

Regeneration of Zinc Particles for Zinc-Air Battery by Spouted-bed Electrochemical  
Reactor



A Thesis Submitted in Partial Fulfillment of the Requirements  
for the Degree of Master of Engineering in Chemical Engineering

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การฟื้นฟูของอนุภาคสังกะสีสำหรับแบตเตอรี่สังกะสี-อากาศโดยเครื่องปฏิกรณ์สเปาเต็ดเบด



วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต

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Field of Study                    Chemical Engineering  
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ในปัจจุบันแบตเตอรี่สังกะสี-อากาศเป็นอุปกรณ์กักเก็บพลังงานที่นิยมอย่างแพร่หลาย  
 เนื่องจาก ความหนาแน่นพลังงานสูง ความเป็นพิษต่ำและติดไฟได้ยาก แบตเตอรี่ทั่วไปถูกนำไปใช้  
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Peerawat Puengthaijaroen : Regeneration of Zinc Particles for Zinc-Air Battery by Spouted-bed Electrochemical Reactor. Advisor: Asst. Prof. Palang Bumroongsakulsawat, Ph.D.

Zinc-air batteries are a promising energy storage system due to its high energy density, low toxicity, and low flammability. They are currently used commercially in low-current devices. Batteries for high-current applications are constructed with zinc particles for increased specific surface areas. Nevertheless, the regeneration of zinc particles from dissolved zincate ions in spent electrolytes has been relatively neglected. We fabricate and study a spouted-bed electrochemical reactor for the regeneration of zinc particles from spent electrolytes. The reactor measures 220 mm high and 130 mm wide with copper as a cathode and stainless steel as an anode. The reactor is separated into two compartments with a cation-exchange membrane. The model spent electrolytes are made by saturating 6 M KOH solutions with ZnO. Stainless steel particles are spouted into the reactor along with the electrolyte as seed particles. Zinc is deposited on stainless steel particles in the cathode compartment electrochemically by imposing potential differences between the anode and the cathode. Effects of zinc particle morphology, current efficiency, and energy consumption are studied. The regenerated zinc deposits are used as an anode in the zinc-air battery to test the performance of the battery.

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## Chapter 1

### Introduction

#### 1.1 Background

Nowadays, energy consumption is a problem that Thailand focuses on because electricity is generated from natural gas at very high rates. Energy from natural gas is non-renewable energy. Therefore, Thailand turns to concentrate on renewable energy. Ministry of energy has a policy Thailand 4.0 that are increasing usage of renewable energy from 6 percent to 20 percent and decreasing usage of natural gas from 64 percent to 37 percent within 2036. However, sources of renewable energy are unstable such as fluctuation of light intensity from the sun. Variance of them has effect on efficiency of energy that is used.

Electrical energy storage has been widely used because it can be applied with renewable energy. The conventional electrical energy storage is Lithium-ion batteries. Lithium-ion batteries have been used for electric vehicles (EVs) and portable consumer electronics since they were revealed in 1991. Nevertheless, their problems are high cost, easy to catch fire and insufficient theoretical energy density for large scale [1]. Then, metal-air batteries have become attractive because of their higher energy densities [2-4]. For example, 13,300 Wh/kg for Li/O<sub>2</sub> [5] and 6,462 Wh/kg for Mg/O<sub>2</sub> [6]. The main advantage of metal-air batteries is that the cathode material is oxygen, which is freely available in air and abundant [7, 8]. Nonetheless, the limitations of metal-air batteries are high cost and electrical rechargeability. Among metal-air batteries, zinc-air batteries have recently been focused because they have the highest energy densities among metal-air batteries. Compared with other metal-air batteries, the zinc-air batteries are low cost, relatively non-toxic and non-polluting. For example, zinc-air batteries showed energy density and discharge capacity higher than lithium-ion batteries and lead-acid batteries [9]. Zinc-air batteries already have commercial applications in railway signal, hearing-aids and medical devices [5]. However, the main problems that prevent zinc-air batteries from a larger market are poor rechargeability and low cycle life.

One of the factors that affects quality regenerated zinc product is morphology of deposited zinc which is associated with longevity. There are many undesirable morphologies such as spongy, mossy and dendrite formations [8]. The ideal morphology that is expected to be deposited from charge process is granular zinc. Hence, the morphologies control is important factor indicating the reusability of regenerated zinc in discharge process. The morphologies of deposited zinc are effects of electrode materials, separator, concentration of electrolyte, additives and process engineering design [8].

A spouted bed reactor [10] is a vertical vessel that contains particles with conical bottom. A jet of liquid is vertically injected through a nozzle at the center of the vessel. If velocity of jet is sufficiently high, it makes particles move up rapidly in the center of vessel. Then, the velocity of jet drops. The particles fall back around the annulus of the bed until velocity becomes high again. The particles in this reactor can be transformed to electrode by incorporated with current feeder. When current can be flowed, metal can be deposited on particles, which are called “seed” particles, so that they grow from initial stage to final stage. In this research, nickel particles that are about 1 mm are chosen as seed particles because stainless particles can be regenerated for using in zinc-air batteries.

In this research, flat spouted bed reactor is investigated for regeneration of zinc particles. Effects of various current densities and time of deposition are studied. Morphologies of zinc particles are characterized by scanning electron microscope. Energy consumption and Faradaic efficiency are investigated. Zinc that is deposited on stainless particles is tested performance in zinc-air batteries.

