# THE STUDY OF AGAR BINDER AND SUPER P ADDITIVE IN POROUS ZINC ANODE FOR ZINC-AIR BATTERIES

**by**

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*MOHAMAD NAJMI MASRI*

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## LIST OF ABREVIATIONS

| | |
|---|---|
| AB | Acetylene black |
| AgNP | Silver nanoparticle |
| Al-air | Aluminium-air |
| Cu | Copper |
| FESEM | Field emission scanning electron microscope |
| FRA | Frequency response analyser |
| Fe-air | Iron-air |
| GPE | Polymer gel electrolyte |
| $H_2O$ | Water |
| ICDD | International Centre of Diffraction Data |
| KOH | Potassium hydroxide |
| Li-air | Lithium-air |
| Li-ion | Lithium-ion |
| $LIC_OO_2$ | Lithium cobalt oxide |
| LiOH | Lithium hydroxide |
| LSV | Linear sweep voltammetry |
| $MnO_2$ | Manganese oxide |
| Mg-air | Magnesium-air |
| NaOH | Sodium hydroxide |
| Ni | Nickel |
| NMP | 1-methyl-2-pyrrolidone |
| $OH^-$ | Hydroxide |
| $O_2$ | Oxygen |
| PTFE | Polytetrafluoroethylene |
| PC | Polycarbornate |

| | |
|---|---|
| PVDF | Polyvinylidene fluoride |
| SEM | Scanning Electron Microscopy |
| SDBS | Sodium dodecyl benzene sulfonate |
| SiC | Silicon carbide |
| SWNT | Single-walled carbon nanotube |
| TEM | Transmission Electron Microscopy |
| $V_{oc}$ | Open circuit voltage |
| XRD | X-ray Diffraction Spectroscopy |
| Zn | Zinc |
| Zn-air | Zinc-air |
| ZnO | Zinc oxide |
| $Zn(OH)_4^{2-}$ | Zincate |

## LIST OF SYMBOLS

| | |
|---|---|
| % | Percentage |
| ~ | Approximately |
| θ | Theta |
| σ | Ionic conductivity |
| < | Less than |
| > | More than |
| ≤ | Less than or equal to |
| $\lambda^{o}$ | Ionic molar conductivity |
| ° | Degree |
| A | Ampere |
| A $m^{-2}$ | Ampere per square meter |
| °C | Degree Celsius |
| ca. | Approximately |
| cm | Centimetre |
| d | Day |
| e.g. | For example |
| *f* | Frequency |
| g | Gram |
| h | Hour |
| i.e. | That is |
| *I* | Current |
| *J* | Current density |
| kg | Kilogram |
| L | Litre |
| M | Molar |

| | |
|---|---|
| m | Meter |
| min | Minute |
| mL | Millilitre |
| mm | Millimetre |
| nm | Nanometer |
| $P$ | Power density |
| $R_b$ | Bulk resistance |
| s | Second |
| t | Thickness |
| $V$ | Voltage |
| wt% | Weight percent |

**KAJIAN MENGENAI PENGIKAT AGAR DAN BAHAN TAMBAH SUPER P DALAM ANOD ZINK BERLIANG UNTUK BATERI ZINK-UDARA**

## ABSTRAK

Bateri zink-udara (Zn-udara) telah difabrikasi menggunakan anod Zn berliang, katod-udara dan elektrolit gel 6 M KOH-sagu. Anod Zn berliang telah disediakan dengan campuran serbuk Zn dan pengikat agar-KOH pada kepekatan yang berbeza untuk mencapai kekonduksian dan ciri-ciri fizikal yang dikehendaki. Agar adalah polimer semulajadi, mudah didapati, mudah disediakan, murah, tidak mencemarkan alam sekitar dan boleh membentuk gel. Kehadiran KOH menyebabkan pertumbuhan struktur jarum ZnO yang meliputi bahan Zn-aktif. Keputusan menunjukkan bahawa pengikat Zn-agar tanpa KOH memberikan keupayaan nyahcas tertinggi iaitu 505 $mAh \cdot g^{-1}$. Walau bagaimanapun, kapasiti nyahcas menurun dengan peningkatan KOH. Selain itu, prestasi elektokimia bagi bateri meningkat dengan kehadiran Super P. Antara kelebihan Super P adalah keaslian yang tinggi, luas permukaan tinggi dan struktur yang sempurna. Kehadiran bahan tambah Super P dalam anod Zn berliang meningkatkan prestasi nyahcas dan kestabilan pada voltan bateri Zn-udara. Kapasiti nyahcas dan ketumpatan kuasa bagi anod Zn yang mempunyai 2 wt% Super P adalah 776 $mAh \cdot g^{-1}$ dan 20 $mW \cdot cm^{-2}$, masing-masing. Imej morfologi dan sifat-sifat struktur juga dianalisis untuk menyokong pemerhatian ini. Super P menjadi penghubung antara serbuk Zn dan meningkatan prestasi elektrokimia bateri Zn-udara.

# THE STUDY OF AGAR BINDER AND SUPER P ADDITIVE IN POROUS ZINC ANODE FOR ZINC-AIR BATTERIES


## ABSTRACT

A zinc-air (Zn-air) battery was fabricated using porous Zn anode, an air cathode, and 6 M KOH-sago gel electrolyte. The porous Zn anode was prepared by mixing Zn powder and agar binder at different concentrations to achieve the desired conductivity and physical properties. Agar is an abundant natural polymer that does not require tedious and costly processing or preparation. Agar is also a gel-forming environmental friendly material. Meanwhile, the presence of KOH causes the growth of ZnO needle structures to cover the Zn-active material. Zn-agar binder without KOH produced the highest discharge capacity of 505 $mAh \cdot g^{-1}$. By contrast, the addition of KOH reduced the discharge capacity. The introduction of Super P improved the electrochemical performance of the batteries. The advantages of using Super P in batteries include high purity, large area, and highly structured body. The use of Super P additive in porous Zn anode enhanced the Zn-air battery discharge capacity because of the efficient and better voltage stability obtained from such an anode. The specific discharge capacity and power density of Zn anode with 2 wt% Super P were 776 $mAh \cdot g^{-1}$ and 20 $mW \cdot cm^{-2}$, respectively. Morphological images and structural properties were also analyzed to support these observations. Super P acted as a bridge in the Zn powders and improved the electrochemical performance of the Zn-air batteries.

