly acceptable and suitable material to be selected due to all of its excellent properties compromising on overall mechanical, chemical, thermal and electrical properties.

Silver nitrate powder (AgNO₃)

First and foremost, as one of the chosen dopant materials to be implemented in the synthesis of doped TiN electrodes, the silver nitrate powder is applied and mixed together with the base titanium nitride powder.

Silver nitrate, $AgNO_3$ is defined and described as the inorganic compound produced in a form of white solid salt, which is known to be a great versatile precursor to numerous other silver compounds as it is known to be the least expensive silver salt compared to others. As a matter of fact, silver nitrate is known to have a broad range of applications in huge various fields such as chemical synthesis, medical and marine industrial applications. In term of stability and versatility, silver nitrate compound is very stable as the nitrate ion can be substituted by other ligands which can properly bonded to silver ion itself compared to other silver compounds such as silver halides.

Moreover, as for the industrial application the silver nitrate is widely used in the targeted field of disinfecting and inactivating the harmful marine microorganism which is typically known as the common pathogen indicator for determining the water contamination levels in water treatment industries. Thus, the presence of silver, Ag ion in silver nitrate compound is being properly evaluated to be implemented in preventing the spread of that pathogens from keep contaminating the treated water as well as in marine environment situation. This is due to the capability of silver's antimicrobial activity which is observed to be an amazing benefit for the inactivation of those harmful marine microorganisms in the targeted marine or water treatment industries.

Zirconium oxide powder (ZrO_2)

A zirconium oxide, ZrO_2 is often described as the white crystalline oxide of zirconium which is also known as the zirconia. Plus, zirconia is also mentioned and listed as one of the advance ceramic materials that is typically being utilized in the production of various different hard ceramics products.

Besides, in terms of hardness or strength the zirconium oxide is defined as an extremely strong with excellent hardness material along with the capability of being easily malleable and ductile. A lot of physical and chemical properties of zirconia are much similar and close to titanium itself, indicating a clear understanding on how good the wear resistant and hardness of zirconia is.

As a brief example, zirconium oxide is always compared to other material as porcelain in the dental industries. Due to zirconia great strength which is about five times stronger and more durable than porcelain, then it is used as the best substitute or replacement for replacing the porcelain. Moreover, as zirconia is also known to possess

other outstanding corrosion properties as well as wear resistant, then it is frequently being applied in the targeted production of electrochemical electrode for prevention of marine bacteria or biofouling activities or industries.

Thus, in the concern of producing better doped titanium nitride electrode, zirconia is also utilized and mixed together with TiN powder which is expected to have better result of electrochemical prevention on marine bacteria or biofouling as it is hard, durable and indestructible for a long period of time which truly a huge benefit for all.

Nickel powder (Ni)

Nickel, Ni is defined as the lustrous silvery-white metal alongside with a gold tint physical appearance. Nickel powder is widely implemented in most of hundreds or thousands of products especially in many productions of nickel alloys with other metals combination such as chromium and titanium. Plus, it is also used to produce the required stainless steel as well as heat resistant steel for the industries. This is because of nickel's great ability regarding the anti-corrosion capabilities, so it is generally chosen to be utilized as the material in providing the needed good corrosion resistant feature on most manufactured metals especially in the marine condition.

On other side, nickel powder is also described as a great alloying element and very much compatible with other metallic elements such as gold, iron, cobalt, aluminium, titanium and others. Therefore, it is known to be massively implemented in the production of related electrochemical or electrolysis activities, making it is as one of the most suitable metallic powders to be applied in the synthesis of doped titanium nitride electrode.

1.4   Objectives

The major objectives for this research are:

a. To investigate and learn the effect of marine fouling and seawater corrosion on doped Titanium nitride electrode.

b. To determine as well as compare the corrosion rate and linear polarization of doped Titanium nitride electrodes ($AgNO_3$-TiN, ZrO_2-TiN and Ni-TiN) when subjected to marine fouling and seawater existence.

1.5   Research scope

In this experiment, it is known that there are three different types of produced sintered doped-titanium nitride electrodes which are defined as the doped $AgNO_3$-TiN electrode, ZrO_2-TiN electrode and Ni-TiN electrode. The main purpose of conducting this research experiment is to investigate and learn the effects of various marine fouling and different types of seawater on the synthesized doped titanium nitride, TiN electrodes, which included the inactivation of marine bacteria in term of electrochemical activity, in order to investigate the crucial effect of those marine fouling and seawater corrosion for each type of the sintered doped electrodes.

The immersion testing is identified as one of the most common corrosion measurement testing that is implemented and conducted in calculating the rate of corrosion on the doped TiN electrodes. The electrochemical impedance spectroscopy and linear polarization (LP) are being applied to measure the electrochemical value properties of the targeted doped titanium nitride electrodes. After the completion of the required testing, the doped TiN electrodes morphologies are observed by using the optical microscope and scanning electron microscope (SEM).