## 1.2 Objectives

1. To study using spouted bed electrochemical reactor for regeneration of zinc particles from electrolyte solutions containing zinc
2. To study effects of current densities and electrolyte flow rates on the performance of zinc regeneration
3. To investigate the performance of using regenerated zinc in zinc-air batteries

## 1.3 Scopes of research

1. The design of spouted bed electrochemical reactor and components are showed in table 1 and table 2 , respectively.
2. Electrolyte for cathode compartment is 500 cm<sup>3</sup> of 6 M KOH saturated with zinc oxide 10 % w/w and electrolyte for anode compartment is 500 cm<sup>3</sup> of 6 M KOH.
3. Zinc deposition at current densities of 10, 20, 30 and 40 mA/cm<sup>2</sup>.
4. The flow rates of the catholyte are set 250 ml/min.
- 5 Performances of using regenerated zinc in zinc-air batteries are tested at a constant current of 250 mA.





## Chapter 2

### Theory and literature reviews

#### 2.1 Theory

##### 2.1.1 Zinc-air battery

A battery is a contained energy device that converts chemical energy to electrical energy. There are main 4 parts in zinc-air battery which are zinc electrode, air electrode, electrolyte and separator. Zinc-air battery design is showed in Figure 1.

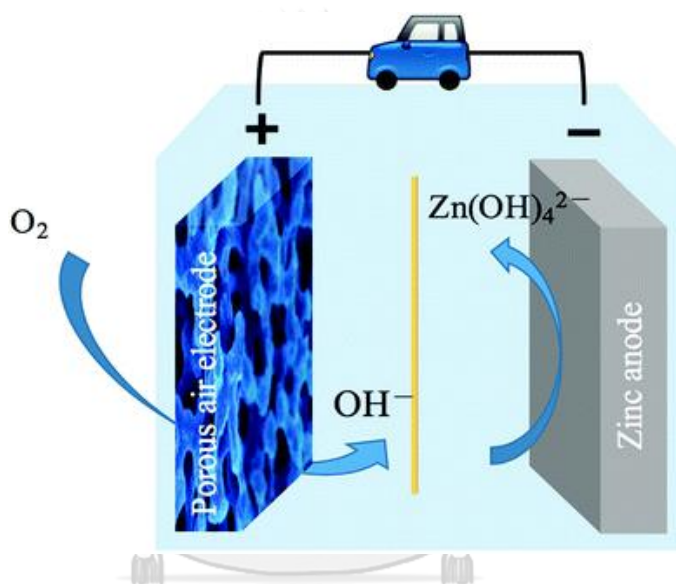
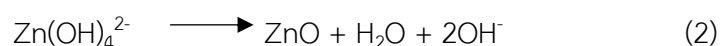
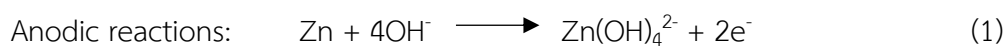


Figure 1 Schematic diagram of a zinc-air battery [4]

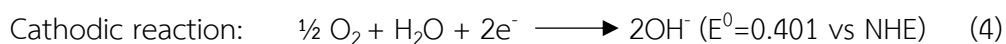
The theoretical energy density of zinc-air battery is about  $1,086 \text{ Whkg}^{-1}$ , it is about 5 times of Li-ion, and operational cost is less than  $10 \text{ \$ Kw}^{-1}\text{h}^{-1}$ , it is small part compared with Li-ion [11]. From Figure 1, the electrochemical reactions pathway of zinc-air battery are summarized as follow.

Discharge



( $E^0 = -1.25\text{V}$  vs normal hydrogen electrode (NHE))





In discharge process, zinc metal is oxidized and react with  $\text{OH}^-$  ions to occur zincate ion ( $\text{Zn}(\text{OH})_4^{2-}$ ). When the number of zincate ions are over solubility limit, zinc oxide is form. In parallel reaction for anode, hydrogen is generated from zinc and water. This reaction causes slow corrosion of metallic zinc. For cathodic reaction, oxygen from air spreads through porous gas diffusion layer and is reduced to produce hydroxyl ion which this reaction is called oxygen reduction reaction (ORR). At the zinc electrode, it is required slight energy to overcome resistance. Hence, the over-potential that is required to operate the reaction is low. Nonetheless, the over-potential at air electrode is higher than zinc electrode. The reaction at air electrode is rate-determining step [12]. By the way, zinc ions have many form. The form of zinc ions depend on PH value of electrolyte [13]. In case of PH above or equal 13, zincate ions is got. In ranges of PH values 9.3 to 12.3, the other forms of zinc ions are produced such as  $\text{Zn}(\text{OH})_y^{2-y}$ ; y ranged 0 to 4;  $\text{Zn}(\text{OH})_4^{2-}$  and  $\text{Zn}(\text{OH})_3^-$ . The form of zinc ions has affected on anodic reaction because each of zinc ions has different capability of received hydroxide ion. The zinc ion that is suitable for zinc-air battery is  $\text{Zn}(\text{OH})_4^{2-}$ . Therefore, 7 M of potassium hydroxide solution is selected that it equals to PH 13. Moreover, there are other factors that affect on the form of zinc ions such as scan rates.