# CHAPTER 1
# INTRODUCTION

## 1.1 Background

Concerns on fluctuating prices of oil and serious environmental issues emphasize the urgent need for alternative energy (Anisur et al., 2013; Bernardes et al., 2004; Espinosa et al., 2004; Sayilgan et al., 2009). Recently, the demand for portable electronic devices has been increasingly driven by energy and power density sources (Dillon and Sun, 2012). The field of electrochemical energy sources has undergone positive development in the last decade. Metal-air batteries have also received considerable attention (Kraytsberg and Ein-Eli, 2012). Among all metal-air battery systems, the Zn-air battery shows high potential as an alternative energy storage device.

Zn-air batteries possess a unique set of attributes, including abundance, low cost, low toxicity, flat discharge, long shelf life, ease in handling, and high theoretical specific energy density (1,084 $Wh \cdot kg^{-1}$) (Lee et al., 2011). Generally, Zn-air batteries are composed of three major parts, namely, Zn as anode, air-cathode, and alkaline electrolyte. The electrolyte used in a Zn-based battery is predominantly aqueous alkaline electrolyte, such as potassium hydroxide (KOH), sodium hydroxide (NaOH), and lithium hydroxide (LiOH) (Sapkota and Kim, 2009).

The use of KOH as electrolyte in Zn-air systems has recently attracted attention because of the high ability of limiting ionic molar conductivity ($\lambda°$) of $K^+$ (73.50 $S{\cdot}cm^2{\cdot}mol^{-1}$) compared with that of $Na^+$ (50.11 $S{\cdot}cm^2{\cdot}mol^{-1}$) (Passaniti et al., 2011; Sapkota and Kim, 2010). Meanwhile, $\lambda°$ of $OH^-$ is 199.1 $S{\cdot}cm^2{\cdot}mol^{-1}$, and the anions are commonly the charge carriers in alkaline systems (Giffin et al., 2012).

The air-cathode is responsible for determining battery activation. The air-cathode as a battery component provides unlimited oxygen ($O_2$) supply as an active material, which can be obtained directly from the environment (Passaniti et al., 2011). These advantages contribute to the relatively small size and flexible designs for Zn-air batteries.

Another component that can enhance the high performance of a battery is the Zn anode. Zn anodes have two types , namely, Zn plate and porous Zn (Ye and Xu, 2007). Zn plates have a lower surface area than porous Zn anodes; the Zn plate is effectively moistened, and the usage of Zn-active material is optimized. By contrast, the porous Zn anode has better contact with the electrolyte because of its higher surface area, thus producing a promising performance rate for Zn-air batteries (Shaigan et al., 2010a).

Typically, a porous Zn anode is prepared from a powder mixture that includes Zn (main component), conductive powder, and binder. Porous Zn anodes can be fabricated using various methods, such as roll-bonding or compression, electrodeposition, and paste drying. Among these processes, paste drying is the simplest technique with promising outcomes.

## 1.2 Problem statement

Recently, a considerable number of studies based on porous Zn anode for Zn-air batteries have emerged (Othman et al., 2002a; Othman et al., 2002b; Ye and Xu, 2007). The development of Zn-air battery systems has shown great improvement from year to year. However, systematic and detailed studies on the use of binders are yet to be found in the literature.

The binder has an important function in tethering; it prevents the absolute disintegration of the active materials, which are normally fine powders or particles (Pejovnik et al., 2008). The binder functions not only as a highly adhesive agent but also as an effective dispersion medium for the active material (Huang et al., 2008a). Polytetrafluoroethylene (PTFE) is the most used binder for Zn-air batteries. Polycarbonate (PC) and sodium silicate have been recently discovered as binders as well (Hilder et al., 2009; Hilder et al., 2012).

Agar binder is introduced to emphasize green material alternatives to polymeric binders such as PTFE and PC. Othman et al. (2002b) introduced agar as a binder that can be used for preparing porous Zn anodes. Moreover, the addition of a few drops of KOH has been reported to enhance the conductivity of the agar binder; however, the exact value of KOH concentration was not specified. No systematic study has explored the effect of KOH addition to the binder, as well as the consequent improvement of porous anodes for Zn-air batteries. A conductivity study on agar mixture with KOH was also considered to ensure quantitative conductivity measurement.

The passivation of Zn-active materials by the formation of zinc oxide (ZnO) during discharge, which limits the usage efficiency of Zn, is also a research interest. The use of additives for porous Zn anodes has been proposed in several studies to overcome this problem (Bass et al., 1988; Duffield et al., 1987a; Müller et al., 1998; Othman et al., 2002b). Hilder et al. (2012) showed that the network in Zn-air batteries is dependent on carbon content because carbon functions as a conductive link between isolated metal particles, thus activating the anode for electrochemical reaction.

In this study, agar-KOH paste was used as a binder for a porous Zn anode. The further improvement was focused on the effects of the addition of Super P to the porous Zn anode on the performance of Zn-air batteries. The porous Zn anode was prepared by mixing Super P and Zn powder in agar binder paste. The performance of the porous Zn anode was characterized by electrochemical investigations and supported by morphological and structural studies. This study aims to verify the effect of agar binder in conjunction with Super P addition to porous Zn anodes for enhancing the performance of Zn-air batteries.

