

STUDY OF CORROSION BEHAVIOUR OF ZINC IN POTASSIUM HYDROXIDE ELECTROLYTE

by

W<mark>AN MA</mark>RINAH IZZATI BINTI WAN I</mark>SMAIL

UNIVERSITI

A report submitted in fulfilment of the requirements for the degree of Bachelor of Applied Science (Materials Technology) with Honours

FACULTY OF EARTH SCIENCE UNIVERSITI MALAYSIA KELANTAN

DECLARATION

I declare that this thesis entitled "Study of Corrosion Behaviour of Zinc in Potassium Hydroxide Electrolyte" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature	:
Name	: <u>Wan Marinah Izzati binti Wan Ismail</u>
Date	;

I certified that the thesis of this final year project entitled "STUDY OF CORROSION BEHAVIOUR OF ZINC IN POTASSIUM HYDROXIDE ELECTROLYTE" by Wan Marinah Izzati binti Wan Ismail, matric number E13A335 had been examined and all the correction recommended by examiners have been done for the degree of Bachelor of Applies Science (Materials Technology) with Honours, Faculty of Earth Science, University Malaysia Kelantan.

University Malaysia Kelantan.
Approved by:
Signature :
Name : <u>Dr. Mohamad Najmi Bin Masri</u>
Date :

i

FYP FSB

ACKNOWLEDGEMENT

Bismillahirrahmanirrahim,

First of all, I am so thankful until today that with God's blessings, I am able to live my life to the fullest academically and physically. On the other hand, I would like to express my greatest gratitude to my Research Project Supervisor, Dr. Mohamad Najmi bin Masri for his countless supervision and guidance throughout completing this thesis. I am particularly in debited for his foresight and vision which inspired me to confront the obstacles on doing this research with patience and passionate. This work would not conceive without the invaluable aids that I gain from him to access the resources and journals for the purpose to write the paper.

Furthermore, I also owe a debt gratitude to my parents who are always supporting me in completing the task. It is with their great hands as well as financial and moral supports that I am able to achieve the great outcomes from his research study.

It is also my utmost responsibility to record my appreciation to Faculty Earth Science, University Malaysia Kelantan Campus Jeli who are willing give permission and providing all needs needed in way to complete this study which is above all a treasure of the thesis. Their help is indeed the most crucial of all course to bring this research to a successful end.

Last but not least, I would also like to thank everyone who are being supportive into collaborating to produce this work of success especially to my colleagues, circle of friends and lecturers. Your kindness is highly appreciated for this glorious outcome. Thank you.

Study of Corrosion Behaviour of Zinc in Potassium Hydroxide Electrolyte

ABSTRACT

Two types of zinc (Zn) was immersed in different concentration of potassium hydroxide (KOH) aiming at the preparation of corrosion behaviour of Zn in KOH, which led by producing the hydrogen evolution gas. Zn that been used in this study were existing commercial Zn and 99.9% pure Zn. In this study, the characterization of Zn was studied, this is including hydrogen evolution gas, corrosion rate, morphology analysis and structural analysis. In this experiment, instruments that used are scanning electron microscopy (SEM) and X-ray diffraction (XRD). The volume of hydrogen evolution gas was increasing until it attain the maximum level concentration of KOH, 6 M. Meanwhile, both sample of Zn that soaked in 6 M KOH had the highest rate of corrosion with 9.95 mpy, respectively. From the SEM micrographs of sample showed that Zn have reacted and corrode when immersed in KOH. The analysis from XRD for both types of Zn showed that the immersion of KOH electrolyte into Zn gives some effect where the surface of Zn showed white patch. This is due to oxide presence at Zn surface.



Kajian Kelakuan Kakisan Zink dalam Elektrolit Pottasium Hidroksida

ABSTRAK

Dua jenis zink (Zn) telah diletakkan di dalam kepekatan Pottasium hidroksida (KOH) yang berbeza bertujuan bagi persediaan kelakuan kakisan Zn dalam KOH, yang akan menghasilkan gas evolusi hidrogen. Zn yang digunakan dalam kajian ini ialah Zn yang komersial dan Zn yang 99.9% tulen. Dalam kajian ini, pencirian Zn telah dilakukan termasuk gas evolusi hidrogen, kadar kakisan, ujian mikograf dan ujian kristal dan komposisi. Dalam eksperimen ini, alatan yang telah digunakan bagi memenuhi analisis untuk mikrograf ialah mikroskop imbasan elektron (SEM) dan pembelauan sinar X-ray (XRD) bagi tujuan analisis komposisi dan kristal. JumLah gas evolusi hidrogen semakin meningkat sehingga ia mencapai tahap maksimum kepekatan KOH, 6 M. Manakala, kedua-dua jenis sampel Zn yang direndam dengan kepekatan 6 M KOH mempunyai kadar tertinggi kakisan dengan 9.95 mpy masingmasing. Dari mikrograf SEM sampel menunjukkan bahawa Zn mempunyai tindak balas dan terhakis apabila direndam dengan KOH. Analisis dari XRD untuk keduadua jenis Zn menunjukkan bahawa rendaman elektrolit KOH ke dalam Zn memberi sedikit kesan di mana permukaan Zn menunjukkan tompok putih. Ini ialah disebabkan oleh kehadiran oksida di atas permukaan Zn. Keseluruhan eksperimen dilakukan dalam masa tiga bulan yang mana setiap sampel direndam selama tujuh hari untuk melihat perkembangannya daripada semasa ke semasa.



TABLE OF CONTENTS

		Page
DECI	ARATION	i
ACKN	NOWLEDGEMENT	ii
ABST	RACT	iii
ABST	RAK	iv
TABL	LE OF CONTENTS	v
LIST	OF TABLES	vii
LIST	OF FIGURES	viii
LIST	OF ABBREVIATIONS	Х
LIST	OF SYMBOLS	xi
CHAI	PTER 1 INTRODUCTION	
1.1	Background of Study	1
1.2	Problem Statement	4
1.3	Objectives and the second se	5
1.4	Scope of Study	5
CHAI	PTER 2 LITERATURE REVIEW	
2.1	Introduction	6
2.2	Properties of Zinc	6
	2.2.1 Electrochemistry of Zinc	6
	2.2.2 Application of Zinc	8
2.3	Corrosion of Zinc in Different Electrolyte	
	2.3.1 Sodium Chloride	10
	2.3.2 Sodium Hydroxide	12
	2.3.3 Potassium Hydroxide	13
2.4	Characterization of Zinc in Potassium Hydroxide	
	2.4.1 Volumetric Measurement	16
	2.4.2 Corrosion Rate	17
	2.4.3 Morphology Observation	18
	2.4.4 Structural Analysis	20

CHAPTER 3 MATERIALS AND METHODS

3.1	Introduction	21
3.2	Preparation of Raw Materials	
	3.2.1 Pure Zn	21
	3.2.2 Commercial Zinc	22
	3.2.3 Preparation of Potassium Hydroxide Electrolyte	23
3.3	Characterization of Zinc in Potassium Hydroxide	
	3.3.1 Volumetric Measurement	25
	3.3.2 Corrosion Rate	27
	3.3.3 Morphology Observation	28
	3.3.4 Structural Analysis	28
3.4	Research Flow Chart for Overall Experiment	29

CHAPTER 4 RESULTS AND DISCUSSION

4.1	Introduction	30
4.2	Characterization of Zinc in Potassium Hydroxide	
	4.2.1 Volumetric Measurement	31
	4.2.2 Corrosion Rate	35
	4.2.3 Morphology Observation	38
	4.2.4 Structural Analysis	40

CHAPTER 5 CONCLUSION AND RECOMMENDATION

5.1	Conclusion	46
5.2	Recommendation	48
REFE	ERENCES	49
APPE	ENDIX	53



FYP FSB

PAGE

LIST OF TABLES

CHAPTER 2 Literature Review			
Table 3.1	Preparation for KOH solution	23	
CHAPT <mark>e</mark> i	R 4 Result and Discussion		
Table 4.1	Crystallinity and Amorphous of commercial Zn in	45	
	concentration KOH		
Table 4.2	Crystallinity and Amorphous of pure Zn in concentration	45	
	КОН		



LIST OF FIGURES

CHAPTER 2 Literature Review

Figure 2.1	EMF Series	7
Figure 2.2	Comparison of the XRD peaks	18
Figure 2.3	Cross-section micrographs of Zn particles	20

CHAPTER 3 Materials and Method

Figure 3.1	Cross section of battery	22
Figure 3.2	Summarization of preparation KOH solution	24
Figure 3.3	Illustration setup for volumetric measurement	25
Figure 3.4	Actual setup for volumetric measurement	26
Figure 3.5	Summary of flow research	29

CHAPTER 4 Result and Discussion

Figure 4.1	Rate hydrogen evolution of commercial Zn in different	27
	concentration of KOH.	32
Figure 4.2	Rate hydrogen evolution of pure Zn in different	22
	concentration of KOH.	55
Figure 4.3	Rate hydrogen evolution in both types of Zn plate in	22
	different concentration of KOH	55
Figure 4.4	Illustration of Zn particles in KOH solution	34
Figure 4.5	Corrosion rate against concentration KOH in both types of	36
	Zn	



PAGE

Figure 4.6	Cross sections of micrograph commercial Zn before	38
	experiment	
Figure 4.7	Cross sections of micrograph pure Zn after experiment	38
Figure 4.8	Cross sections of micrograph commercial Zn before	39
	experiment	
Figure 4.9	Cross sections of micrograph pure Zn after experiment	39
Figure 4.10	Comparison peak analysis for Zn Plate before experiment	40
Figure 4.11	Comparison peak analysis for XRD of commercial Zn in	43
	different KOH solution	
Figure 4.12	Comparison peak analysis for XRD of pure Zn in different	43

KOH solution

UNIVERSITI MALAYSIA

LIST OF ABBREVIATIONS

X-Ray Diffraction	
Scanning Electron Microscope	
Electromotive Forces	EMF
Zinc	Zn
Pota <mark>ssium Hydr</mark> oxide	КОН
Optical Microscope	OM

UNIVERSITI MALAYSIA KELANTAN

LIST OF SYMBOLS



FYP FSB

xi

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Most people are familiar to the corrosion by the appearance of the degradation of rooftop (which is using zinc (Zn)) rusting of metal, and corrosion in batteries. However, the corrosion is appearing safe to almost everyone is at least familiar with the corrosion by defined it in general terms as the degradation of a material, usually a metal, or its properties because of a reaction with its environment (Roberge, 2008).