1.6 Outline of Chapter

To sum up, totally there are about five chapter that are consisted in the thesis. Introduction, objectives and scope of work regarding the project was discussed in chapter one. Whereas chapter two is on concept, theory and literature review related to the different sintered doped titanium electrodes affecting the efficiency of electrochemical inactivation for each of them. Meanwhile chapter three was explaining on experimental details and characterization approaches for the project. Then, the results and discussion of the project was focused on the chapter four. Finally, chapter five is mentioning the conclusion and recommendations for future work.

CHAPTER 2

LITERATURE REVIEW

2.1   Introduction

A corrosion is the erosion of a material's characteristics as a result of interactions with the environment including the seawater situation. It's a natural occurrence that happens on metal that needs to be prevented. According to research, the annual expenses of corrosion are considerable since it is critical to assure the safe usage of the building or component. There are numerous types of corrosion classifications, including general corrosion, galvanic corrosion, pitting, and stress corrosion cracking, depending on the morphology of the attack and the type of environment it is subjected to. (Shaw, 2006). Besides, corrosion also reduces component lifetime owing to surface roughness, weakens the component, and causes component failure. It's critical to keep precise records of previous corrosion in order to improve and prevent the failure from happening again. Different components have different concerns that must be considered while choosing materials and designing them. (Garbatov et al., 2016).

When different types of materials are electrically connected in the same environment, galvanic corrosion occurs, which can be regulated by material selection, coatings, inhibitors, and cathodic protection. (Khadom and Abod, 2017). Plus, the existence of anode and cathode is also detected when the dissimilar materials are coupled. In comparison to the metal cathode, which will corrode slower or even inhibit corrosion from occurring, the anode will corrode faster and expedite the corrosion stage in order to prevent the targeted metal product or sample from being affected by rapid corrosion especially in seawater environment along with presence of marine fouling organisms. The cathode will be made of a less noble metal, while the anode will be made of a more noble metal. Previous research has shown that having a smaller anodic layer helps reduce and ameliorate severe corrosion in a highly conducting electrolyte areas compare to

cathode. As a result of the larger cathode, more oxygen is reduced, resulting in a higher galvanic current. (Hasan, 2014).
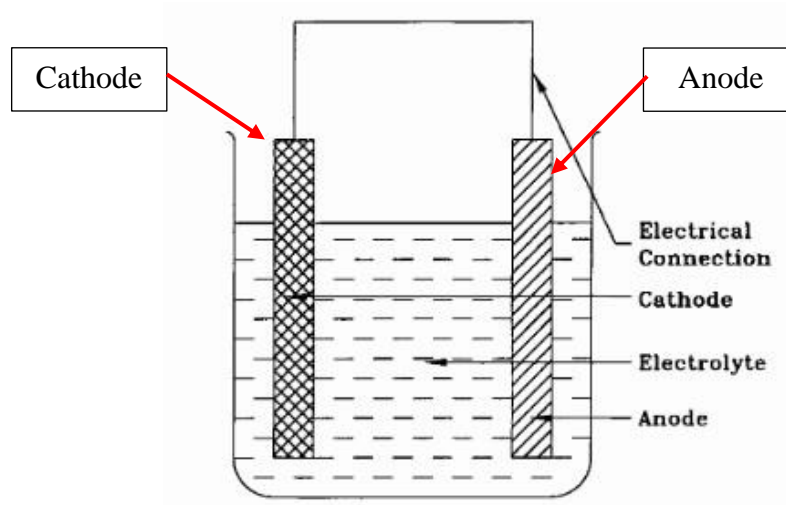
Figure 2.1: Galvanic cell

From Figure 2.1, An electrolyte is a conductivity solution used to transfer ions, and current flow requires an electrical connection. Corrosion occurs at the anode when a metal loses an electron and transforms into an ion in the solution.

$$M \longrightarrow M^{Z+} + Ze^-$$

At the cathode, it attracts electrons from the anode and consumes them for the reaction. This reaction could result in the formation of a metal layer, as well as oxygen reduction and hydrogen evolution. (Tavakkolizadeh, 2001)

$$N^{Z+} + Ze^- \longrightarrow N$$

$$2H_2O + O_2 + 4e^- \longrightarrow 4OH^- \, pH > 7$$

$$2H^+ + 2e^- \longrightarrow H_2 \, pH < 7$$

11
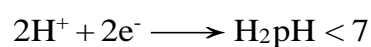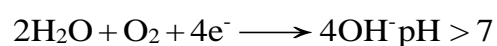
2.2　The EMF and Galvanic Series

The electromotive force series (EMF) is a half-cell potential system that ranks metals according to their reactivity. Metals at the top of the series are the most noble, with a positive electrochemical potential, while metals at the bottom are the most active, with a negative electrochemical potential. Electron flow will occur when the two types of metals are joined due to the potential difference. The nobility determines corrosion resistance. The slower a metal's tendency to corrode is, the more noble it is. Furthermore, EMF can be utilized to forecast the occurrence of galvanic corrosion. (Revie and Uhlig, 2008).