## 1.3 Objectives

The main objectives of this research are as follows:

(i) To determine the optimum conductivity of agar and KOH binder,

(ii) To study the electrochemical properties of porous Zn anode with agar-KOH in Zn-air batteries, and

(iii) To determine the effect of Super P addition on the properties of porous Zn anodes in Zn-air batteries.

## 1.4 Scope of Work

This research was performed in three stages. The initial stage involved the characterization of agar binder by conductivity and potential window. Then, agar binder in the porous Zn anode for a Zn-air battery system was studied. Subsequently, the effect of Super P addition was also determined by electrochemical characterization. Finally, morphological and structural analyses were also conducted.

## 1.5 Organization of Thesis

This thesis is divided into several chapters. The literature review provides information and summarizes the results related to porous Zn anodes in Zn-air battery systems. The relationships between Zn-air batteries and other assessment criteria involved in porous Zn anodes, such as binder and filler, are also reviewed in Chapter 2. Chapter 3 describes the experimental procedures including sample preparation to characterization. The results and discussion are presented in Chapter 4. Finally, Chapter 5 concludes the study with several suggestions for further research.

# CHAPTER 2
# LITERATURE REVIEW

## 2.1 Introduction

This chapter presents the theories on which this research was based. The construction of Zn-air batteries using porous Zn anode, as well as the steps of its preparation, is also discussed. The relationships between Zn-air batteries and other assessment criteria involving porous Zn anodes, such as binder and filler, are also explained. Zn-air battery assessments with regard to porous Zn anodes are also included.

## 2.2 Zinc-air Batteries

Metal-air batteries are a unique battery technology. These batteries are also called "breathing batteries" because absorb oxygen from the environment. It is also similar to fuel cells because they represent a "marriage" between battery (the anode) and fuel cell (the cathode). In particular, metal-air batteries are different from other types of batteries because of the virtual limitless supply of air, which enables the batteries to offer many advantages compared with other batteries. In short, cathode active material is not stored in the battery. These batteries produce electrical energy through the electrochemical reaction between the oxygen ($O_2$) present in air and the anode that is oxidized. The superiority of metal-air batteries over conventional types of batteries is based on the high specific energy.

Although Zn-air is one of the most popular metal-air batteries, other metal-air batteries have also been considered include:

(i) *Lithium-air (Li-air)* – This battery has the highest energy storage density, but its use is limited by safety issues and fast degradation under ambient conditions. In particular, the highly reactive Li should be isolated from moisture ($H_2O$) and $O_2$ that can permeate the anode. Thus, complex and stable long-term separator is required in this battery (Hummelshøj et al., 2010; Thapa et al., 2011; Yu. Aleshin et al., 2011; Zhang et al., 2010),

(ii) *Aluminium-air (Al-air)* - This battery is low cost and innocuous. However, it generates a large amount of heat and is highly corrosive (hydrogen evolution reaction), which affects the efficiency of the anode (Li et al., 2007; Mohamad, 2008; Tang et al., 2004; Wang et al., 2010a),

(iii) *Magnesium-air (Mg-air)* – Mg is abundant and lightweight. However, Mg undergoes rapid self-corrosion (Chen et al., 2006; Li et al., 2006; Ma et al., 2010; Sathyanarayana and Munichandraiah, 1981), and

(iv) *Iron-air (Fe-air)* - Passivation during discharge and high self-discharge result in its thermodynamic instability in alkaline-based electrolyte (Hang et al., 2006; Hang et al., 2007; Ito et al., 2011; Watanabe et al., 2006).

Most Zn-air batteries are designed for low-rate applications, although a high-rate version is also available (Levy and Bro, 1994). Their uses range from electric bus application (Goldstein et al., 1999) to the smallest commercially available Zn-air battery, which is approximately 50 $mm^3$ in size (Heller, 2006). Zn-air batteries have been used for hearing aid applications since the mid-1980s (Neburchilov et al., 2010; Pytches, 1983; Read, 2002a; Root, 2010; Sparkes and Lacey, 1997; Zhang et al., 2008).

The unique properties of Zn-air batteries make them indispensable in military (Brownlee et al., 1969; Jamaludin et al., 2010; Knapp et al., 1969) and safety applications, such as railway signals (Culter, 1996; Pistoia, 2005; Pistoia, 2008). The emergence of sophisticated devices has stimulated new research work focusing on the longevity and energy density of batteries. Hence, longer durability, superior performance, dependability, and cost effectiveness are the properties of a good battery.

Electric Fuel Corporation promoted small-size versions of Zn-air primary batteries for use in mobile telephones. These batteries provide three to five times more "talk-time" than rechargeable batteries, which is useful when recharging is not readily possible. As a primary battery, the Zn-air battery can be used straight from the packet without the need for a preliminary charge (Goldstein et al., 1999). Latest developments on Zn-air batteries have also prompted the energy industries to produce commercial rechargeable Zn-air batteries (Badarulzaman et al., 2009; Masri, 2008; Pistoia, 2008; Zhang, 2004).

### 2.2.1 Components of Zinc-air Battery

Figure 2.1 shows the basic components of a Zn-air battery. A Zn-air battery consists of an alkaline electrolyte, and it operates using a steady supply of oxygen from air. $O_2$ is reduced at the air-cathode, forming a hydroxyl ($OH^-$) ion that migrates through the electrolyte to the Zn anode. This reaction produces electrons, which are transported through the external circuit to the air-cathode, thereby generating electricity. The $OH^-$ ions react to form zinc oxide (ZnO), which is a by-product of the reaction.