Naturally, corrosion happens when the metal surface is exposed to the oxygen (O_2) . For an example, the alkaline battery. In a part of alkaline battery is using Zn as an anode. Zn is a type of metal that corrode when it react to the presence of O_2 or actual material loss by the corrosion (Callister et al., 2007).

Basically, corrosion occurs with different forms including that no visible weight change or degradation in certain form of corrosion, yet properties change and cause the material may fail unexpectedly because of certain changes within the material. Such changes may change the ordinary visual examination or weight change determinations. Literally, it is causing stress concentration as a material reducing load carrying capability. Meanwhile, mostly corrosion happens to the metal where the metal is exposed to the oxygen and under the moist condition. During corrosion there are two main reactions occur oxidation and reduction. Oxidation is a reaction where metal will lose the electron by a species and increase in oxidation number. While, reduction is a reaction where the metal is gaining of electron or being used to convert water or oxygen to hydroxide.

The major of corrosion obviously happen at the alkaline battery where the leakage is happening. Alkaline batteries are classification in type of primary batteries dependent upon the reaction between Zn and manganese dioxide. The term of alkaline battery refers by usage of alkaline electrolyte, commonly usage potassium hydroxide (KOH) (Deyab, 2015). In general, battery system consists of three part include anode, cathode and the electrolyte. As we know the name, the term of Zn is familiar in manufactured of alkaline battery.

Zn is chosen as an anode in alkaline battery because of its properties that excellent combination of physical and electrochemical properties. In addition, Zn also have a high specific energy and power density (Szczesniak et al., 1998), rechargeable, zero emission, recyclable and sustainable (Nakata et al., 2016). Other than that, Zn in alkaline solution as it is functioning of current density, temperature, solution composition and porosity of the electrode.

This properties of the Zn that make it valuable corrosion resistance is its ability to form a protective layer that consist of zinc oxide (ZnO) and hydroxide (OH[¬]) or various basic salts, depending on the nature of the environment. The function of the protective layers is to cover the surface of the metal, the corrosion proceeds at a greatly reduced rate (Goodwin, 2010).

However, in the alkaline battery electrolyte is important as it is functioning as a catalyst that conducts or promote the movement of ions from cathode to anode during charge or in reverse on discharge. There are several types of electrolyte that can be used such as sodium hydroxide (NaOH), sodium chloride (NaCl) and potassium hydroxide (KOH). Basically, alkaline battery used the KOH as an electrolyte in battery system because it can act as a strong base that can conduct the movement of ions from cathode to anode. Thus, able the electrochemical reaction in the battery system to occur.

The different concentration of KOH determines the limitations of the free charge carrier when the concentration increased. The free ions would tend to come closer to each other's. On the other hand, KOH solution with a concentration of 30 wt.-% shows the highest ionic conductivity, a good solubility of ZnO and relatively low viscosity, which is beneficial for high power density flow battery applications (Bockelmann et al., 2016, Mainar et al., 2016)

In addition, the battery can give some effect where it can undergo the leakage. The battery leaks because of the discharge of batteries (chemistry of the battery changes and some hydrogen gas is generated). This out-gassing process increases pressure in the battery. Eventually, the excess pressure either ruptures the insulating seals at the end of the battery, or the outer metal canister. The disadvantages of corrosion to the materials will make the materials facing serious problem which tend to damage internal and external of the material such as cracking (Safizadeh et al., 2014).

KELANTAN

1.2 Problem Statement

Corrosion of metal is happened when the metal reacts to the environment such as the presence of O_2 , reaction toward acidity and alkaline level of environment and the moisture content of surrounding. In the alkaline battery, the problem with Zn frequently facing corrosion because of the electrolyte. For this reason, the behaviour of the Zn is depending on the concentration of KOH is being used. Inherently, at low concentration of KOH, few charge carriers existed so that ionic conductivity correspondingly kept low in value so that the corrosion towards the Zn is least. (Srivastava et al., 2000). The addition of higher concentrations of KOH increased the ionic conductivity due to an increase in the number of OH^- ions available in the electrolyte (Jamaludin et al., 2010).

In the previous study, there are many researchers that study on the concentration of 2, 4 and 6 M of KOH with Zn (Szczesniak et al., 1998, Nazeri et al., 2014, Puapattanakul et al., 2013) to reveal their characterization and conductivity. But, no researcher that doing towards concentration of KOH in 2, 4, 6 and 8 M with Zn by revealing their volume hydrogen evaluation gas, corrosion rate and characterization of Zn plate.

MALAYSIA KELANTAN

1.3 Objectives

The aims of this research are:

- i) To evaluate the volume of hydrogen evolution gas of Zn with different concentration of KOH electrolyte.
- ii) To determine the rate of corrosion of Zn with different concentration of KOH electrolyte.
- iii) To observe the morphology and structural of Zn with different concentration of KOH electrolyte.

1.4 Scope of Study

The main scope of this work was to study the corrosion behaviour of the Zn plate towards KOH electrolyte. In order to achieve the objective, this work is divided into three major parts. The initial part was to evaluate the volume of hydrogen evolution gas. The hydrogen evolution gas is the by product from the reaction of Zn and KOH electrolyte. With the evaluation of volume hydrogen evolution gas, it will reveal the corrosion behaviour and characterization of the Zn for the second part.

The further study of variances KOH to the Zn, the morphology and structural analyse had been carried out. The morphology of Zn that immersed into different concentration of KOH was evaluated. While, the structural was done after the morphology. This testing needed to analyse the structural of the Zn. Where, XRD was used to examine the structural of the Zn. Meanwhile, SEM was used for analytical the morphological structure of Zn.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter revealed the properties and characterization of Zn that consider taking as an anode. While, the chemical reaction of Zn towards concentration of KOH. The reactions that occur will give some effect to the Zn structure and its morphology.

2.2 **Properties of Zinc**

Uses of zinc (Zn) as the main material is depending on few factor such as its properties, uses and its function. For example, usage of Zn as alloy and die casting are important to the industries. Furthermore, zinc oxide (ZnO) is widely used in the manufactured of many products such as battery, paint, inks and electronic devices. This is due to its properties of high discharge efficiency and high safety features associated with its manufacturing process and use.

2.2.1 Electrochemistry of Zinc

There are various applications in that using Zn as the main metal such as in the construction, roof, coating for the protection of steel from corrode and being the materials that used in sacrificial anode. Besides, Zn is one of the most metals in electroplating and it is favourable anode in primary batteries due to its properties high discharge efficiency and high safety features associated with its manufacturing process and use (El-Sayed, Mohran, & Abd El-Lateef, 2012). While, regarding another researcher Zn metal is a favourable anode in primary batteries because of its high capacity (0.82 Ah/g) (Ein-Eli et al., 2003).

Accordingly, to the standard electromotive force (EMF) series that showed in Figure 2. Zn has the value of -0.763 which is more anodic (easy to be oxide/release electron). The function of EMF series is to know the corrosion tendencies of metals.



Figure 2.1 EMF Series

Furthermore, Zn is a material that can be an electrode that has a large surface area, fairly dense, volume consumption is about three times lower than for magnesium and dimension of the Zn anode are correspondingly smaller. The corrosion undermines the coating is prevented and the coating remains firmLy attached to give its maximum life. Moreover, the property which gives Zn this valuable corrosion resistance is its ability to form a protective layer consisting of ZnO and OH⁻, or of various basic salts, depending on the nature of the environment (Goodwin, 2010).

2.2.2 Application of Zinc

Due to high specific energy, high specific power, low cost and room temperature mechanical properties, Zn can be made into various alloys with many other metals (Xie et al., 2015). Mainly, in the form of galvanization, Zn-based alloys and ZnO, it has applications in the automobile, construction and shipbuilding industries and batteries.