The half-cell reactions are written as decrement in the EMF series. The series progresses from positive to negative, passing through the hydrogen reaction at 0.00 V

$$2H^+ + 2e^- \longrightarrow H_2 \quad E^0 = 0.00 \text{ V}$$

From figure 2.3, the Au has the highest positive potential values in the series, with potential values of +1.498 V.

$$Au^{3+} + 3e^- \longrightarrow Au \quad E^0 = +1.498 \text{ V}$$

The series from the table with the most negative values is Li, which has potential values of -3.040 V. (McCafferty, 2010).

$$Li^+ + e^- \longrightarrow Li \quad E^0 = -3.040 \text{ V}$$

In diverse media, such as saltwater, sulfuric acid, and artificial perspiration, the EMF series is frequently ranked differently. By connecting the metal or alloy to the voltmeter's negative terminal and the reference electrode to the positive terminal, the series can be established. (Ahmad, 2006).
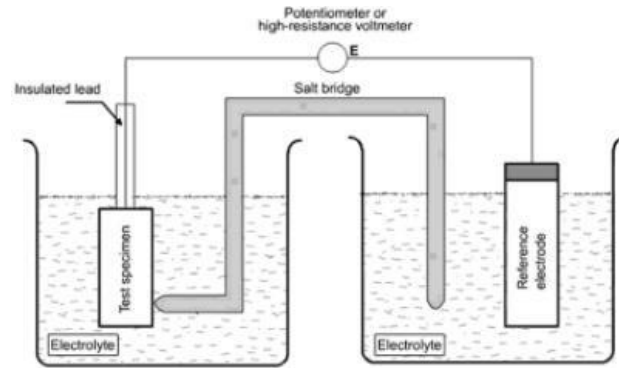
Figure 2.2: Laboratory technique for measuring the single electrode (corrosion) potential, E_{corr} of metals and alloys in aqueous environments. Use of salt bridge (Ahmad, 2006)

Reaction	E^0(V vs. SHE)	
$Au^{3+} + 3e^- \rightarrow Au$	+1.498	Noble
$Pt^{2+} + 2e^- \rightarrow Pt$	+1.18	↑
$Pd^{2+} + 2e^- \rightarrow Pd$	+0.951	
$Hg^{2+} + 2e^- \rightarrow Hg$	+0.851	
$Ag^+ + e^- \rightarrow Au$	+0.800	
$Cu^+ + e^- \rightarrow Cu$	+0.521	
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.342	
$2H^+ + 2e^- \rightarrow H_2$	0.000	
$Pb^{2+} + 2e^- \rightarrow Pb$	−0.126	
$Sn^{2+} + 2e^- \rightarrow Sn$	−0.138	
$Mo^{3+} + 3e^- \rightarrow Mo$	−0.200	
$Ni^{2+} + 2e^- \rightarrow Ni$	−0.257	
$Co^{2+} + 2e^- \rightarrow Co$	−0.28	
$Cd^{2+} + 2e^- \rightarrow Cd$	−0.403	
$Fe^{2+} + 2e^- \rightarrow Fe$	−0.447	
$Ga^{3+} + 3e^- \rightarrow Ga$	−0.549	
$Ta^{3+} + 3e^- \rightarrow Ta$	−0.6	
$Cr^{3+} + 3e^- \rightarrow Cr$	−0.744	
$Zn^{2+} + 2e^- \rightarrow Zn$	−0.762	
$Nb^{3+} + 3e^- \rightarrow Nb$	−1.100	
$Mn^{2+} + 2e^- \rightarrow Mn$	−1.185	
$Zr^{4+} + 4e^- \rightarrow Zr$	−1.45	
$Hf^{4+} + 4e^- \rightarrow Hf$	−1.55	
$Ti^{2+} + 2e^- \rightarrow Ti$	−1.630	
$Al^{3+} + 3e^- \rightarrow Al$	−1.662	
$U^{3+} + 3e^- \rightarrow U$	−1.798	
$Be^{2+} + 2e^- \rightarrow Be$	−1.847	
$Mg^{2+} + 2e^- \rightarrow Mg$	−2.372	
$Na^+ + e^- \rightarrow Na$	−2.71	
$Ca^{2+} + 2e^- \rightarrow Ca$	−2.868	
$K^+ + e^- \rightarrow K$	−2.931	↓
$Li^+ + e^- \rightarrow Li$	−3.040	Active