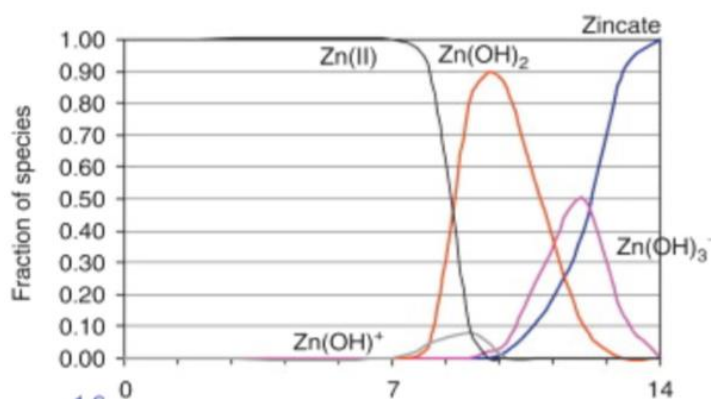
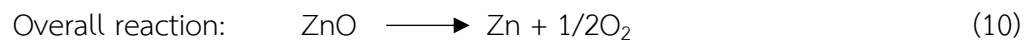
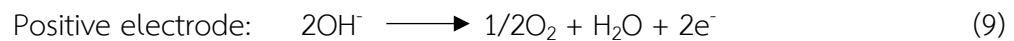
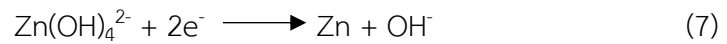
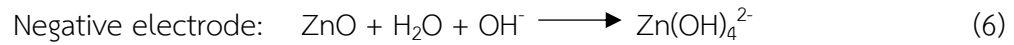


Figure 2 The diagram of zinc ions or zinc compounds at different PH values and room temperature [14].

Charge



In charge process, zinc is deposited from zincate solution at negative electrode. Oxygen is generated at positive electrode that is called oxygen evolution reaction (OER).

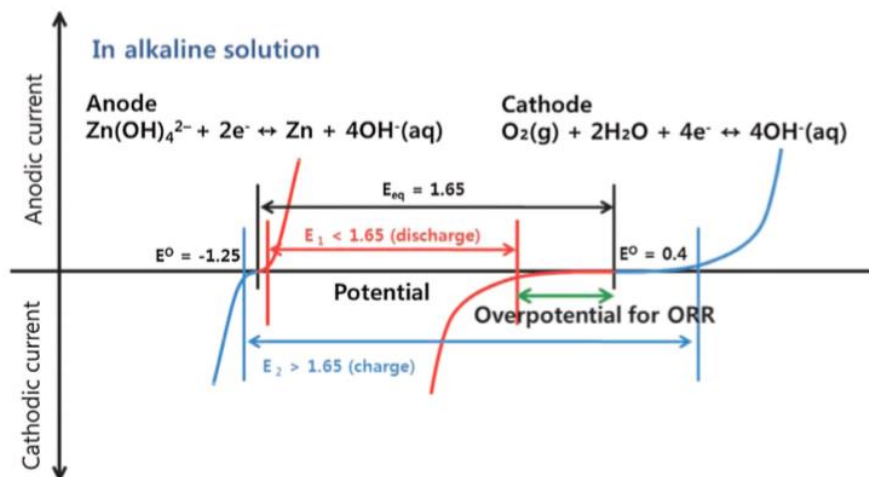


Figure 3 The polarization curve of zinc-air battery. Black line shows the equilibrium potential of zinc-air battery. Red line shows the potential during discharged process and blue line shows the potential during charged process [12].

From figure 3, the theoretical potential of zinc-air batteries is 1.65 V. Notwithstanding, the potential of discharged process is lower than 1.2 V in practice in order to get enormous current densities. Charged process is activated when a considerable potential, generally 2 V or above, is charged. Both potential discharged and charged process are divergent from equilibrium potential due to a large over-potential of oxygen reaction at air electrode. The main factors that influence on over-potential of

oxygen reaction are activation loss and dendritic formation. Activation loss is the loss of energy owing to slowness of electrochemical reaction that can be decreased by porous high efficiency bifunctional catalyst. Dendritic formation which is occurred at zinc electrode is another major problem for regeneration in zinc-air battery. The dendritic growth causes short cycle-life and a large over-potential. Moreover, it obstructs not only reactions but also flow of electrolyte at zinc electrode. It is broadly formed at zinc electrode during charged-discharged cycles.

#### 2.1.1.1 Zinc electrode

Zinc metal has widely chosen as a negative electrode for many systems ,for example, zinc-carbon, zinc-nickel and zinc-air [15]. The remarkable characteristics of zinc metal are high specific energy density, low cost, non-polluting, reversibility and wealth. The ideal morphology of zinc that is used for electrode is granules. In theory, the more surface area of zinc particles is high, the electrochemical reaction performance is better. Nonetheless, surface area of zinc particles escalates; consequently, side reaction takes place following equation (3) and finally it causes longevity challenge in battery. From equation (3), zinc reacts with water. Hydrogen is generated in system. This reaction isn't generate current which it is corrosion. Hydrogen that is produced causes swelling battery.

#### 2.1.1.2 Electrolyte

Electrolyte that is mostly used in zinc-air battery is strong base such as potassium hydroxide (KOH) and Sodium hydroxide (NaOH). KOH has been used over than NaOH due to its higher oxygen diffusion coefficients, lower viscosity, superior ionic conductivity [16]. Normally, 7 M or 30%w/w KOH solution is used owing to its maximum electric conductivity. Therefore, we use 7 M KOH as electrolyte in this research.

#### 2.1.1.3 Separator

The main function of separator in battery separates negative electrode from positive electrode. Separator that is suitable in zinc-air battery are high ionic conductivity and electrical resistance. Furthermore, separator should be strong

structure because of dendritic growth of deposited zinc in rechargeable zinc-air battery. The well-known separators have been used that are polyethylene (PE), polypropylene (PP), polyamide and polyvinyl alcohol (PVA). Normally, commercial separator for zinc-air battery that is used is laminated nonwoven separators such as Celgard 5550 [17]. Laminated nonwoven separators have 3 layers structure which are PP/PE/PP. The PP layers is fabricated to sustain the coherence of the separator. PE is designed to shut down zinc-air battery when the battery is overheat. Celgard 5550 is showed in figure 4.