Currently, its consumption among non-ferrous metals is second only to aluminium and copper. Therefore, practically corrosion problems of Zn and Zn-alloys, a high overvoltage for the O_2 reduction may be beneficial but the H_2O_2 generated May cause pitting or attack of the inorganic/organic protection coatings (Pilbáth et al., 2008).

i) Galvanization

As in moist air, a protective layer is easily produced on the surface of Zn, which prevents further atmospheric corrosion. Zn is widely used in the galvanization industry. Galvanization is primarily used in steel and surface coatings on steel structures (example. galvanized sheet) for automobiles, construction and shipbuilding.

ii) Zinc Alloy

Zn casting alloys account for about 20% of annual zinc usage. These alloys are commonly alloyed with 4% aluminium to improve cast ability and strength. Smaller quantities of Zn alloys containing 8, 12, or 27% aluminium, termed ZA alloys, are also utilized. Die castings can be made readily on account of the low melting points and the good flow properties of Zn alloys. Continuous casting is also used, mainly for production of hollow cylinders for bearing materials but also as stock for machining of Zn shapes (F.E.Goodwin, 2010).

Currently, 20% of zinc applications are made up from Zn alloy. However, in western countries, they have realized that Zn alloy can be directly used as the covering material for roofs, extending the service life from 5-10 years to 120-140 years. In fact, Zn can be recycled. Thus, in the long times run, when it comes to Zn consumption, the ratio of galvanization will decrease while Zn alloy will gradually increase.

iii) Battery

A battery is a device that contains active materials that convert chemical energy to electrical energy by means of an electrochemical oxidation-reduction (redox) reaction. Usually, battery is divided into three part where anode, cathode and electrolyte.

Zn is the main material that mostly used for anode in battery system. Such as alkaline, Zn-air battery which in metal-air battery, Zn-Ni battery and Zn-Br battery. In the Zn-air electrochemical power source possesses the highest energy density compared to other Zn anode batteries, which prominently due to its free an unlimited oxygen supply from the ambient air (Othman et al., 2002). While, the alkaline battery has a superior performance at the higher current drains and low temperatures and its better shelf life.



2.3 Corrosion of zinc plate in others solution or electrolyte

Corrosion is happening to the Zn due to the reaction of Zn toward the environment. Different electrolyte will cause different form of corrosion to the zinc. Below the explanation to the Zn in NaOH, NaCl and KOH. Where the product of corrosion can be Zn hydroxide chloride, Zn hydroxide carbonate, Zn oxide, and Zn hydroxide as well-known as zincate.

2.3.1 Sodium Chloride

The corrosion layer that forms on the surface of Zn when it is exposed to NaCl media was characterized where the composition of ZnO, zinc hydroxide, $Zn(OH)_2$ and Zn hydroxide chloride, $Zn_5(OH)_8(Cl)_2$. $2H_2O$ (Mouanga et al., 2007, (Mouanga et al., 2010). While, Zn hydroxide carbonate was presence $(Zn_5(OH)_6(CO_3)_2$. $2H_2O$) during the exposure of Zn in NaCl solution. However, the $(Zn_5(OH)_6(CO_3)_2$. $2H_2O$) layer can be considered as porous layer, according to the passive region is not observed during anodic polarization experiments conducted in an aerated NaCl solution (Lin et al., 2012).

The chemistry reaction that happen in Zn when it immersed in NaCl:

The cathodic reaction corresponds to the reduction of O_2

$$0_2 + 2H_20 + 4\bar{e} \to 40H^-$$
 (2.1)

The anodic reaction involves the dissolution of Zn

$$\operatorname{Zn} \to \operatorname{Zn}^{2+} + 2\bar{\mathrm{e}}$$
 (2.2)

It can be expected that the Zn^{2+} and the OH^{-} react to produce Zn hydroxide

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

The pH may be high enough at very active cathodic sites for zincate ions, $Zn(OH)_4^{2-}$ to form according to equation 2.4.

$$\operatorname{Zn}(\operatorname{OH})_2 + 2\operatorname{OH}^- \to \operatorname{Zn}(\operatorname{OH})_4^{2-}$$
(2.4)

In the presence of NaCl, chloride ions (Cl⁻) migrate to anodic sites where Zn hydroxide chloride, $Zn_5(OH)_8Cl_2$ is formed according to (2.5)

$$5Zn(OH)_{2}+2Cl^{-}+H_{2}O \rightarrow Zn_{5}(OH)_{8}Cl_{2}H_{2}O+2OH^{-}$$
(2.5)

(Boshkov et al., 2002) reported that Eq. (2.1) leads to a local increase in pH value in the depth of the corrosion damages and has, as result, the formation of $Zn_5(OH)_8Cl_2$ in the pits and their neighbourhood areas.

Zn hydroxide carbonate, $Zn_5(OH)_6(CO_3)_2$ was also detected on Zn surface after immersion in NaCl solution. Its formation depends on the absorption of atmospheric CO_2 into the surface electrolyte and the formation of bicarbonate and carbonate according to (2.6) and (2.7)

$$CO_2 + 2OH^- \to CO_3^{2-} + H_2O$$
 (2.6)

$$CO_3^{2-} + H_2O \to HCO_3^{-} + OH^{-}$$
 (2.7)

Sodium ions (Na⁺) at cathodic areas also react with carbonate ions to form sodium carbonate. Some of carbon detected on Zn surface is due to the presence of sodium carbonate on the sample surfaces.

The formation of $Zn_5(OH)_6(CO_3)_2$ is given by the reaction of $Zn(OH)_2$ and HCO_3^- according to (2.8)

$$55Zn(OH)_2 + 2HCO_3^- + 2H^+ \rightarrow Zn_5(OH)_6(CO_3)_2 + 4H_2O$$
 (2.8)

Considering the characterization of the corrosion layer formed on the top of Zn that reported by some authors in the literature, in the atmospheric conditions, $Zn_5(OH)_8Cl_2$ and $Zn_5(OH)_6(CO_3)_2$ are the main corrosion products of Zn.

2.3.2 Sodium Hydroxide

A passivation layer forms on the top of Zn surface during the immersion in concentrated NaOH electrolyte. This phenomenon well known, in the electrolyte of NaOH, where the dissolution of Zn produces the Zn hydroxide $Zn(OH)_2$ which is not soluble in water at high pH value near to 14 (Mouanga et al., 2010).

The Chemical reactions:

ZnO and Zn(OH)₂ were detected on Zn surface after immersion in NaOH solution. It can be expected that the zincate can produce ZnO or Zn(OH)₂. The overall reaction is given by (2.9) and (2.10).

$$Zn(OH)_{4}^{2} \leftrightarrow ZnO + H_{2}O + 2(OH)^{-}$$
 (2.9)

$$Zn(OH)_2 \rightarrow ZnO + H_2O \tag{2.10}$$

Zn hydroxide carbonate was also detected on Zn surface after immersion in NaOH solution. This corrosion product is formed as proposed in Eq. (2.6)–(2.8).

The main corrosion products formed on the Zn surface after immersion in NaOH solution are ZnO, $Zn(OH)_2$ and $zZn_5(OH)_6(CO_3)_2$. Corrosion products formed on the Zn surface in this work correspond well to those reported in the literature (Mouanga et al., 2007).



2.3.3 Potassium Hydroxide

Strong base is a substance that increasing the concentration of OH⁻ where hydrolyses completely can accept proton and donate a pair of electrons. Strong base usually used as electrolyte. Electrolyte is a substance that containing a free ion which are carrying electric current in the electrolyte.

KOH is chosen as an electrolyte because of it character as a strong base that allow the current to flow, do not gas off and remain in the cell. Besides, it contained loosely bound semi-solid jelly granules and limited amount of free KOH electrolyte available to the Zn electrode due to the high water retentivity of the gel (Othman, 2002).

However, (Iwakura et al, 2002) reported that the highest conductivity in polymer gel-KOH mixtures are achieved at 6 M KOH concentration and give maximum impact on corrosion behaviour. Besides, the failure of anode is due to capacity of ionization (OH) ions. Based on the previous study the failure of the anode is due to the oxidation of Zn which formed ZnO layer (Mohamad, 2006).

Researcher reported that 6 M of KOH is the maximum concentration due to the very high ionic conductivity and high mobility of OH^- anion in water solutions. KOH is mostly used because apparently K^+ is the highest ionic conductivity after H_3O^+ among the cations and OH^- has the highest ionic conductivity among the anions.



Thus, KOH proposed in literature that chloride ions may react with zincate to form Zn hydroxyl chloride complex that has a higher solubility that zincate, thus it make hinder formation of ZnO and increase utilization (Ippolito et al., 2016).