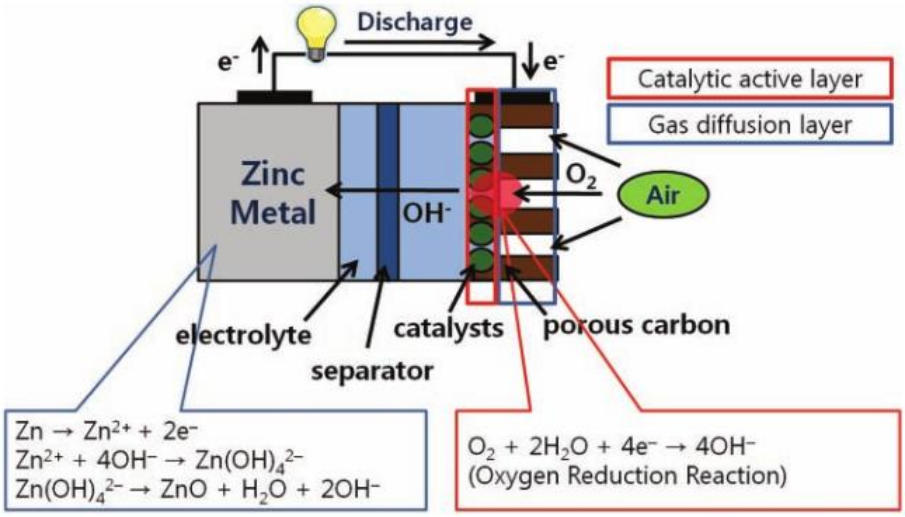


Figure 2.1: Schematic diagram of the basic configurations of a Zn-air battery (Lee et al., 2011)

The use of an air-cathode or gas diffusion electrode distinguishes Zn-air batteries from other batteries; battery weight is considerably reduced, resulting in a compact and simplified battery design (Barak, 1980; Chamran et al., 2007; Williford and Zhang, 2009; Zhang, 2004). Figure 2.2 demonstrates a schematic illustration of the basic components of different air-cathode designs. Air-cathodes reduce $O_2$ to produce $OH^-$, which is soluble in an aqueous electrolyte.

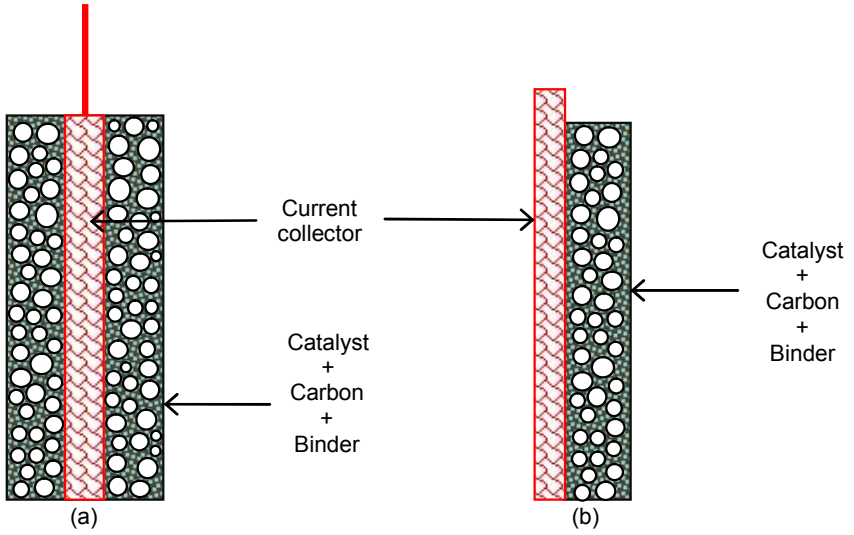


Figure 2.2: Layers of air-cathode with different states of current collector; (a) internal and (b) side

An air-cathode has huge hydrophobic channels to maximize $O_2$ diffusion (Eom et al., 2006; Li et al., 2010). Chemical and dimensional stability, sufficient porosity, and high electronic conductivity are required in an air-cathode (Singhal and Gopalan, 2000). Typically, an air-cathode consists of four main materials, namely, the catalyst, carbon, current collector, and binder (Durkot et al., 2007; Wang and Zhou, 2010). The most widely reported catalyst is manganese oxide ($MnO_2$) impregnated with carbon (Cao et al., 2003; Feng et al., 2005; Wei et al., 2000).

The infinite supply of $O_2$ from the environment provides advantages to the Zn-air battery system. Figure 2.3 illustrates the air flow through the air-cathode material as it catalytically promotes the reduction of $O_2$ in the electrolyte. Further concerns on $O_2$ flowing into the air-cathode was studied by Eom et al. (2006). The air-cathode is generally durable and remains constant during Zn-air battery discharge (Mohamad, 2006a).