Figure 2.3: Standard electrode potentials at 25^0C (McCafferty, 2010)
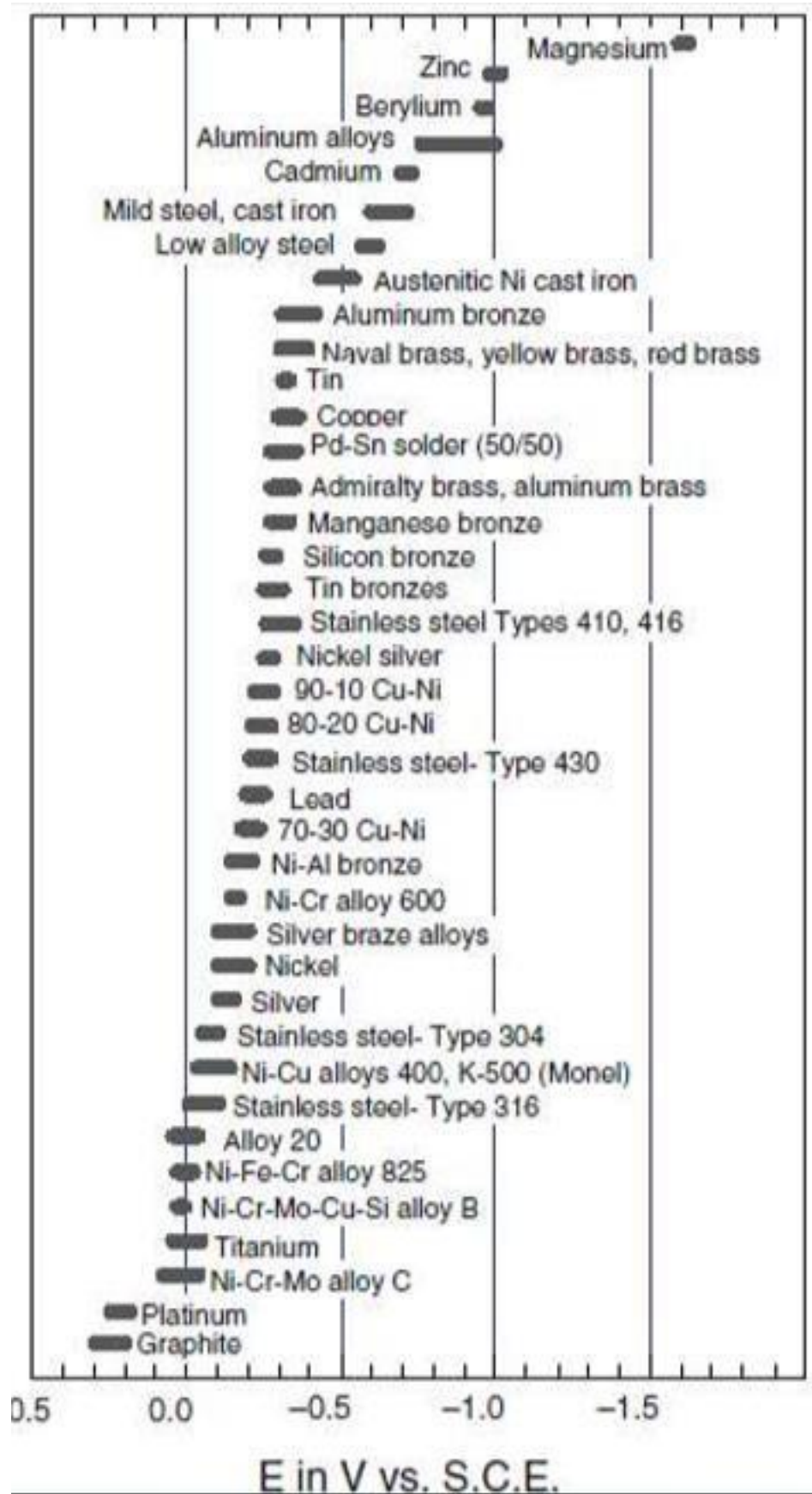
Figure 2.4: Galvanic series in seawater (McCafferty, 2010)

2.3   Pourbaix Diagram

Pourbaix diagram is a potential-pH diagrams of compact summary thermodynamic data. The data obtain can be related to any metal in water for electrochemical and corrosion behavior. From the potential and pH values in the diagram, the reaction of the metal can be estimated. Either it's in the stable region where the corrosion does not take place, immunity region where it does not react, or in the reaction region which can form specific oxides or complex ions. Therefor the pH or potential can be adjusted to meet the requirement values for stable region to avoid corrosion (Revie and Uhlig, 2008).