The electrochemistry reaction:

i) Zinc Plate in Potassium Hydroxide Electrolyte

The Zn plate anode chemistry discharge in an alkaline electrolyte is represented by equation (2.11):

$$\operatorname{Zn} + \frac{1}{2}O_2 + H_2O + 2(OH)^- \to \operatorname{Zn}(OH)_4^2$$
 (2.11)

The reaction of Zn in Zn-air batteries during discharge are simultaneous and the use of an O_2 -reducing catalyst in an air-cathode results in the reduction of the O_2 adsorbed from the surrounding air (Iyuke et al., 2003; Genies et al., 2003) The reactions are presented in equation (2.12):

$$0_2 + 2H_20 + 4e \leftrightarrow 40H^- \tag{2.12}$$

The reaction of the preliminary discharge at the Zn electrode can be expressed by equation (2.13) (Othman, 2002) :

$$\operatorname{Zn} + 40\mathrm{H}^{-} \leftrightarrow \operatorname{Zn}(0\mathrm{H})_{4}^{2^{-}} + 2\mathrm{e}$$
(2.13)

This reaction proceeds until the zincate $[Zn(OH)_4^2]$ ion reaches saturation point because the super saturation rate is time dependent. This effect is caused by the solubility of the anion in the electrolyte. Thus, the stable solubility stage is exceeded upon complete discharged, which results in the formation ZnO precipitate (Alias et al., 2010; El-lateef et al., 2015). This reaction can be presented as equation (2.14):

$$\operatorname{Zn}(\operatorname{OH})_{4}^{2^{*}} \leftrightarrow \operatorname{ZnO} + \operatorname{H}_{2}\operatorname{O} + 2(\operatorname{OH})^{-}$$

$$(2.14)$$

The overall battery reaction may be simplified as equation (2.15) (Kar et al., 2014) :

$$Zn + \frac{1}{2}O_2 \leftrightarrow ZnO \tag{2.15}$$

The tendency of Zn to corrode during battery storage remains difficult problem that should be addressed. Hence, researches have investigated the electrochemical reaction involved in alkaline solution. The predominant oxidized products of the aforementioned reactions are generally believed to be $Zn(OH)_4^2$. Nevertheless, most researchers believe that the passive film contain ZnO.

ii) Reaction in the Electrolyte

Where the reaction at the electrolyte is given as following:

$$Zn + KOH \rightarrow ZnO + \frac{1}{2}H_2 + K^+$$
(2.16)

When the Zn is immersed into the electrolyte, the reaction of this strong base electrolyte to the Zn is reacted. The KOH break their bond where the O_2 is deposited at the surface of the Zn. Which the form of ZnO is the passive film that function as to protect the Zn itself from corrode. The K⁺ remain in the solution. Its due to its properties that high in ionic conductivity. The production of H₂ in the electrolyte will release to the air.



2.4 Characterization of Zinc in Potassium Hydroxide

Characterization of Zn in KOH were used to look out or observed the changes in microstructure or behaviour of Zn itself. Characterization that had been used were volumetric measurement where to observe the reaction of alkaline solution toward Zn, corrosion rate where to identify the changes or differential of Zn before and after experiment, morphology observation which was used to observe the microstructure of Zn and structural analysis where to find if there were any impurities exist in the Zn after immersion in KOH solution.

2.4.1 Volumetric Measurement

The expected result that can be achieved through this research is the corrosion behaviour of Zn in different concentration of KOH electrolyte. The volume of H_2 evolution gas is increasing with different concentration of KOH until it is achieved the optimum concentration 6 M of KOH and the graph will constant at 8 M of KOH. It is because 6 M of KOH give maximum impact on corrosion behaviour. This is stated in the previous study, (Lal et al., 2012, Vercher et al., 2015, Soc, 1969). The hydrogen is constructed by using the method of volumetric measurement.



2.4.2 Corrosion Rate

The corrosion of metals can be occurred in salt solution, fresh water and alkaline or basic solution. Corrosion can be happened when only dissolved in present of O_2 . Water solution rapidly dissolve O_2 from the air or the chemical composition itself and this is the source of the oxygen required in the corrosion process.

In this research, the reaction that occur when Zn is exposed to the water resulting ZnO is the whitish deposit on the surface. This is due to the water ionized into H^+ and OH^- . It is further known that a H^+ has a valence 1 and it required three H^+ with the corresponding three positive charges to combine with the three OH^- ions held by the Zn.

$$2Zn + O_2 + 2H_2O \rightarrow Zn(OH)_2$$
 (2.17)

$$Zn(OH)_2 \leftrightarrow ZnO + H_2O \tag{2.18}$$

In need to be noted that, there is no oxidation or reduction (electron transfer) during the reaction of Zn and water as in Eq. 2.18. In this case, the valences of the elements on the left of each reaction remain what it is on the right. The valence electron for Zn unchanged throughout the course of these reactions, and it is consequently not possible to divide these reactions into individual oxidation and reduction process.

On top of that, the corrosion that be analyse in this research by looking at their corrosion rate that occur to the Zn plate is increasing as the concentration of KOH is increase. This is influence of the amount of OH⁻that hydrolyses completely.



2.4.3 Morphology Observation

Scanning electron microscopy (SEM) has the unique ability to analyse sample surface by using electron. Electron have wavelength that is shorter from light with this speciality of wavelength it is enable to produce higher resolution higher. Higher resolution allows higher magnification without losing important data. The image is achieved from the detection of "secondary" electrons that are released from the sample as a result of it being scanned by very high energy "primary" electrons (Staff, n.d.).

SEM was designed for continuing analyse towards solid surface and the depth focus of SEM can reach more than optical microscope (OM) that only allow image production from two-dimensional angle. Furthermore, SEM has depth of field that is larger where it allows a larger sample focus at one time. The preparation sample of SEM easier than OM where the sample need to be in dried and conductive. All of this reasons makes SEM as one of machines that be used in this research.

SEM has been used long time ago until now. This is because of wide-array of applications in detailing by three-dimensional and topographical. There are limitations while using the SEM such as the machines has to be kept in high vacuum which indirectly give a cost and electrons are high energy particle which will easily be affected by any matter they encounter. Thus, the interaction results in emission of all the lower forms of energy.

KELANTAN

The results for micrograph of Zn plate with different concentration of KOH will be slightly same as the previous study showed in the Figure 2.3. It shows the micrographs of the Zn powder that was added with the various concentration of KOH after having been kept for seven days to dry (Masri et al., 2009).



Figure 2.3 Cross-section micrographs of Zn particles with (a) pure agar (b) 0.2 M (c) 0.4 M and (d) 0.6 M KOH (Masri et al., 2009).



2.4.4 Structural Analysis

X-Ray Diffraction (XRD) been used in this characterization because of to decide raw material purity, impurities, and phase that obtain when the Zn soaked in KOH electrolyte. The started point at $2\theta = 20^{\circ}$ to 90° . The analysis of XRD was useful in analysis phase where each of metal and sample had their own pattern, but usually it is called as fingerprint. This technique will identify the crystallization phase, amorphous phase and mostly used as informant to know element presence in sample.

The results for structure of Zn plate with different concentration of KOH will be slightly same as the previous study showed in the Figure 2.2. It shows the structural pattern of dried Zn anode's electrode. (Masri et al., 2009).



Figure 2.2 Comparison of the XRD peaks of (a) pure agar (b) Zn powder and Zn with (c) pure agar (d) 0.2 M (e) 0.4 M and (f) 0.6 M KOH (Masri et al., 2009).

CHAPTER 3

MATERIALS AND METHOD

3.1 Introduction

In this research, the materials will be used are Zn plate (99.9% purity, Merck), potassium hydroxide (Merck), commercial Zn plate and diesel oil. Water that will be used is distilled water.

3.2 Preparation of Raw Materials

This section had been explained briefly about the preparation of the sample from the raw material that needed to start the experiment until sample of end of the experiment. Process and flow chart were used to discussed it briefly.

3.2.1 Pure Zn

The sample of Zn is taken from the other place. Before proceeding to the next step, the bulk of the Zn was cut into dimensions 2 cm. After that the sample had been experienced grinding process. The purpose of the grinding process is to remove the passive film that coated at the surface of the Zn.

The grinding process of the Zn sample was run with various grade of grit paper (180-1200 grit). As the process of grind is complete the next step was polished the surface of the material by using diamond paste until the surface is mirror finishing. The step of polished was did in order to examine the surface morphology of Zn.



3.2.2 Commercial Zinc

Commercial Zn was placed inside of the battery where the function of commercial Zn is mostly used as an anode's electrode. Thus, battery was cut at the outermost layer which of it is function as protection layer to the commercial Zn from being rust as being showed in Figure 3.1.

After the protection layer being removed, the layer of commercial Zn was cut into dimensions 2 cm carefully to avoid from disturbing the other parts of battery. The next step is similar to section (3.2.1).



Figure 3.1 Cross section of battery



3.2.3 Preparation of Potassium Hydroxide Electrolyte

The preparation of KOH had been obtained by the molarity measurement using equation below. Then, the KOH pellet was weighted and dissolved in the distilled water.

$$MV = \frac{\text{grams}}{\text{molar mass}} \tag{3.1}$$

where:

M = Mole, (mol/L)

V = Volume, (L)

To prepare 2, 4, 6 and 8 M of KOH in 0.3 L of water, need to use the equation above:

The molecular mass:

K = 39 g/mol

O = 16 g/mol

H = 1 g/mol

Molar mass KOH = 39 + 16 + 1 = 59 g/mol

Table 3.1 was showed the solution that been used in this experiment. The calculation is appeal on the Appendix 1.

Concentration (M)	Volume (L)	Molar Mass (g/mol)	Grams (g)
2	0.03	59	3.36
4	0.03	59	6.72
6	0.03	59	10.08
8	0.03	59	13.44

Table 3.1 Preparation for KOH solution

To dilute the solution, distilled water were used the tap water is containing the impurities (minerals, suspended solids and contaminants). The impurities will precipitate out of the water when subjected to electrolysis. Precaution need to be taken during the mixture of solution. It need to be done in fume chamber due to KOH that release sharp gas that can harm when inhale. The steps can be summarized as Figure

3.2.