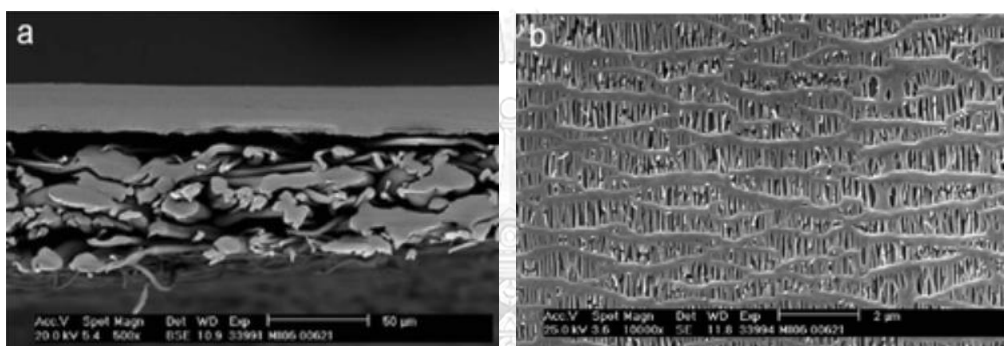


Figure 4 Structure of laminated nonwoven separator membrane (Celgard 5550) is used in zinc-air battery (a) A cross-section and (b) a top-view of the separator [17].

#### 2.1.1.4 Air electrode

From equation (4) or ORR, oxygen diffuses through catalyst particles layer to contact electrolyte that is showed in figure 5. The reaction can be occurred both two (solid and liquid) and three (solid, liquid and gas) phases. Rates of reaction in three phases are faster than two phases because liquid has oxygen solubility and diffusivity lower than gas. The structural design of air electrode is complex since air electrode have two sides that one side contacts with electrolyte and another one contacts with atmosphere. Therefore, the selection chemistry for air electrode should have hydrophobic property. The hydrophobic property controls the amount of water both sides that should be different. The side that contacts with atmosphere should confine water at the catalyst layer in order to facilitate oxygen from atmosphere occuring maximum reaction. Another one has hydrophilic property because it requires water to happen the reaction. But, If it has extream hydrophilic property, it will cause flooding [15] that makes efficiency of catalyst decrease. Gas diffusion

electrode that has been widely used is polytetrafluoroethylene (PTFE) - bonds carbon layers. Well balanced hydrophilicity and hydrophobicity in air electrode can restrain extreme flooding. The ratio of carbon and PTFE should be properly varied [18, 19]. Oxygen permeability is required maximum so, the GDEs should be as thin as possible.

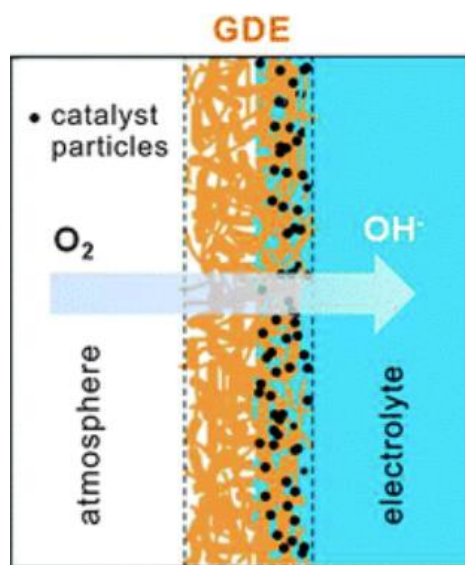


Figure 5 The architecture of gas diffusion electrode. Oxygen diffuses through atmosphere to occur ORR on electrocatalyst [17].

#### 2.1.1.5 Application of rechargeable zinc-air batteries

In the 1960s, rechargeable zinc-air batteries were investigated for powering portable military electronic equipment because of their high energy density and easy recharging. Electronic vehicles (EVs) have been evolved by rechargeable zinc-air batteries since 1990s. Cooper and co-workers [20] created a self-feeding feature that added zinc pellets and the alkaline electrolyte to minimize the refueling time to less than ten minutes for 15 kW, 55 kWh battery unit. The advantages of EVs powered by rechargeable zinc-air batteries which is compared with conventional vehicles are safety, low cost, better performance and time of refueling.

### 2.1.1.6 The obstruction of zinc-air batteries

#### 2.1.1.6.1 Morphologies of zinc deposits

Shape changes and dendrite growth are due to high solubility of zinc and migration of zinc. The migration of zinc causes irreversible loss of capacity and stimulates dendritic formation. The dendritic formation pierces through separators and causes short circuit. There are five main types of deposited zinc that are dendrite, mossy, spongy, boulder, layer-like and filament shown in figure 6. The appearances of boulder deposits have hexagonal structure, transparent planes and sharp angles. Layer-like has epitaxial growth and occurs at the beginning of deposition. Mossy deposits have intertwined folds with diameter in ranges of 50-200 nm and lengths which aren't more than 5  $\mu\text{m}$ . Dendritic formation looks like tree or leaf and it can be hexagonal columns if deposition is slowly operated. Layer and boulder of zinc deposits are formed in the early stage of deposition. They are substituted by other morphological pattern later. Mossy deposits is formed at low current densities as dendrite deposits is formed at high current densities. Cluster deposits start to form at very high current densities which cluster is highly branched dendrite.