Nernst equations and solubility data for metal and its species was used to construct the pourbaix diagram. From the attached pourbaix diagram, the pH value is on the horizontal axis whereas the redox potential is on the vertical axis. Based on pourbaix diagram for water at 25^0C as shown in figure 2.5 below. There are 3 regions present in the diagram upper, middle and lower. Upper region is where water electrolyzed anodically to O_2. Water has electrolyzed as cathodic to H_2 at the lower region. Whereas at the middle region, water is stable and won't decompose (McCafferty, 2010).
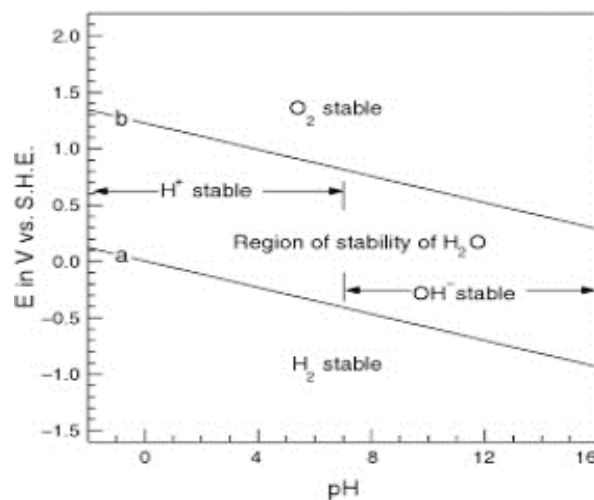
Figure 2.5: Pourbaix diagram for water at 25^0C (McCafferty, 2010)

2.4   Pourbaix Diagram for Titanium

From the diagram below in figure 2.6, it shows that there is a horizontal and vertical line presented in the diagram. The horizontal line indicates that pH which related to neither H^+ and OH^- does not involve in the reaction. Whereas the vertical line indicates reaction involving H^+ and OH^- but not electron. In different oxidation state, corrosion of Ti can happen in acid and neutral solutions.
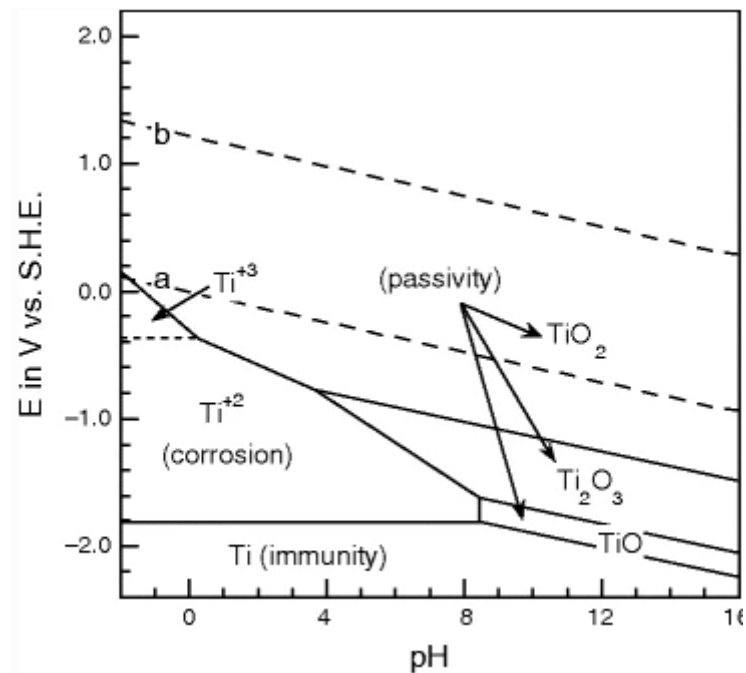
Figure 2.6: Pourbaix diagram for Titanium at 25^0C (McCafferty, 2010)

At pH 1.76 represent equation $2Ti + H_2O \longrightarrow TiO + 2H^+$ is equilibrium. Thus, this means that when the pH is more then 1.76, TiO is stable because formation of oxide film will act as protective film which will show some protection against corrosion. The iron oxide is in a passivation region which means Ti reacts in these will be forming protective oxide films but this only acceptable when it accounted by diffusion-barrier oxide layer. When the pH starts to drop, which is lower than 1.76 corrosion will occur without any protection this is because the ferric ions in solution are stable. $TiO + 2H^+ + 2e^- + H_2O$ equilibrium reaction represent by the sloping line between Ti^{2+} and TiO.

Therefore, this is similar just like before to the right side of the sloping line protection oxide layer will be form, whereas on if it move to the left side of the slopping line corrosion will occurred (McCafferty, 2010).