Figure 3.2 Summarization of preparation KOH solution

UNIVERSITI MALAYSIA

3.3 Characterization of Zinc in Potassium Hydroxide

3.3.1 Volumetric Measurement

Measurement was carried out by immersion of Zn (pure and commercial) in the different concentration of KOH (2, 4, 6 and 8 M) and connected a tube to the burette inside of the beaker that contain tap water as showed in Figure 3.3. While, the container is contained of Zn plate that immersed in the KOH concentration. Top of the KOH solution is oil. The function of the oil is to collect or prevent the bubbles produce from moving randomLy. So, the bubbles were directly flow to the rubber tube. This procedure was taken for calculate and compare between the volume of hydrogen gas that released by the Zn to concentration of KOH.



Figure 3.3 Illustration of Volumetric Measurement: (a) experiment setup and

(b) enlargement of burette scale



Figure 3.4 Actual experiment setup for volumetric measurement that run for (a) single and (b) multiple evaluation.

3.3.2 Corrosion Rate

Measurement corrosion rate was done after the Zn is immersed in different concentration of KOH for certain time. It involves two methods. There are weight loss and corrosion rate

Weight
$$Loss = weight$$
 of Zn before – weight of Zn after (3.2)

The formula chosen is the simplest and longest-established by estimating corrosion losses in metal and the equipment by using weight loss analysis. A weight sample of the metal under consideration was introduced into the process and later removed after a reasonable time interval. The metal was cleaned from the solution or residue by using distilled water and is reweighed. The weight loss is converted to a corrosion rate (CR) as follows (Polarization & Resistance, n.d.):

$$CR == \frac{W x k}{D x A x T}$$
(3.3)

where;

$$W = Weight Loss, (g)$$

- k = Constant variable/K-factor
- D = Metal Density, (gcm^{-3})
- A = Area of metal, (A)
- T = Time, (hr)

The density of Zn and value of k is constant.

D =
$$7.14 \text{ gcm}^{-3}$$

 $k = 3.45 \times 10^6$

3.3.3 Morphology

Scanning electron microscopy (SEM) was utilized to observe the surface and cross-sectional of the Zn. The results gave corrosion behaviour of Zn-active materials occurs during the preparation or before application in the volumetric measurement.

SEM characterization of both types of Zn products after immersed in KOH was carried out by using a Hitachi Table top TM3030Plus scanning electron microscope and the distance of operator and machine is $6200 \ \mu\text{m}$. In this research, 1x, 2x, 5x, 10x and 20x of magnification had been used in order to take the micrograph of sample. Constant value of accelerating voltage, emission current and filament current with 15000 Volt, 36900 nA and 1850 mA respectively.

3.3.4 Structural

X-ray diffraction (XRD) was used to observed the composition of the Zn plate. The crystalline phase was identified using the International Centre of Diffraction Data (ICDD) powder diffraction database. Besides, XRD can identified the changes of structure Zn plate. In this experiment, the machines that being used is Bruker. The using of 2θ at the value 10° to 90°.





3.4 Research Flow Chart for overall experiment

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

This chapter will be discussed the result that obtained from the experiment will indirectly reveal the Zn behavior, characteristics and properties. This include the effect of the concentration of KOH that imposed to the surface of KOH. The characterization in this chapter is key factor that involving volumetric measurement, corrosion rate, and structural characterization. While, the morphology characterization obtained in order to support towards key results.

4.2 Characterization of Zinc in Potassium Hydroxide

In this experiment, the characterization of Zn in KOH will assessed by its properties and behaviour on the changing trend of volumetric measurement, corrosion rate, structural and morphology. The Zn that been used are existing commercial and pure with the concentration of KOH of 2, 4, 6 and 8 M.



4.2.1 Volumetric Measurement

A typical set of data is shown in Figure 4.1 and 4.2. The slope of these lines served as a measure of the hydrogen evolution that effect from Zn that immersed in different concentration of KOH. This rate was measured in 2, 4, 6 and 8 M KOH. Both Zn types commercial and pure were used and every run was made at room temperature.

Figure 4.1 shows that the data of commercial Zn (ZC) that immersed in different concentration of KOH. In 2 M of KOH showed that gradually decline for 170 hours. 0.1 mL of water was decreased every eight hours. It is happening because the low of KOH concentration used. This will slow the movement of ion to attack the surface of Zn and unproductive air bubble is produced.

The pattern lines for 4 M of KOH showed that lines are drawn through most of the data points. However, surprisingly at 110 hours there is small difference that there is indicates a lower volume of water at the increasing of time. Every four hours the volume of water decreasing by 0.1 mL.

Compared to 6 M that slightly decrease in pattern until at the 17 hours, but, then steeply dropped up to 45 hours and steadily until 170 hours. The water constantly decreases by 1.0 mL every hour. While at 8 M of KOH, showed data that decrease steadily for 82 hours and volume of water remain constant from 82 hours until 170 hours. The water keep diminished by 0.6 mL for every hour.





Figure 4.1 Rate of hydrogen gas for commercial Zn that immersed in different concentration of KOH

Figure 4.2 showed that the data of pure Zn that immersed in KOH. In 2 M of KOH solution is slightly declined up to 16 hours and dropped dramatically to hour of 17. The declination of water continued till 30 hours and then remain constant. The water consistently reduced by 1.4 mL for every hour.

For 4 M of KOH that the volume of water seems to have little effect, but, surprisingly the plummeted happens at hour of 47 and in 53 hours the lines is shot up till constantly decreased. For every hour the water reliably lessens by 0.1 mL for every hour.

Meanwhile, 6 M of KOH shows the pattern was slightly decline and steeply down between 16 to 20 hours. 20 hours to 170 hours the volume water remain constant. The volume of water dependably dropped by 2.3 mL for every hour. Lastly, 8 M of KOH shows the pattern of line is gently decline from the beginning to the end. Volume of water dropped by 0.1 mL for every hour.



Figure 4.2 Rate of hydrogen gas for pure Zn that immersed in different concentration of KOH

In short, Figure 4.3 shows that the combination all the pattern of figures above. The volume of water for each concentration of KOH are decrease and 6 M of pure Zn is the highest reaction that loos the volume of water while 2 M of commercial Zn is the lowest reaction to loss the volume of water.



Figure 4.3 Summary of rate of hydrogen evolution from Zn in KOH

Figures above shows the trend lines for commercial Zn (Fig. 4.1) and pure Zn (Fig. 4.2) that immersed in different concentration of KOH. This figures explained that the significant of the time was influenced the KOH reacted to the Zn surface thereby caused hydrogen evolution happen. The existing of hydrogen evolution is causing by the corrode on the reactions of KOH and Zn. Where, the reactions of

$$Zn + 2H_2 0 \rightarrow ZnO + H_2$$
(4.1)

take place. The Zn is reacted to the KOH and caused the white patch on the surface after the observation at the end of experiment. Figure 4.4 shows the illustration of reactions happen in the media.



Figure 4.4 Illustration of Zn plate immersed in KOH solution

MALAYSIA KFI ANTAN

4.2.2 Corrosion Rate

Figure 4.5 shows the trend line of corrosion rate for both types of Zn. For commercial Zn it showed the increasing of line when the concentration of KOH at range 2 to 4 M, then the concentration rate rise dramatically until the rate reach the peak level which when then concentration of KOH is 6 M. At peak of 6 M, the corrosion rate started decrease at concentration of 8 M.

While for pure Zn trend line was showed the fluctuation in the corrosion rate over the concentration of KOH. The corrosion rate is decrease when the concentration of KOH is 2 to 4 M with 5.68 mpy and 2.84 mpy respectively. Then, the lines are increasing at the peak of 6 M with 9.95 mpy respectively. When the concentration of KOH is more than 6 M, the corrosion rate starts to decrease again with 8.53 mpy respectively.

On top of that, as compared to the trend line for both types of Zn in 6 M of KOH was recorded the highest corrosion rate with 9.95 mpy compared to other commercial Zn in 2, 4 and 8 M with 2.84 mpy, 4.26 mpy and 5.68 mpy and pure Zn in 2, 4 and 8 M with 5.68 mpy, 2.84 mpy and 8.53 mpy respectively. This case is agreed with higher mole of KOH exhibits higher corrosion rate. This is because 6 M is the optimum concentration for KOH and give maximum impact on corrosion behaviour (Iwakura et al, 2002).

KELANTAN

However, 2 M of commercial Zn and 4 M of pure Zn do not exhibit this severe corrosion condition possibly due to insufficient of oxygen. On withdrawal of Zn immersed in concentration of KOH were noticed that white patch (oxide) is formed. This proves that the corrosion process depends largely on O_2 content, besides the pH level of KOH. This case also agrees with (Uzorh, 2013) that stated corrosion of Zn depends on the amount of O_2 dissolved in the media. The disadvantage of lots consumption oxygen from the atmosphere it will cause physical damage such as cracking in the cathode after discharge (Lee et al., 2011).



Figure 4.5 Corrosion rate against concentration in both types of Zn



No other reported work was found for the corrosion rate of commercial Zn and pure in KOH solutions except for a few data reported by (Jamaludin et al., 2010). They found, as we have, that the corrosion rate decrease with increasing concentration of KOH. Result such as those shown on Figure 4.5 are the basic data against which factors or conditions can be compared.