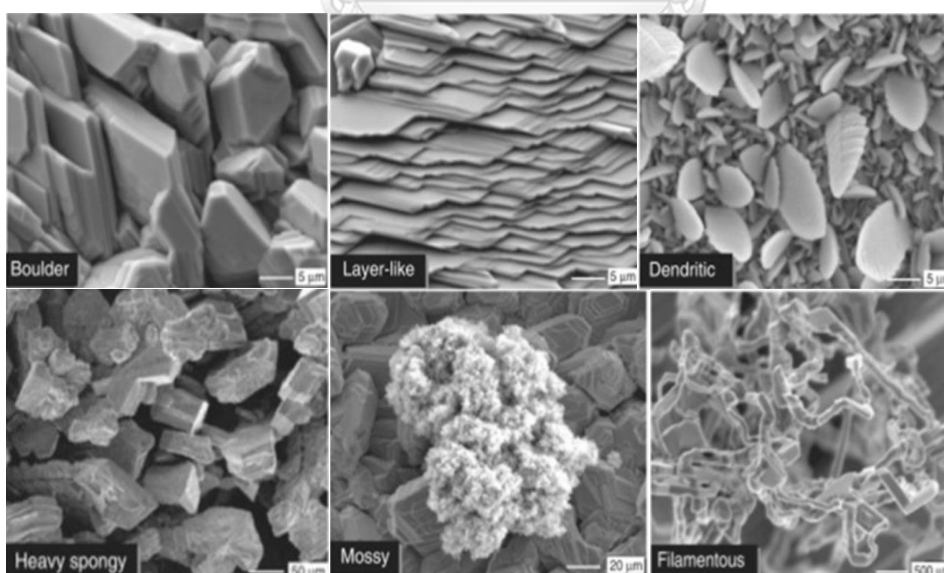


Figure 6 The different morphologies of deposited zinc [14].

#### 2.1.1.6.2 Zinc passivation

Zinc passivation takes place dissolution of metal which makes a surplus zinc and hydroxide ions in electrolyte close to electrode creating a compact solid film. The film acts as obstacle to  $\text{OH}^-$  ion and causes capacity and capability of zinc anode decrease. There are two types of zinc oxide film. The first type is a result of precipitation of solution causing porous of film that  $\text{OH}^-$  ion is hard to diffuse to surface of metal. The another type is a result of changing PH values of electrolyte that makes concentration of  $\text{OH}^-$  ion change. Using the high concentration of alkaline solution minimizes zinc passivation but, it causes shape changes. The another way that reduces passivation is using additives. An additives with electrolyte enhances electrode surface and inhibits passivation film such as silicate ( $\text{SiO}_3^{2-}$ ) [21].

#### 2.1.1.6.3 Carbonation

Hydroxide ion reacts with carbon dioxide to produce carbonate ( $\text{HCO}_3^-$ ) or bicarbonate ( $\text{CO}_3^{2-}$ ) components. The reactions are shown as following



An effect of carbonate components causes poor conductivity because diffusion of carbonate ion is slower than hydroxide ion. Air electrode is clogged up due to low solubility of carbonate ion and high viscosity of electrolyte. Hence, oxygen is hard to diffuse.

#### 2.1.2 Spouted-bed reactor

A Spouted-bed reactor is a bed of particles that is filled in vertical column with conical bottom. A jet of fluid is fed through a nozzle at the center of the bottom of the reactor. If the velocity of the fluid is sufficiently high, it makes particles move up rapidly in the center of bed. Then, the fluid velocity drops. The particles fall back around the annulus of the bed until the fluid velocity becomes high again [10]. The diagram of spouted-bed reactor is shown in figure 7. There are three



sections of spouted-bed reactor that are spout, annulus and fountain. The annulus is like packed bed that is as a moving electrode. The spout and annulus correspond to fluidized bed that doesn't touch with current feeder.

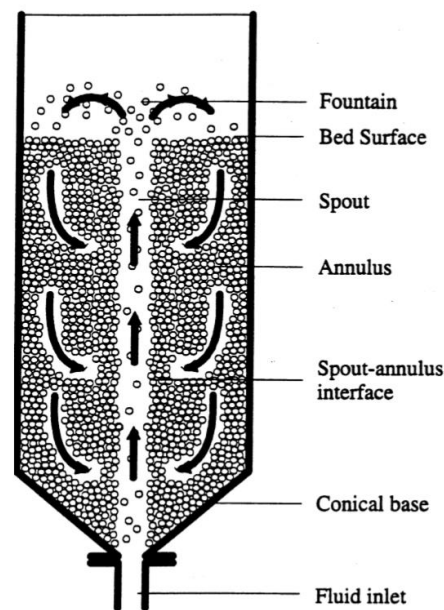


Figure 7 Sketch of spouted-bed reactor [10]

In this research, spouted-bed reactor has investigated to use in metal electrodeposition from alkaline solution. The bed is connected with negative electrode and metal is deposited on particles due to cathodic reaction. Generally, the anodic reaction evolves oxygen.

### 2.1.3 Electrodeposition

When the charged process is operated, the metal electrodeposition of zinc on stainless steel substrate occur. According to Peng Wen Jie [22], the mechanism electrodeposition of zincate solution was proposed as followed :



Two charged transfer in equation 14 and 15 step by step. The first reaction of receiving electron was slow reaction which it showed this step was rate-determining step.

## 2.2 Literature reviews

In the present, Zn-air fuel cell (ZAFC) has been widely investigated in many researches because it is a promising energy source. ZAFC has been applied for hearing-aids and medical devices. There are two electrochemical systems in ZAFC i) power generation system ii) Zn regeneration system. In this research, we focus on Zn regeneration system with spouted bed electrode. In these literatures, we can be mainly divided three parts that are Zn-air batteries, zinc regeneration and spouted bed electrode (SBE).