2.5   Pourbaix Diagram for Silver

From diagram below it shows that pourbaix diagram of Silver (Ag). The result of Silver just as shown in the diagram which is because the dissolution of Silver occurs in acid solution and basic solution. Same as other pourbaix diagram, the diagram of Ag is obtained from Nernst equation and it is a diagram of an equilibrium potential as a function of pH from acidic to basic.
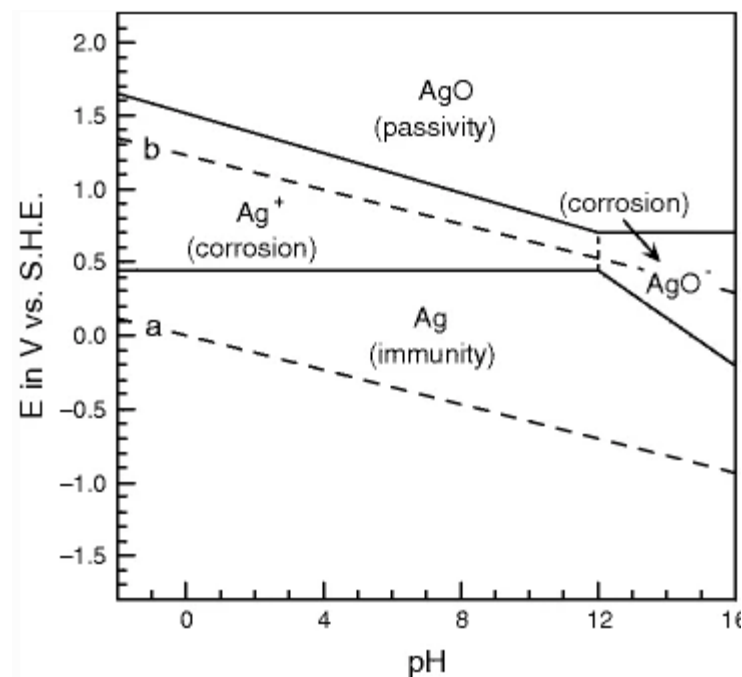
Figure 2.7: Pourbaix diagram for Silver at 25^{0}C (McCafferty, 2010)

Figure 2.7 shows that at lower and higher pH values, Ag have higher corrosion rate whereas at intermediate pH it forms a passivation which is lower corrosion rate. The thermodynamic information agrees with kinetic data. At the upper side of horizontal anodic lines, the produced oxidized product is stable. Whereas on the lower side

horizontal anodic equilibrium line, solid silver, Ag is stable hence it immune to corrosion and cannot be dissolved (McCafferty, 2010).

2.6   Pourbaix diagram for Zirconium Oxide (zirconia)

As displayed in the diagram below, it is known to be the pourbaix diagram for Zirconia, ZrO_2. The result of ZrO_2 is shown as below due to the formation of oxide impurities which has led to the existence of ZrO_2 contamination which further proceeding to be easily corroded. Same as other pourbaix diagram, the diagram of Ag is obtained from Nernst equation and it is a diagram of an equilibrium potential as a function of pH from acidic to basic.
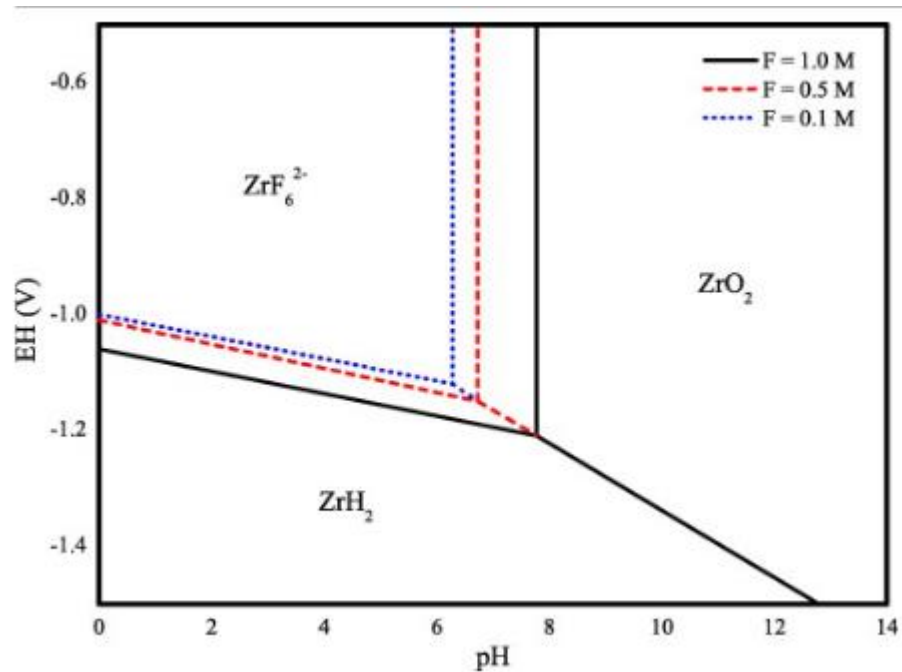
Figure 2.8: Pourbaix Diagram for Zirconia at 25^0C (Raghavan, 2012)

Figure 2.8 shows that at lower and higher pH values, Zr_2O have higher corrosion rate whereas at intermediate pH it forms a passivation which is lower corrosion rate. The thermodynamic information agrees with kinetic data. At the upper side of horizontal anodic lines, the formed oxidized product is stable. Whereas on the lower side horizontal anodic equilibrium

line, solid zirconia, Zr_2O is stable thus, it immune to corrosion and cannot be dissolved (McCafferty, 2010).