A possible mechanism involves the following process:

$$2\mathrm{H}_{2}\mathrm{O} + 2\mathrm{e} \to \mathrm{H}_{2} + 2\mathrm{O}\mathrm{H}^{-} \tag{4.2}$$

$$Zn + 20H^{-} \rightarrow Zn(0H)_{2} + 2e$$
(4.3)

$$Zn + 2 OH^{-} \rightarrow ZnO + H_2O + 2e$$
(4.4)

Reactions (4.2) and (4.3) may each involve several steps as in the anodic treatment of Zn.

Combining (4.2) and (4.3), the overall reaction is

$$Zn + 2H_2O \rightarrow H_2 + Zn(OH)_2$$

$$(4.5)$$

Combining (4.2) and (4.4) gives

$$Zn + 2H_2 0 \rightarrow ZnO + H_2$$
(4.6)

These reactions do agree with the effect of KOH concentration on the rate of corrosion. As KOH concentration increases, the activity of the water decrease, resulting in a higher rate for reaction (Soc, 1969).



4.2.3 Morphology

In addition to the morphology result before and after immersion of Zn, corrosion effects during Zn dissolution had been a major challenge. Two types of zinc been used commercial Zn and pure Zn. The SEM investigation was carried out on the surface of Zn. In the interior of sample look alike plain surface that does not have any contaminants on the surface for both sample Zn. Examples are shown in Figure 4.6 and 4.7.



Figure 4.6 Cross sections of micrograph commercial Zn before experiment with (a) 1x magnification (b) 2x magnification



Figure 4.7 Cross sections of micrograph pure Zn before experiment with

(a) 2x magnification (b) 5x magnification

Apart from that, Figure 4.8 showed 'sea-like' oxide film, consisting of coral shape crystals, was found on the Zn grains with diameters on the order of 10 μ m and 3 μ m for magnification 10X and 20X respectively. Figure 4.9 showed of 'seaweed-like' found in pure Zn sample. The appearance of oxide in both types of Zn existed with white patch and the black area is Zn.



Figure 4.8 Cross sections of micrograph commercial Zn after experiment with
(a) 10x magnification (b) 20x magnification



Figure 4.9 Cross sections of micrograph pure Zn after experiment with (a) 5x magnification (b) 10x magnification



4.2.4 Structural

Figure 4.10 showed that the pattern of both types of Zn before the experiment start. It can be showed that the peak at commercial Zn more that peak at pure Zn. This is due to the chemical composition more in commercial Zn such as Zn, Magnesium (Mg), Aluminium Oxide (AlO), Chromite (Cr), Iron(II) Oxide (FeO), Magnesium Oxide (MgO), Nickel Oxide (NiO), Zinc Oxide (ZnO) and Titanium Oxide (TiO) compared to the pure Zn that contain 99.9% of Zn.

Consisting of chemical composition more than one type its due to the application of Zn that need to be commercialized in application of battery. Both types of Zn are an inorganic metal but the difference to commercial Zn that contain mineral ion, Cr.



Figure 4.10 Comparison peak analysis for Zn Plate before experiment

Figure 4.11 and 4.12 showed that the combination pattern of Zn plate that soaked in different concentration of KOH electrolyte. In both figures can be discussed that point (a) both of sample does not react to any chemical and at the point (b), (c), (d), and (e) the reaction beginning to happen. To get better sense of the specific issues that need to be addressed by explaining the process by 20.

During, the immersion of Zn plate in strong alkaline electrolytes, metallic Zn, oxidizes to aqueous Zn^{2+} ions, which form a stable complex with OH^- known as zincate, $Zn(OH)_4^{2-}$ at point $2\theta = 20^\circ$ (4.7). Zincate will precipitate as ZnO when the solution is saturated at point $2\theta = 40^\circ$ (4.8), however its solubility increases with pH, which delays passivation.

During discharge, if the zincate concentration exceeds the local solubility limit, ZnO will precipitate on the surface of the Zn as what is typically known as type ZnO. This layer is loose and porous, and does not directly passivate or block the surface of the Zn. There is impact of ion transport between the electrolyte and Zn surface, impeding OH^- and $Zn(OH)_4^{2-}$ transport.

$$\operatorname{Zn} + 40\mathrm{H}^{-} \to \operatorname{Zn}(\mathrm{OH})_{4}^{2^{-}} + 2\mathrm{e} \tag{4.7}$$

$$\operatorname{Zn}(\operatorname{OH})_4^2 \to \operatorname{ZnO} + \operatorname{H}_2\operatorname{O} + 2(\operatorname{OH})^-$$
 (4.8)

At high anodic over potentials, in a zincate-saturated solution (or local environment), there is a solid state transition directly from Zn(s) to ZnO(s), without the dissolution step (4.9).

At $2\theta = 60^{\circ}$, corrosion occurs ZnO forms on the Zn surface, hindering any further dissolution, and any remaining zinc is effectively rendered electrochemically inactive. Therefore, any zinc trapped under the passivation layer will be not be utilized at a useful potential (Davies et al., 2016).

$$Zn + 2 OH^{-} \rightarrow ZnO + H_2O + 2e$$

$$(4.9)$$

Based on this understanding, the ability for zincate ions to diffuse away from the Zn surface will impact the rate of ZnO growth and corrosion occur during Zn dissolution. Therefore, corrosion effects are expected to be felt more rapidly at higher concentration. It follows, then, that high surface area electrodes are gives an exposition towards oxide in the solution. Unfortunately, high surface area zinc electrodes are more susceptible to corrosion through parasitic surface reactions, resulting more oxide on the surface. This happening at $2\theta = 70^{\circ}$:

$$\operatorname{Zn} + \frac{1}{2}\operatorname{O}_2 \to \operatorname{ZnO} \tag{4.10}$$

The reaction kept continued till the $2\theta = 90^{\circ}$. The hydrogen evolution half-reaction (4.11), couples with the Zn oxidation half-reaction (4.10) to give the parasitic hydrogen evolution reaction Eq. 4.12:

$$H_2 0 + \bar{e} \rightarrow 0H^- + \frac{1}{2}H_2$$
 (4.11)

$$Zn + 2H_2O \rightarrow ZnO + H_2 \tag{4.12}$$



Figure 4.11 Comparison peak analysis for XRD of (a) commercial Zn and Zn with (b) 2 M of KOH,

(c) 4 M of KOH, (d) 6 M of KOH and (e) 8 M of KOH



Figure 4.12 Comparison peak analysis for XRD of (a) pure Zn and Zn with (b) 2 M of KOH,

(c) 4 M of KOH, (d) 6 M of KOH and (e) 8 M of KOH

The rust formed on Zn as a consequence of atmospheric exposure comprise of oxides an amorphous or crystalline nature that shown in Table 4.9 and 4.8. In particular, amorphous commercial Zn is highly abundant at 4 M with 41.7% continued with 8, 6 and 2 M with 26.7%, 19.0% and 16.3% respectively. For Table 4.10 high rate to low of amorphous in pure Zn at 2, 8, 6, and 4 M with 41.9%, 29.3%, 28.5%, and 23.6% respectively. ZnO is highly abundant atmospheric corrosion layers and has been widely reported in the literature (Fuente et al., 2016).

However, XRD only provides a good characterisation of crystalline rust. Highest to low crystallinity for commercial Zn are immersion in 2, 6, 8 and 4 M with 83.7%, 81.0%, 73.3% and 58.3% respectively. Meanwhile, crystallinity in order high to low in pure Zn with concentration KOH are 4, 6, 8 and 2 M with 76.4%, 71.5%, 70.5% and 58.1%. For micro-XRD patterns, care must be taken to ensure that the number of diffracting grains is sufficient, and the measurements were performed. Since the results obtained at similar locations were generally within the error associated to the counts provided by the phases present, only the results obtained from representative diffraction patterns are included in Table 4.1 and 4.2.



_			
	Concentration (M)	%-Crystallinity	%-Amorphous
	2	83.7	16.3
	4	58.3	41.7
	6	81.0	19.0
	8	73.3	26.7

Table 4.1 Crystallinity and Amorphous of commercial Zn in concentration KOH

Table 4.2 Crystallinity and Amorphous of pure Zn in concentration KOH

%-Crystallinity	%-Amorphous
58.1	41.9
76.4	23.6
71.5	28.5
70.5	29.5
	%-Crystallinity 58.1 76.4 71.5 70.5



CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

In this experiment, the study of corrosion behaviour of zinc in potassium hydroxide electrolyte was already done. The corrosion was prepared by using technique of corrosion rate by producing hydrogen evolution gas. The electrolyte that been used in this research is KOH with concentration of 2, 4, 6 and 8 M. Therefore, the conclusion was described according to the characterization that had been done. The conclusions were drawn from the characterization of volumetric measurement, corrosion rate, morphology analysis and structural analysis.

i) Volumetric Measurement

Can be conclude that, the volume of hydrogen evolution gas was produced higher when the Zn is soaked in maximum concentration of KOH, 6 M.

ii) Corrosion rate

Higher concentration of KOH led to high corrosion happened to the surface of Zn. The corrosion was lower the reaction till it achieves at optimum concentration of KOH.

KELANTAN

iii) Morphology Observation

From this research, it can be concluding that the surface or microstructure of Zn Plate will have major effect when it soaked in high concentration of KOH.

iv) Structural

Higher concentration of KOH will produce more oxygen that can led the Zn deposited to ZnO.

It can be concluding, from this research that 6 M of KOH is an optimum concentration that can give maximum impact to the surface of Zn.