### 2.2.1 Zinc-air battery

Zinc-air batteries is an attractive choice for energy sources because they have well balance for energy densities, kinetics, reversibility and stability. In addition, they are easy to operate, low cost and excellent rechargeability [23]. J.F. Cooper [24] studied that zinc-air systems showed power level from 170 to 350 Wh/kg. Moreover, power level can be increased to 500-600 Wh/kg in the future. Zinc-air batteries are the highest energy density of primary batteries, so they are used in many applications. O. Hass [25] developed and showed that zinc anode and spent electrolyte was replaced by fresh particles, so it was possible to make rechargeable zinc-air batteries. The rechargeable zinc-air batteries have many problems such as cycle life, non-uniform morphologies and inefficiency of air catalyst.

### 2.2.2 Zinc regeneration

A major problem for zinc regeneration that related to longevity is a morphology of zinc. There are various undesired morphologies that cause obstacle for zinc regeneration such as dendrite and spongy forms showed in figure 2.6. The morphologies of zinc deposits are main factor to determine reusability of regenerated zinc in discharge process. Hence, granular zinc is desired from

deposition. The different morphologies of zinc deposits showed different characteristics of them. XG Zhang [26] studied characteristics of zinc deposits. There are many factors that determine morphology of zinc such as electrode materials, additives and solution chemistry [14]. R.D.Naybour [27] investigated the morphologies of zinc deposits at various current densities that showed dendrites created at high current densities ( $100 \text{ mA/cm}^2$  or over), layer mixed with granules at moderate current densities (between 4 and  $20 \text{ mA/cm}^2$ ) and mossy morphology at low current densities (lower than  $4 \text{ mA/cm}^2$ ). McBreen et al. [28] have studied using Cu, Au, Cd, Pb, Ti, Sn and In as a negative electrodes and effect of morphologies zinc deposits. For positive electrodes in regeneration zinc system, Au, Pt are always selected for laboratory scale, but steel, Ni are always selected for industrial process. P.J.Sonneveld [29] found that glassy carbon electrodes were hardly selected for the regeneration of zinc from zincate solution because glassy carbon electrodes tended to cause mossy formation of zinc deposits. Additives are critical role in electrolyte and electrode because they affect on structure and morphology of zinc deposits. J.L Zhu [30] found that lanthanum and neodymium hydroxides coated on zinc electrode could suppress the shape change of zinc electrode. The effect of addition Bi ions in electrolyte was investigated by J.M.Wang [31] so, he found that Bi ions impeded dendrite growth due to the distribution of Bi on zinc electrode surface. Spongy forms were inhibited by Pb and  $\text{Na}_2\text{WO}_4$  [32]. Tetrabutyl ammonium bromide (TBAB) has exhibited that impeded the dendritic formation [25, 31]. R. Shivkumar [33] showed that ZnO was used as an additives shown positive effect such as decreasing the electrode corrosion and increasing the cycle life and discharge capability. Conductivity of electrolyte increases when concentration of KOH increases to about 30% by weight then it decreases at over 30% by weight. Hence, the electrolyte is used about PH 6-7.

### 2.2.3 Spouted-bed reactor

Salas-morales studied using spouted-bed electrochemical reactor for electrowinning process [10]. There were two types of spouted-bed reactor that were cylindrical and flat shapes showed in figure 8. Cell voltages for cylindrical cell were higher than flat cell. Therefore, energy consumptions of flat cell were lower than cylindrical cell. Current efficiencies were same both cells. A.verma [34] investigated angle of bed that found 60 degree prevented dead zones. Dead zones which are area of stationary particles. Dead zones generally occurred 45 degree. The flow rates of electrolyte shall be suitable with height of bed. If flow rates were low, the bed was packed bed. If flow rates were high, the bed was fluidized bed. Moreover, minimum spouted flow rates were independent on other variables except height of bed and particles size. There was installation a draft tube to minimize expansion of fluid jet and reduce pressure drop. The draft tube also serves as current feeder.