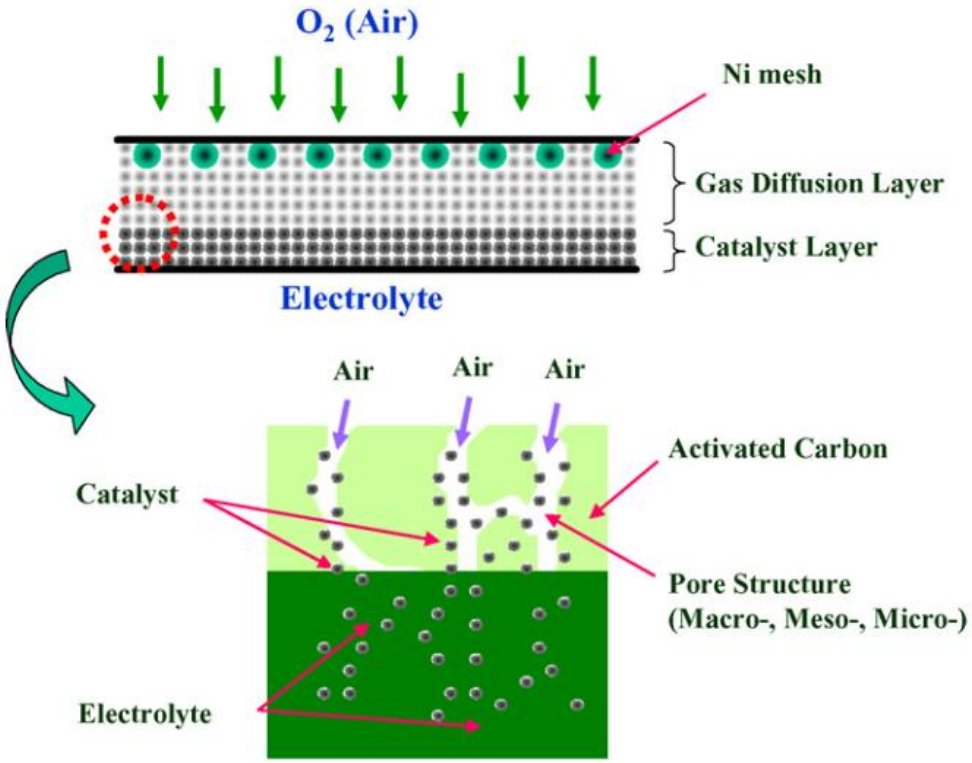


Figure 2.3: The illustration on behaviour of oxygen from atmosphere into the air-cathode in Zn-air battery (Eom et al., 2006)

The choice of electrolyte highly depends on the electrodes used. The characteristics of the electrolyte that must be considered are conductivity and viscosity (Blomgren, 1999). The majority of Zn-air batteries use aqueous alkaline solutions, particularly potassium hydroxide (KOH), because of its high conductivity and excellent ability to control the reduction of $O_2$ ions into $OH^-$ anions anions (Almeida et al., 2009; Barak, 1980; Dell and Rand, 2001; Dirkse and Kroon, 1971; Koscher and Kordesch, 2004; Miura et al., 1988; Putt and Merry, 1992; Pytches, 1983; Zhang, 1996; Zheng et al., 2004).

The capacity of Zn-air batteries is attributed to the type of air-cathode material and the concentration of KOH in the electrolyte. However, the anode is another key factor in determining battery performance (Akuto et al., 2001; Hang et al., 2005; Linden, 2001; Winter and Brodd, 2004; Yang et al., 2004). A number of factors must be considered to optimize the anode materials, such as the material cost for the alkaline battery (Koretz et al., 1995; Muller et al., 1998; Roundy et al., 2004), abundance of resources, non-toxicity (Chao et al., 2008; Chen et al., 2011; Chen et al., 2010; Vatsalarani et al., 2009), low equilibrium potential, and high over-potential of the reaction of hydrogen with Zn (Chao et al., 2008; Chen et al., 2011; Chen et al., 2010; Smedley and Zhang, 2007; Zheng et al., 2004).

### 2.2.2 Chemistry of Zinc-air Batteries

The Zn anode chemistry as the Zn-air battery discharges in an alkaline electrolyte (Linden and Reddy, 2001a; Reddy, 2010b) is represented by Equation 2.1:

$$Zn + \frac{1}{2}O_2 + H_2O + 2(OH)^- \rightarrow Zn(OH)_4^{2-} \quad (2.1)$$

The reactions of Zn in Zn-air batteries during discharge are simultaneous, and the use of an oxygen-reducing catalyst in an air-cathode results in the reduction of the $O_2$ adsorbed from the surrounding air (Chang, 1963; Foller, 1986; Genies et al., 2003; Mohamad et al., 2003; Wang et al., 2010b; Wu et al., 2007; Yang and Zhou, 1995). The reactions are presented in Equation 2.2:

$$O_2 + 2H_2O + 4e \rightleftarrows 4OH^- \quad (2.2)$$

The reaction of the preliminary discharge at the Zn electrode can be expressed by Equation 2.3 (Reddy, 2010b):

$$Zn + 4OH^- \rightleftarrows Zn(OH)_4^{2-} + 2e \quad (2.3)$$

This reaction proceeds until the zincate [$Zn(OH)_4^{2-}$] ion reaches saturation point because the supersaturation 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 discharge, which results in the formation of ZnO precipitate (Tan and Mohamad, 2010; Yap et al., 2009). This reaction can be presented as Equation 2.4:

$$Zn(OH)_4^{2-} \rightleftarrows ZnO + H_2O + 2(OH)^- \quad (2.4)$$

The overall battery reaction may be simplified as Equation 2.5 (Chodosh et al., 1966; Chodosh et al., 1967; Cretzmeyer et al., 1976; Culter, 1996; Malone et al., 2004; Pistoia, 2008):

$$Zn + \frac{1}{2}O_2 \rightleftarrows ZnO \quad (2.5)$$

The tendency of Zn to corrode during battery storage remains a difficult problem that should be addressed. Hence, researchers have investigated the electrochemical reaction involved in alkaline solutions (Culter, 1996; Dirkse and Timmer, 1969; Zhang and Zhang, 2003). The predominant oxidized products of the

aforementioned reactions are generally believed to be $Zn(OH)_4^{2-}$. Nevertheless, most researchers believe that the passive films contain ZnO (Buchholz, 1980; Dirkse and Timmer, 1969; Goldstein and Koretz, 1998; Graedel, 1989; Rudd and Breslin, 2000; Yang et al., 2004).

The status of Zn can be identified by two different colors, namely, grey (fresh Zn) and white (incompletely discharged Zn). Deiss et al. (2002) claimed that ZnO could form and remain on the Zn electrode after discharge. Many researchers have proposed mechanisms of ZnO formation based on material, preparation, and methodology (Bockris et al., 1972; Cai and Park, 1996; Chang and Prentice, 1984; Chang and Prentice, 1989). The growth morphology enables the tuning of reaction conditions to obtain the desired properties, such as the shape and size (*ca.* nanoscale) of a material and even the by-product of the Zn-air battery system for a specific application.