5.2 RECOMMENDATION

There are few recommendations that can be used after gaining the experience running this research for future research. First, the time that been used for soaking Zn plate in KOH is seven days. I suggest that to take a little bit longer of time to analyze the effect on the surface of Zn and the volume of hydrogen evolution gas will be produced more. Second, when the time is longer, the corrosion can be seen higher from this research due to the corrosion that happening on surface. This is happening because of the reactions of oxide indirectly to the surface of Zn.

Next, in this research the electrolyte that being used was KOH. So, for the future research, the addition of other electrolyte can be used as other parameter. The purpose of this recommendation because from two or more electrolytes that will be tested to the same sample, we can figure out deeply and make the comparison of which one is better for industrial.

Lastly, recommendation for industrial. In this research, one of the sample that able to used is commercial Zn that can be found in battery. It is recommended for do the technique of coating on the surface of Zn due to the behavior of Zn that can be corrode to high concentration of electrolyte. For example, metallic coating. This will provide a layer that changes the surface properties of the work piece to those of the metal being applied and can provide a durable, corrosion resistant layer and core material provides the load-bearing capability. Metal coating that can be used such as Chromium (Cr), Copper (Cu) and Nickel (Ni).



REFERENCES

- Roberge, P. R. (2008). *Corrosion engineering: principles and practice* (pp. 370-375). New York: McGraw-Hill.
- Alias, S. S., Ismail, A. B., & Mohamad, A. A. (2010). Effect of pH on ZnO nanoparticle properties synthesized by sol – gel centrifugation. *Journal of Alloys and Compounds*, 499(2), 231–237.
- Bockelmann, M., Kunz, U., & Turek, T. (2016). SC. *Electrochemistry Communications*.
- Boshkov, N., Petrov, K., Vitkova, S., Nemska, S., & Raichevsky, G. (2002). Composition of the corrosion products of galvanic alloys Zn – Co and their influence on the protective ability, *157*, 171–178.
- Callister, W. D., & Rethwisch, D. G. (2007). *Materials science and engineering: an introduction* (Vol. 7). BOOK, Wiley New York.
- Davies, G., Hsieh, A. G., Hultmark, M., Mueller, M. E., & Steingart, D. A. (2016). Utilization of Hyper-Dendritic Zinc during High Rate Discharge in Alkaline Electrolytes, *163*(7), 1340–1347.
- Deyab, M. A. (2015). Application of nonionic surfactant as a corrosion inhibitor for zinc in alkaline battery solution. *Journal of Power Sources*, 292, 66–71.
- Ein-Eli, Y., Auinat, M., & Starosvetsky, D. (2003). Electrochemical and surface studies of zinc in alkaline solutions containing organic corrosion inhibitors. *Journal of Power Sources*, *114*(2), 330–337.
- El-lateef, H. M. A. B. D., & Mohran, H. S. (2015). Role of nickel alloying on anodic dissolution behavior of zinc in 3 . 5 % NaCl solution . Part II : Potentiodynamic , potentiostatic and galvanostatic studies. *Transactions of Nonferrous Metals Society of China*, 25(9), 3152–3164.
- El-Sayed, A. R., Mohran, H. S., & Abd El-Lateef, H. M. (2012). Corrosion study of zinc, nickel, and zinc-nickel alloys in alkaline solutions by Tafel plot and impedance techniques. *Metallurgical and Materials Transactions A: Physical Metallurgy and Materials Science*, 43(2), 619–632.
- F.E.Goodwin. (2010). Corrosion of Zinc and its Alloys. *International Lead Zinc Research Organization*, 1, 2078–2093. Journal Article.
- Fuente, D. De, Alcántara, J., Chico, B., Díaz, I., Jiménez, J. A., & Morcillo, M. (2016). Characterisation of rust surfaces formed on mild steel exposed to marine atmospheres using XRD and SEM/Micro-Raman techniques. *Evaluation and Program Planning*.

- Genies, L., Bultel, Y., Faure, R., & Durand, R. (2003). Impedance study of the oxygen reduction reaction on platinum nanoparticles in alkaline media, *48*, 3879–3890.
- Ippolito, N. M., Belardi, G., Medici, F., & Piga, L. (2016). Utilization of automotive shredder residues in a thermal process for recovery of manganese and zinc from zinc carbon and alkaline spent batteries. *WASTE MANAGEMENT*.
- Iwakura, C., Nohara, S., Furukawa, N., & Inoue, H. (2002). The possible use of polymer gel electrolytes in nickel/metal hydride battery. *Solid State Ionics*, *148*(3–4), 487–492.
- Iyuke, S. E., Bakar, A., Amir, A., Kadhum, H., Daud, W. R. W., & Rachid, C. (2003). Improved membrane and electrode assemblies for proton exchange membrane fuel cells, *114*, 195–202.
- Jamaludin, A., Ahmad, Z., Ahmad, Z. A., & Mohamad, A. A. (2010). A direct borohydride fuel cell employing a sago gel polymer electrolyte. *International Journal of Hydrogen Energy*, 35(20), 11229–11236.
- Kar, M., Simons, T. J., & Macfarlane, D. R. (2014). Ionic liquid electrolytes as a platform for rechargeable metal air batteries : a perspective. *Physical Chemistry Chemical Physics*, *16*, 18658–18674.
- Lal, B., Sahin, M., & Ayranci, E. (2012). Volumetric studies to examine the interactions of imidazolium based ionic liquids with water by means of density and speed of sound measurements. *Journal of Chemical Thermodynamics*, 54, 142–147.
- Lee, J. S., Kim, S. T., Cao, R., Choi, N. S., Liu, M., Lee, K. T., & Cho, J. (2011). Metal-air batteries with high energy density: Li-air versus Zn-air. Advanced Energy Materials, 1(1), 34–50.
- Lin, Z., Li, X., & Xu, L. (2012). Electrodeposition and Corrosion Behavior of Zinc-Nickel Films Obtained From Acid Solutions : Effects of TEOS as Additive, 7, 12507–12517.
- M.N. Masri, A. A. M. (2009). Effect of adding potassium hydroxide to an agar binder for use as the anode in Zn–air batteries. *Corrosion Science*, *51*, 5. Journal Article.
- Mainar, A. R., Leonet, O., Bengoechea, M., Boyano, I., Meatza, I. De, Kvasha, A., ... Blázquez, J. A. (2016). Alkaline aqueous electrolytes for secondary zinc – air batteries : an overview, (February), 1032–1049.
- Mohamad, A. A. (2006). Zn/gelled 6 M KOH/O2 zinc-air battery. *Journal of Power Sources*, 159(1 SPEC. ISS.), 752–757.

- Mouanga, M., & Berçot, P. (2010). Comparison of corrosion behaviour of zinc in NaCl and in NaOH solutions; Part II: Electrochemical analyses. *Corrosion Science*, *52*(12), 3993–4000.
- Mouanga, M., Berçot, P., & Rauch, J. Y. (2010). Comparison of corrosion behaviour of zinc in NaCl and in NaOH solutions . Part I : Corrosion layer characterization. *Corrosion Science*, *52*(12), 3984–3992.
- Mouanga, M., Ricq, L., Douglade, J., & Berc, P. (2007). Effects of some additives on the corrosion behaviour and preferred orientations of zinc obtained by continuous current deposition, 283–289.
- Nakata, A., Arai, H., Yamane, T., Hirai, T., & Ogumi, Z. (2016). Preserving Zinc Electrode Morphology in Aqueous Alkaline Electrolytes Mixed with Highly Concentrated Organic Solvent Cdl Re Rct Zw, *163*(2), 50–56.
- Nazeri, M. F. M., & Mohamad, A. A. (2014). Corrosion measurement of Sn-Zn leadfree solders in 6 M KOH solution. *Measurement: Journal of the International Measurement Confederation*, 47(1), 820–826.
- Othman, R., Yahaya, A. H., & Arof, A. K. (2002). Zinc-Air Cell with KOH-Treated Agar Layer between Electrode and Electrolyte Containing Hydroponics Gel. *Journal of New Materials for Electrochemical Systems*, 5(3), 177–182.
- Pilbáth, Z., & Sziráki, L. (2008). The electrochemical reduction of oxygen on zinc corrosion films in alkaline solutions. *Electrochimica Acta*, *53*(7), 3218–3230.
- Polarization, L., & Resistance, E. (n.d.). Corrosion Coupons & Weight Loss Analysis.
- Puapattanakul, a., Therdthianwong, S., Therdthianwong, a., & Wongyao, N. (2013). Improvement of Zinc-Air Fuel Cell Performance by Gelled KOH. *Energy Procedia*, 34, 173–180.
- R. OTHMAN, A. H. Y. and A. K. A. (2002a). A zinc–air cell employing a porous zinc electrode fabricated from zinc–graphite-natural biodegradable polymer paste. *Applied Chemistry*, 32, 1347–1353. Journal Article.
- R. OTHMAN, A. H. Y. and A. K. A. (2002b). Zinc-Air Cell with KOH-Treated Agar Layer between Electrode and Electrolyte Containing Hydroponics Gel. *Electrochemical System*, 5, 177–182. Journal Article.
- Safizadeh, F., Ghali, E., & Houlachi, G. (2014). ScienceDirect Electrocatalysis developments for hydrogen evolution reaction in alkaline solutions e A Review. *International Journal of Hydrogen Energy*, 1–19.