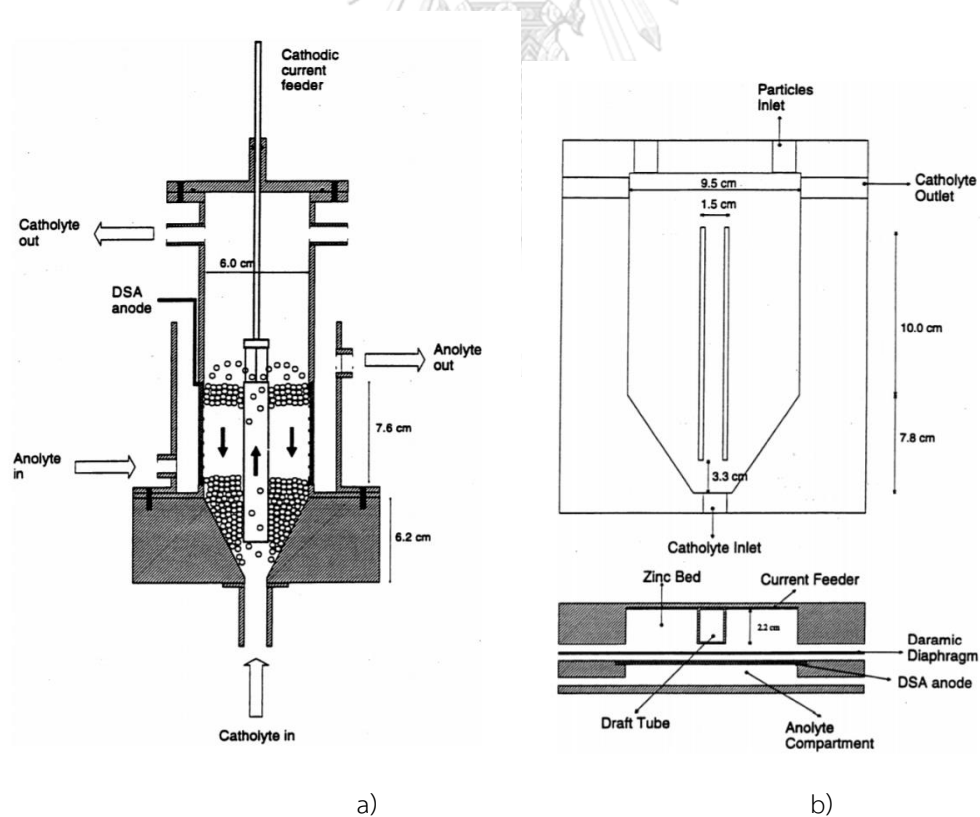


Figure 8 Two types of spouted-bed reactor [10]

a) Cylindrical b) Flat

Jiricny [35] studied electrodeposition zinc on zinc wire from hydroxide electrolyte. It was found that spouted-bed electrochemical reactor can be used to regenerate particles from spent electrolyte. In most cases, electrical energy consumption is low for current densities under  $1,500 \text{ A/m}^2$ . Particles can be grown from 0.4 to 1 mm for long term experiment (58.5 hours) that was showed in figure 9. The final particles exhibited porosity although they had rough surface. It was found that high current efficiency (above 95 percentages) was attained for various current densities.

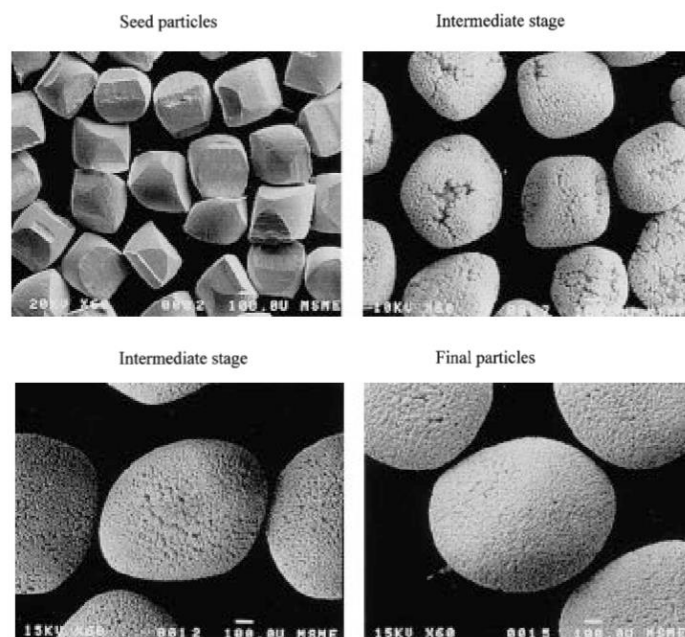


Figure 9 SEM micrographs of zinc particles at different stage of growth [35]

P.A.Shirvanian [36] investigated copper recovery from acidic solution by cylindrical spouted-bed reactor. It was found that current efficiencies were function of temperature and PH values. A slowly of moving bed was desirable because particles can touch with current feeder. The particles bed must keep moving to prevent agglomeration of particles. The anode and cathode electrode should set as near as possible. Spouted-bed electrowinning of zinc from chloride solution was studied [37]. At higher current densities, cell voltage increased, and minimum energy consumption was  $3.8 \text{ kWh/kg}$  at current density  $2,000 \text{ A/m}^2$  because current efficiency increased with low current densities.

## Chapter 3

### Methodology

#### 3.1 Cell design and fabrication

The anodic and cathodic compartments of the cell for electrochemical regeneration of zinc are made from two pieces of milled plexiglass 220 x 80 mm<sup>2</sup> that are showed in figure 10. The diminishing zone is 60 degree measured against the horizon to prevent dead zones. The catholyte and anolyte inlets and outlets are 5 mm in diameter. A cathode current collector is a copper plate of 220 x 80 mm<sup>2</sup> and an anode is a stainless steel plate of the same size. Between the anode and cathode compartments is Teflon fabric reinforced Nafion membrane. Silicone gaskets are inserted between layers of cell components for sealing. C-clamps are used for holding the cell together.