The possible structures of ZnO include combs (Pan et al., 2005; Yang et al., 2002), rods (Boyle et al., 2002; Gonzalez-Valls and Lira-Cantu, 2010; Lee et al., 2007; O'Brien et al., 1996), spherulitic prisms (Verges et al., 1990), helices (Tian et al., 2002), porous structures (Wang et al., 2004), tetrapods (Al-Azri et al., 2010; Wang et al., 2004), belts (Kong et al., 2004; Kong and Wang, 2003), propellers (Gao and Wang, 2004), flowers (Al-Azri et al., 2010; Xu et al., 2009), wires (Al-Azri et al., 2010; Yang et al., 2002; Zhao et al., 2003), spheres (Alias et al., 2010; Verges et al., 1990), plates (Tian et al., 2002), rosettes (Tan and Mohamad, 2010), and needles (Mohamad, 2006; Othman et al., 2001b; Tan and Mohamad, 2010). Figure 2.4 shows the scanning electron microscopy (SEM) images of the examples of ZnO.

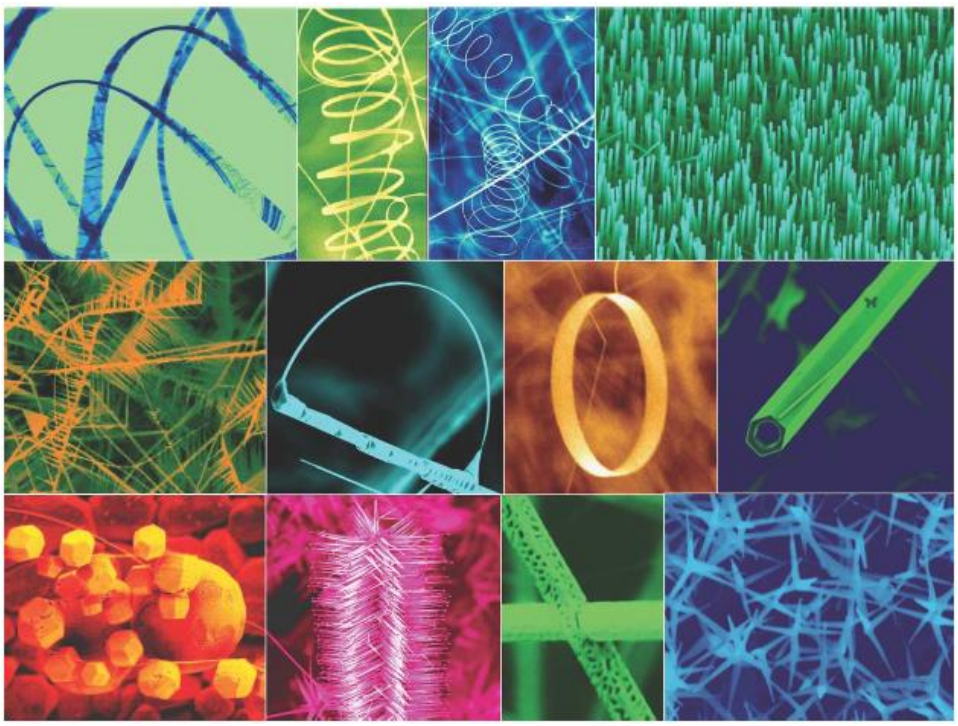

Figure 2.4: A collection of ZnO SEM images (Wang, 2004)

### 2.2.3 Classification of Anode in a Zinc-air Battery

Zn-air battery anodes are classified into two main groups, namely, solid and porous Zn. Zn powder, fiber, lamination, and deposition are included in the porous group. The classification of Zn-air anodes is summarized in Figure 2.5.

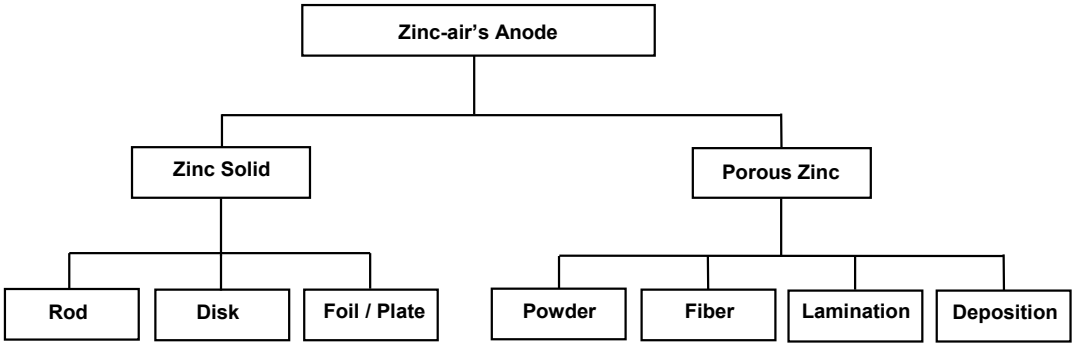


Figure 2.5: The Classification of anode utilization in Zn-air battery

Batteries with a porous anode normally demonstrate 40% higher capacity than those with planar Zn (Minakshi et al., 2010). The electrolytes flow more freely across the entire surface of Zn powder when the surface area is increased. However, a few stringent conditions involving the surface area of the materials used must be met in the fabrication of batteries. In particular, the surface area of Zn particles can affect the properties of the battery, such as (Stanley and Thornton, 2002):

(i) Lifetime of the battery,

(ii) Discharge rate of the battery, and

(iii) Ease of preparation of the battery components.