2.7 Pourbaix Diagram for Nickel

The pourbaix diagram of nickel is depicted in the diagram below (Ni). Because nickel dissolves in both acidic and basic solutions, the outcome is exactly as depicted in the diagram. The Ni pourbaix diagram is similar to the other pourbaix diagrams in that it is derived from the Nernst equation and depicts an equilibrium potential as a function of pH from acidic to basic.
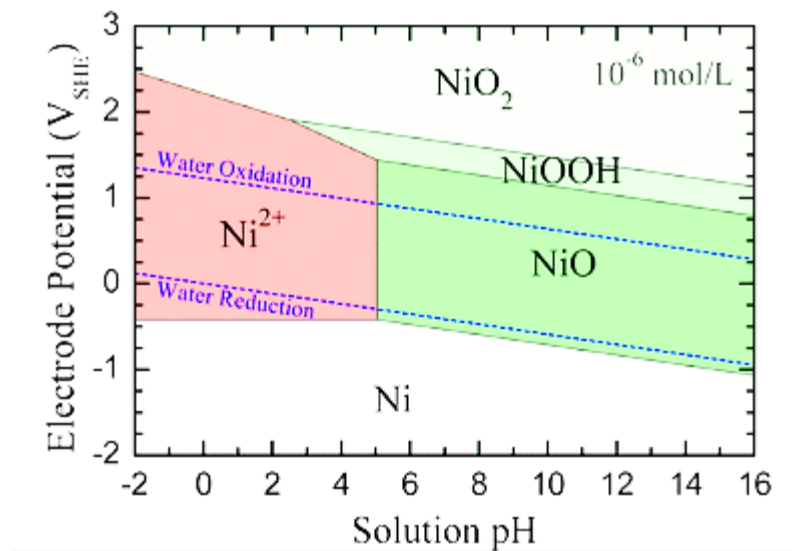
Figure 2.9: Pourbaix Diagram for Nickel at 25^0C (Abazari et al., 2019)

Figure 2.9 demonstrates that Ni corrodes more quickly at lower and higher pH levels than it does at intermediate pH levels, where it forms a passivation that has a reduced corrosion rate. The kinetic data and the thermodynamic information are consistent. The resulting oxidized product is stable at the top of horizontal anodic lines. Solid Ni is substantially more stable on the lower side of the horizontal anodic equilibrium line than solid silver, which makes it resistant to corrosion and impossible to dissolve (Abazari et al., 2019).

2.8   Cathodic Protection

Cathodic protection is one the efficient method to lower down possibilities of corrosion to occur by using direct current (dc). The connection takes place from anode through electrolyte and followed by cathode which is the part that needs protections. The current that flow from the connection through the electrolyte is ionic current not electrical current. It can be done by reducing the potential different between anode and cathode. Hence to protected the structure from other source, current is applied so that the potential for the whole structure is the same (Revie, 2011).

In addition, the objective of cathodic protection is reducing or prevent corrosion from occur. These goals can be achieved by supply more electron which obtain from dc part to the metallic part that need protections. From this action, the cathodic reaction rate is rising while the anodic reaction is decreasing. Due to shifting of cathode potential to anode hence the potential different is eliminated and corrosion is hardly to occur. As the transferring of electron take place, the cathodic reaction polarizes in the direction of local action anode potential. Cathodic protection is completed when the metallic structure become more negative. Corrosion can be prevented by minimizing the potential different between anode and cathode. Hence the lower the potential different, the cathodic protection is more efficient (Ahmad, 2006).

Usually, the hull of the ship which the bottom part that is in contact with the seawater will be painted and the paint is one of the methods to prevent corrosion. Therefore, cathodic protection is one of the effective techniques that is implemented in order to protect the ship hull when the paint protection breakdown and unable to give full protection performance. In actual practice, cathodic protection has been used to protect water storage tanks, buried pipelines, steel reinforcing bars in concrete structures located in marine environment and many other structure (McCafferty, 2010).

2.9   Types of Cathodic Protection

Impressed current cathodic protection (ICCP) and sacrificial anode cathodic protection are the two categories of cathodic protection (SACP). The term "sacrificial anode cathodic protection," also referred to as "galvanic anodes," comes from the process of anodes sacrificing themselves to preserve the cathode, the structure. A galvanic cell is constructed for this form of protection, with the more active metal serving as the anode and the less active metal serving as the cathode. In fresh water, magnesium is preferred above zinc and aluminium alloy, while zinc and aluminium alloy are the most frequently used metals as anodes in underground applications. SACP does not require external power, but the protective current is produced by the electrochemical cell attached to the cathode, which is the structure that has to be protected. (Revie, 2011)

When only a few hundred milliamperes to 4 or 5 A of current are needed, SACP is the preferred option. SACP can be used to protect offshore structures since they typically only need minimal current usage. Examples of SACP in use include well-coated, electrically separated structures, offshore structures, ship hulls, hot-spot pipeline protection, and heat exchanger water boxes. The benefits of SACP include the fact that it does not require external power, requires less maintenance, is simple to install, does not significantly modify cathodic interference, and requires less inspection than other inventions. While the drawbacks include the need for a suitable coating, the high cost of replacement, the limited current output, and the absence of adjustability without resistors in anode circuits (Revie, 2011).