Soc, J. E. (1969). The Corrosion of Zinc in ?KOH? Solutions, *116*(2), 162–165.

- Srivastava, N., & Chandra, S. (2000). Studies on a new proton conducting polymer system : poly (ethylene succinate) + NH 4 ClO 4, *36*.
- Staff, E. M. (n.d.). Sample preparation for Scanning electron microscopy (SEM) SEM services include :, 1–2.
- Szczesniak, B., Cyrankowska, M., & Nowacki, A. (1998). Corrosion kinetics of battery zinc alloys in electrolyte solutions). *Science*, 130–138.
- Uzorh, E. A. C. (2013). Corrosion Properties of Plain Carbon Steels, 18–24.
- Xie, X., Yang, Z., Feng, Z., Zhang, Z., & Huang, J. (2015). Electrochemical properties of ZnO added with Zn-Al-hydrotalcites as anode materials for Zinc/Nickel alkaline secondary batteries. *Electrochimica Acta*, 154, 308–314. Journal Article.



APPENDIX

1) CHAPTER 3

Concentration (M)	Volume (L)	Molar Ma <mark>ss (g/mol)</mark>	Grams (g)
2	0.03	<mark>59</mark>	3.36
4	0.03	59	6.72
6	0.03	59	10.08
8	0.03	59	13.44

3.2.3 Preparation of KOH

$$MV = \frac{grams}{molar mass}$$

Example dilution of 2 M KOH:

$$(2)(0.03) = \frac{g}{59}$$

= 2x0.03x59

= **3.36** g

MALAYSIA KELANTAN

2) CHAPTER 4

4.2.1 Volumetric Measurement

		Zinc Con	nmercial			Pure	e Zn	
Time (h)	2 M of	4 M of	6 M of	8 M of	2 <mark>M of</mark>	<mark>4 M</mark> of	6 M of	8 M of
	ZC	ZC	ZC	ZC	ZP	ZP	ZP	ZP
1	48.8	46.0	46.1	46.5	<mark>46.7</mark>	<mark>48</mark> .3	46.9	48.0
3	48.8	46.0	43.1	44.7	<mark>42.5</mark>	<mark>48</mark> .0	40.0	47.7
4	48.8	46.0	42.1	44.1	<mark>41.1</mark>	<mark>47</mark> .9	37.7	47.6
16	48.6	45.7	30.1	36.9	24.3	<mark>46</mark> .7	10.1	46.4
17	48.6	45.7	29.1	36. <mark>3</mark>	22.9	<mark>4</mark> 6.6	7.8	46.3
20	48.6	45.8	26.1	34.5	18.7	46.3	0.9	46.0
22	48.6	45.8	24.1	33.3	15.9	46.1	0.0	45.8
26	48.5	45.7	20.1	30.9	10.3	45.7	0.0	45.4
30	48.5	45.6	16.1	28.5	4.7	45.3	0.0	45.0
44	48.3	45.3	2.1	20.1	0.0	43.9	0.0	43.6
45	48.3	45.3	1.1	19.5	0.0	43.8	0.0	43.5
47	48.3	45.3	0.0	18.3	0.0	39.1	0.0	43.3
53	48.2	45.2	0.0	14.7	0.0	<mark>4</mark> 3.0	0.0	42.7
54	48.2	45.2	0.0	14.1	0.0	<mark>42</mark> .9	0.0	42.6
68	48.1	44.8	0.0	5.7	0.0	41 .5	0.0	41.2
80	47.9	44.5	0.0	1.5	0.0	<mark>40</mark> .3	0.0	40.0
82	47.9	44.5	0.0	0.0	0.0	<mark>40</mark> .1	0.0	39.8
84	47.9	44.4	0.0	0.0	0.0	<mark>39</mark> .9	0.0	39.6
86	47.9	44.4	0.0	0.0	0.0	<mark>39</mark> .7	0.0	39.4
88	47.8	44.3	0.0	0.0	0.0	39.5	0.0	39.2
90	47.8	44.3	0.0	0.0	0.0	39.3	0.0	39.0
92	47.8	44.2	0.0	0.0	0.0	39.1	0.0	38.8
94	47.8	44.2	0.0	0.0	0.0	38.9	0.0	38.6
98	47.7	44.1	0.0	0.0	0.0	38.5	0.0	38.2
102	47.7	44.0	0.0	0.0	0.0	38.1	0.0	37.8
106	47.6	44.0	0.0	0.0	0.0	37.7	0.0	37.4
110	47.6	39.9	0.0	0.0	0.0	37.3	0.0	37.0
114	47.5	39.8	0.0	0.0	0.0	36.9	0.0	36.6
118	47.5	39.7	0.0	0.0	0.0	36.5	0.0	36.2
126	47.4	39.5	0.0	0.0	0.0	35.7	0.0	35.4
138	47.3	39.2	0.0	0.0	0.0	34.5	0.0	34.2
145	47.3	39.1	0.0	0.0	0.0	33.8	0.0	33.5
152	47.2	38.9	0.0	0.0	0.0	33.1	0.0	32.8
153	47.2	38.9	0.0	0.0	0.0	33.0	0.0	32.7
154	47.2	38.9	0.0	0.0	0.0	32.9	0.0	32.6
158	47.2	38.9	0.0	0.0	0.0	32.5	0.0	32.2
161	47.1	38.7	0.0	0.0	0.0	32.2	0.0	31.9
164	47.1	38.7	0.0	0.0	0.0	31.9	0.0	31.6
165	47.1	38.7	0.0	0.0	0.0	31.8	0.0	31.5
166	47.1	38.7	0.0	0.0	0.0	31.7	0.0	31.4

167	47.1	38.6	0.0	0.0	0.0	31.6	0.0	31.3
168	47.0	38.6	0.0	0.0	0.0	31.5	0.0	31.2
170	47.0	38.6	0.0	0.0	0.0	31.3	0.0	31.0
	_							
difference	8h	4h	1h	1h	1h	1h	1h	1h
	0.1	0.1	1.0	0.6	1.4	0.1	2.3	0.1

For fig 4.1.1,4.1.2,4.1.3,4.1.4,4.1.5,4.1.6,4.1.7,4.1.8,4.1.9

4.2.2 Corr<mark>osion rate</mark>

i. Commercial Zn

Initial experiment

Concentration (M)/ Reading (g)	2	4	6	8
First	0.290	0.300	0.530	0.590
Second	0.280	0.320	0.540	0.570
Third	0.290	0.340	0.550	0.600
Average	0.287	0.320	0.540	0.587

After experiment

Concentration (M)/ Reading (g)	2	4	6	8
First	0.285	0.319	0.533	0.583
Second	0.286	0.316	0.532	0.582
Third	0.285	0.317	0.533	0.583
Average	0.285	0.317	0.533	0.583

ΜΑΓΑΥΡΙΑ



Weight loss of commercial Zn

Concentration (M)		2	4	6	5	8
Weight Loss (g)		0.002	0.003	0.0	007	0.004
Corrosion Rate of c	ommercial Zn					
Concentration (M)	Weight Loss (g)	Area (cm ²)	Density (g/cm3)	Time (hr)	k	CR (mpy)
2	0.002	2	7.14	170	3.45x10 ⁶	2.84
4	0.003	2	7.14	170	3.45x10 ⁶	4.26
6	0.007	2	7.14	170	3.45x10 ⁶	9.95
8	0.004	2	7.14	170	3.45x10 ⁶	5.68

Example calculation for 2 M of KOH:

a) Weight loss:

Weight Loss = Initial reading – Final reading

= 0.287 - 0.285

= **0.002** g

b) Corrosion rate:



ii. Pure Zn

Initial experiment

Concentration (M)/	2		(Q
Rea <mark>ding (g)</mark>	2	4	0	ð
First	0.400	0.380	1.070	1.060
Second	0.390	0.400	1.060	1.065
Third	0.380	0.389	1.070	1.060
Average	0.390	0.390	1.067	1.062
After experiment				
Concentration (M)/	2	4	6	8
Reading (g)	2		Ū	0
First	0.386	0.390	1.057	1.056
Second	0.386	0.385	1.062	1.056
Third	0.386	0.388	1.059	1.056
Average	0.386	0.388	1.059	1.056
Weight loss of pure Zn				
	2			0

Concentration (M)	2	4	6	8
Weight Loss (g)	0.004	0.002	0.007	0.060

Corrosion rate of pure Zn

Concentration (M)	Weight Loss (g)	Area (cm ²)	Density (g/cm3)	Time (hr)	k	CR (mpy)
2	0.004	2	7.14	170	3.45x10 ⁶	5.68
4	0.002	2	7.14	170	3.45x10 ⁶	2.84
6	0.007	2	7.14	170	3.45x10 ⁶	9.95
8	0.006	2	7.14	170	3.45x10 ⁶	8.53

Example calculation for 2 M of KOH:

a) Weight loss:

Weight Loss = Initial reading – Final reading

= 0.004 g

b) Corrosion rate:

 $CR(mpy) = \frac{Weight Loss (g)xk}{Density (gcm⁻³)xArea (cm²)xTime (hr)}$ $= \frac{0.004x3.45x10^{6}}{7.14x2x170}$ = 5.68 mpy

UNIVERSITI