A large surface area can result in very rapid anode degradation. Meanwhile, a very small surface area may not meet battery specifications. The discharge rate of a battery is also determined by the area of exposed surface (Sparkes and Lacey, 1997). Ease of preparation should also be considered, and this includes the adhesion performance of the paste (binder) used to produce neutral gaps between the active materials.

## 2.3 Design of the Battery

The size, shape, performance, and design parameters of a battery are considered variables that can be customized for a variety of specific geometry and dependence functions. A battery can be placed at arbitrary locations within an electronic device. As a result, free design of electronic devices can be achieved in terms of available energy sources and may allow for new possibilities in performance, such as increased discharge capacity. Regardless of the shape and

design, the assembled battery should not suffer from electrolyte leakage or the premature entry of air. Hence, batteries are sealed in numerous ways to prevent leakage (Cheiky, 1995; R.M, 2000). Designs with bigger diameters and thinner walls are preferred. Other factors to be considered in designing batteries are air and electrolyte (Root, 2010).

The popular use of Zn-air batteries in battery research laboratories can be attributed to the stability of the battery materials. Cells for Zn-air batteries can be easily fabricated under ambient air and without the use of sophisticated equipment. The development in battery design focuses on three key objectives, namely:

(i) Full Zn utilization for complete reaction,

(ii) Maximization of the active area of the air-cathode to reduce $O_2$, and

(iii) Determination of the functionality and cost of batteries.

Conventional Zn-air batteries have large volumes, usually around 30 $mm^3$ (Chao et al., 2008). Hence, the recent trend in Zn-air battery design leans toward lighter, thinner, and smaller sizes. The two types of extensively developed commercial Zn-air batteries are the button cells and low-rate industrial batteries. The cross-section of button Zn-air batteries used for hearing aids is shown in Figure 2.6. Zn-air batteries offer a capacity advantage because of air-cathode mass, and their design is similar to that of Zn-mercuric oxide button cells. The battery design uses an anode paste of amalgamated Zn powder in a gelled KOH electrolyte (Knapp et al., 1969) and an air-cathode (Putt and Merry, 1992).

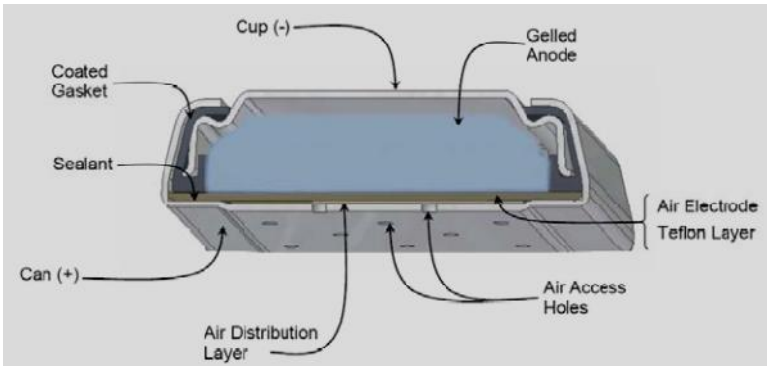


Figure 2.6: Schematic diagram of cross-section commercial Zn-air battery (Energizer, 2013)

Anode thickness is consistent with specific capacity requirements. Industrial Zn-air batteries are of a prismatic configuration and are also encased in molded plastic. This type of battery has a promising service life (2 years to 3 years), with a maximum continuous drain rate of $\leq$ 1 A (Putt and Merry, 1992). Another battery design suitable for military applications is reported elsewhere (Knapp et al., 1969).

Figure 2.7 demonstrates the condition that has always been a drawback to Zn-air battery design. The state of the porous Zn anode before discharge can be seen in Figure 2.7a. The growth of ZnO needles after discharge can cause an internal short circuit or leakage (Cooper and Krueger, 2006; Shaigan et al., 2010b); thus, the available space must be within an exact range to overcome this problem (Figure 2.7b). In small spaces, the continuous growth of ZnO needles connects the anode and the air-cathode (Figure 2.7c).

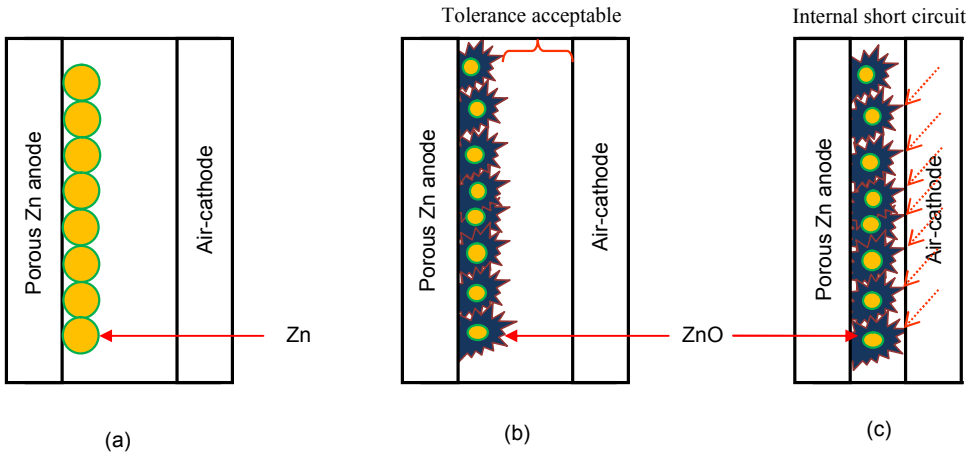


Figure 2.7: Condition of porous Zn anode, (a) before and after discharge as function of range in between the anode and air-cathode; (b) ideal and (c) inferior range

## 2.4 Porosity and Surface Area

A porous Zn anode system typically consists of an active material (Zn powder), additives, and binders. Additives increase the conductivity and life span of the active material. Binders essentially act as holders for the active material. Zn-air batteries typically use anodes made from powders of active materials, which is Zn, to obtain the highest possible surface area per unit weight or volume (Winter and Brodd, 2004). This method is highly useful in meeting the current demand for new and emerging miniature devices, which are being developed yearly, while increasing the surface area of the anode and the capacity of the battery.