While a power source is used to give cathodic protection from impressed current. Anodes formed of a substance with an extremely low or nearly inert dissolving rate receive the current. The protective current is only introduced into the electrolyte by the anodes. The power supply for ICCP is often a transformer rectifier, which has the job of reducing incoming alternating current (ac) and converting it to direct current (dc). High silicon, cast iron that contains chromium, graphite, and scrap steel are some of the common anodes employed. Anodes made of magnetite and lead-silver are also employed, while lead-silver can only be utilized in seawater. (Revie, 2011).

When a high current of 500 A or more is necessary, ICCP is typically employed. In addition, it can be used to replace the SACP system for low current requirements. The most frequent examples of ICCP applications are long transmission pipelines, intricate subsurface structures, pilings, marine constructions, and ship hulls. Similar to SACP, ICCP has benefits and drawbacks. The benefits include tunable output, high current capacity, application to poorly coated or uncoated structures, and decreased replacement costs. The restrictions include the need for steady power, periodic maintenance and inspections, the requirement for experienced workers before to installation, and the possibility of cathodic interference. (Revie, 2011).

2.10   Cathode Material (doped Titanium nitride)

Titanium nitride, TiN, has been applied and presented as an excellent replacement for sacrificial anode in place of employing zinc in this current and advanced materials era to defend ships or any harbor constructions from the attack of seawater corrosion. Since more and more navy ships and vessels are using titanium nitride as sacrificial anodes on an annual basis, titanium nitride has become widely employed throughout the world (Rousseau et al., 2009). On the other hand, titanium itself must be present and was chosen because of its superiority as a noble metal.

This is due to the fact that when titanium is combined with other metals, titanium itself serves as the cathode while the other metals that are connected act as anodes and corrode. Additionally, titanium is recognized for having high redox potentials, which are lower or more negative than steel under the same circumstances, so it will deliver SACP to the steel structure in (Mouanga et al., 2013). The anode and cathode, which represent the structure that needs protection, must be electrically linked and situated in a conducting environment for the protection action to be effective. While precise placement and the necessary number of anodes are necessary for the anode to work properly (Kim, 2017).

Additionally, although magnesium (Mg), compared to aluminium (Al) and zinc (Zn), has the largest negative potential value, it is more suitable for on-shore structures as this is because the electrolyte which the soil or water contains has higher resistivity. If the cathode is used in salt water, the coating at the cathode will disintegrate due to the considerable difference in electron potential between the anode and cathode, which is more negative in potential. For saltwater, TiN and Al or Zn are preferred because of their reduced resistance (Ahmad, 2006). Moreover, the electrochemical properties as well as other related resistivity towards seawater corrosion and marine fouling will be greatly improved in comparison to regular or ordinary titanium electrode with the addition of dopants mixed and sintered with the titanium nitride electrode (the use of silver nitrate, zirconia, and nickel).

2.11   Anode Material

For anode, due to its excellent mechanical qualities, mild steel is one of the most often used building materials for marine structures. In addition to being one of the most plentiful elements on Earth, it is also less expensive than other metals. It may also be welded, making it perfect for creating a variety of constructions. Typical applications for mild steel include ships, drilling platforms, offshore structures, undersea pipelines, and

cable. Mild steel, on the other hand, has a low corrosion resistance, making it unsuitable for corrosive environments like saltwater, which contains between 3% and 3.5 percent sodium chloride. Protection is therefore necessary to stop the metal structure from keep corroding in the seawater or marine environment (Yang, 2010).

2.12   Electrolyte (Seawater)

The compound that might exist in seawater are Na^+, Mg^{2+}, Ca^{2+}, K^+, Sr^{2+} as the major cation. Whereas the major anion is Cl-, SO_4^{2-}, HCO_3^-, Br^-, CO_3^{2-}, $B(OH)_4^-$, F^-. Almost all this element can be found in most seawater which will lead to the properties of the ocean. Salt particle in seawater or marine environment contribute to pitting corrosion by deposited on the metal structure or surface of the metal structure (Ahmad, 2006).

2.13   Effect of seawater pH on the corrosion rate

Corrosion of seawater and marine fouling has left a severe impact on world-wide activities, the impact includes from structure deterioration to economic. Even in a natural environment degradation of structure occurs and it cannot be control but can be prevented. The corrosion occurs when the actual atomic, molecular, or ironic transport process takes place at the interface of the structure. Metal type and environment media do play important roles for corrosion rate. Commonly, the corrosion rate increase as the acidity of the environment media increase (Kim, 2017).

Generally, higher and lower pH does leave remarkable effects on the corrosion rate. By having higher pH, it will leave a significant effect on film formation by causing thickening of the passive film due to its iron oxide being more stable in alkaline solutions for stainless steel. It is very different in acidic solutions. This is because it will be forming

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