The dispersion of porous Zn anode ingredients is controlled by several factors, such as the size and shape of the particle, density, volume fraction of individual components, and interparticle interaction (Hong et al., 2002). These elements affect the mixing efficiency of the paste preparation step, thus dispersing powder in the porous Zn anode. The specific surface area is defined as the area of the surface where the electrochemical reaction between the electrolyte and Zn occurs and produces an electric current(Hilder et al., 2009). The correlation can be simply expressed by Equation 2.6:

$$\text{Specific surface area} = \frac{\text{Effective surface area } (m^2)}{\text{Weight of active materials } (g)} \tag{2.6}$$

Another method used to calculate the surface area is based on micrograph image-processing software. The ImageJ software can also be used for simple processing. The calculation is based on the porous and solid images, and the observations are differentiated according to color. For this quantitative technique, evaluation depends only on the appearance of the micrograph rather than on that of the overall sample. The porosity can also be calculated according to the following Equation 2.7 (Othman et al., 2002b):

$$\text{Porosity} = \frac{V_{pore}}{V_{total}} \text{x } 100\% \tag{2.7}$$

Porosity refers to the fractional volume that is not filled with solids. Porosity is determined by the binder concentrations described in Equation 2.7, where $V_{\text{pore}}$ is the total pore volume within the electrode and $V_{total}$ is the total electrode volume. Porosity and the distribution of porous space in the anode play a significant role in the anode performance in the batteries (Deiss et al., 2002), and their effects are mainly determined by the shape of the Zn particles and the design of the anode. Meanwhile, the important parameters that characterize the porous Zn anode are specific surface area, effective surface, porosity, and physical stability.

## 2.5 Classification of Porous Zinc Anode

The reported porosity percentage generally varies between 10% and 70% of the amount of anode (Knapp, 1968; Warszawski, 1979). However, the performance of porous Zn anodes depends on both the active materials and the processing parameters (Biegler et al., 1983; Maja et al., 2000; Wang et al., 2006a). Table 2.1 summarizes the classification of porous Zn anodes. Figure 2.8 also illustrates the common Zn anode designs. Figure 2.8a shows the Zn plate/foil (solid) commonly used in Zn-air research. Zn deposition (Figure 2.8b) can increase the active surface area similar to that in the fiber approach (Figure2.8c). Laminated/compressed (Figures 2.8d) and powder porous (Figures 2.8e) Zn anodes are slightly similar, but their fabrication methods are different.

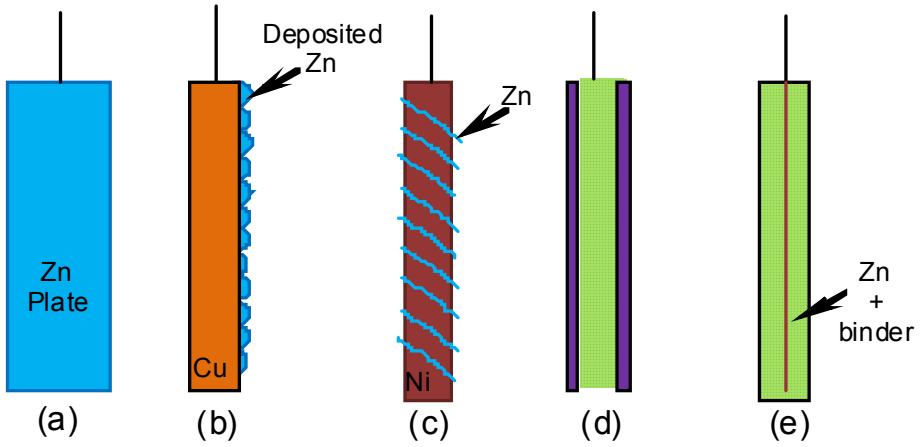


Figure 2.8: The basic design of (a) plate/foil, and porous Zn anode; (b) deposition, (c) fiber, (d) laminated/compressed and (e) powder

### 2.5.1 Zinc Electrodeposition

Electrodeposited Zn is considered as a type of porous Zn anode. Zn is known as one of the most electropositive metals (Koscher and Kordesch, 2004). Thus, pure Zn may be electrodeposited using an aqueous electrolyte, leading to the improvement in the surface area on the substrate (Freitas and De Pietre, 2005; Naybour, 1968; Pal and Chakravorty, 2006; Wang et al., 2006a). The Zn particles are deposited on the surface of the current collector, such as copper (Cu) or nickel (Ni).

Table 2.1: The summary of porous Zn anodes

| Types | Processing | Zn Form | Ref. |
|---|---|---|---|
| Electrodeposition | Obtained by the current collector as deposited zincate. | Surface morphology; Spongy, dendrite, layer-like, mossy | Wang et al. (2006a) |
| Fiber | Anode porosity and shape according to the processes, including:<br>i. Packaging<br>ii. Pressing<br>iii. Fusing<br>iv. Molten rolling<br>v. Cutting | Needle, wire, filament, strands, or threads | Headrick et al. (2002); Heller (2006); Zhang (2006) |
| Lamination | Continuous mesh or perforated. Anode porosity and shape dominance via rolling or stacking. | Sandwich, stack | Zhang and Zhang (2004); Zhang et al. (2001); Zheng et al. (2004) |
| Powder | Anode porosity as determined via gelling/binder and anode's shape controlled by the anode cavity/casing | Powder | Othman et al. (2002b) |