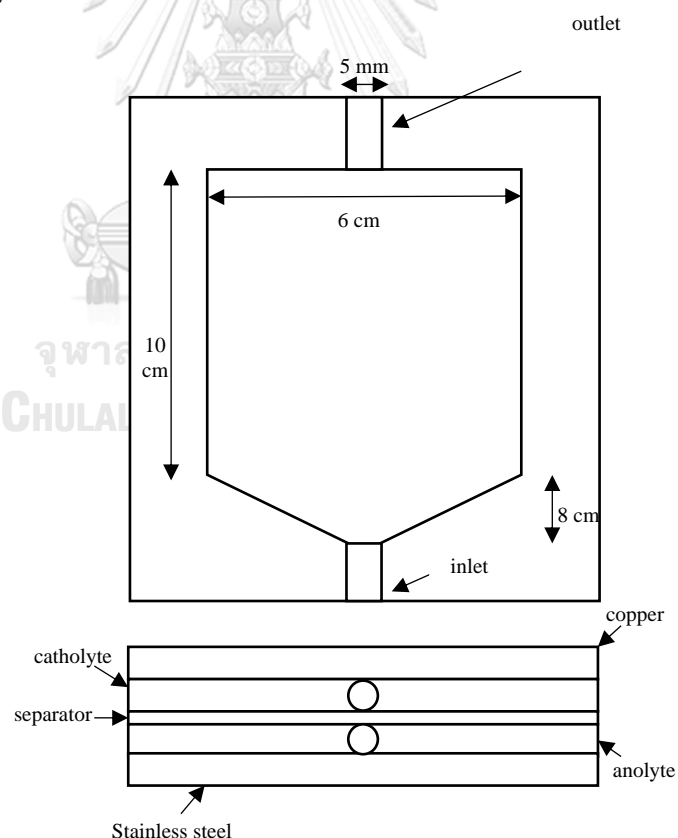


Figure 10 Engineering drawing of spouted bed reactor

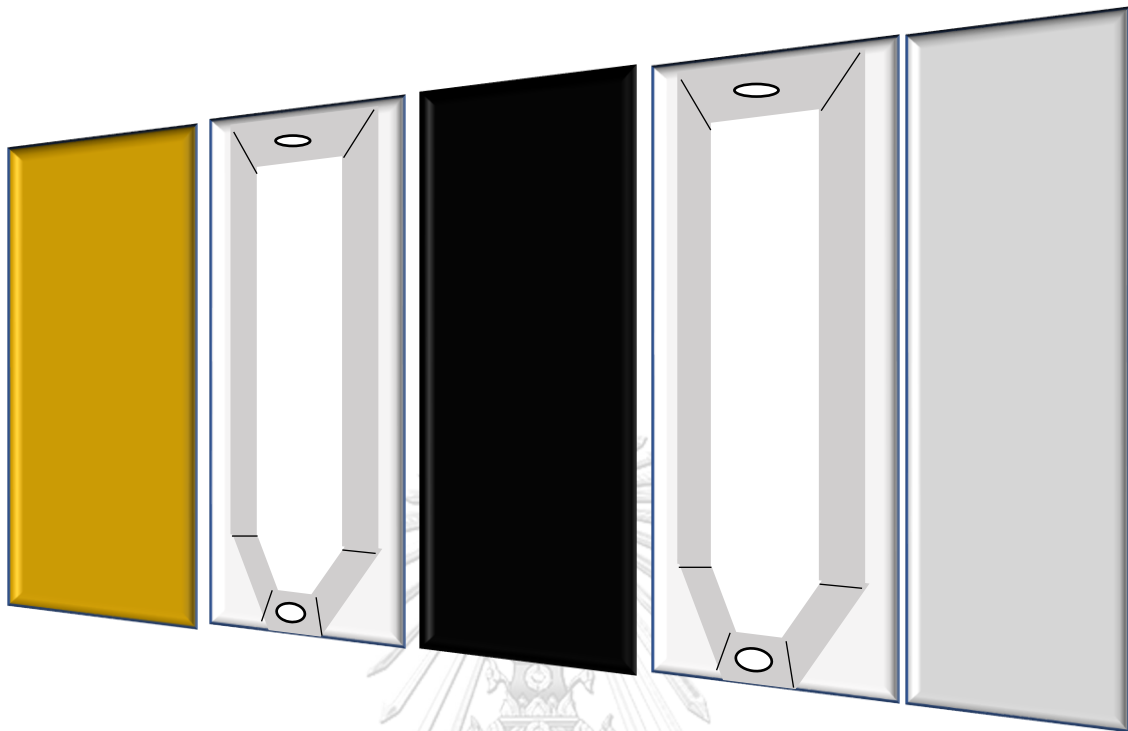


Figure 11 spouted bed reactor

Table 1 Design of cell

Cell	Dimension (cm)
Height	22
Wide	13
Inlet and outlet	0.5

Table 2 Design of component

Component	Material
Anode electrode	Stainless steel
Cathode electrode	Copper
Separator	Cation-exchange membrane
Cathode current collector	Copper
Anode current collector	Copper
Body	PLEXIGAS
Catholyte	500 cm <sup>3</sup> of 6 M KOH saturated with Zinc oxide 10 % w/w
Anolyte	500 cm <sup>3</sup> of 6 M KOH

### 3.2 Chemicals

Potassium hydroxide pellets (AR) and zinc oxide (AR) were purchased from QRec. 1 mm spherical stainless steels were obtained from a local supplier. Copper plate (220×80 mm<sup>2</sup>) and stainless steel plate (220×80 mm<sup>2</sup>) were obtained from a local supplier.

### 3.3 Preparation of electrolytes

500 cm<sup>3</sup> of 6 M KOH is used as anolytes. The catholyte is 500 cm<sup>3</sup> of 6 M KOH saturated with 10 wt % of zinc oxide.

### 3.4 Procedure

5 grams of stainless steel particles are placed in the cathode compartment of the cell which stainless steel particles are supported by stainless mesh. Both electrolytes are pumped to the cell from separated tanks by a peristaltic pump that flow rates are set at 250 ml/min. Battery metric is connected to the current collector to supply 10, 20, 30 and 40 mA/cm<sup>2</sup>. The cell is connected to battery metric in order to use BA500WIN software. Each batch operation is carried out for 4 hours. Then, the particles were removed from the cell, washed with DI water, dried and analyzed.



### 3.5 Characterization

The morphologies of the zinc particles were characterized by scanning electron microscope (SEM) and EDX for approximate chemical composition of the regenerated zinc particles.

### 3.6 Faradiac efficiency

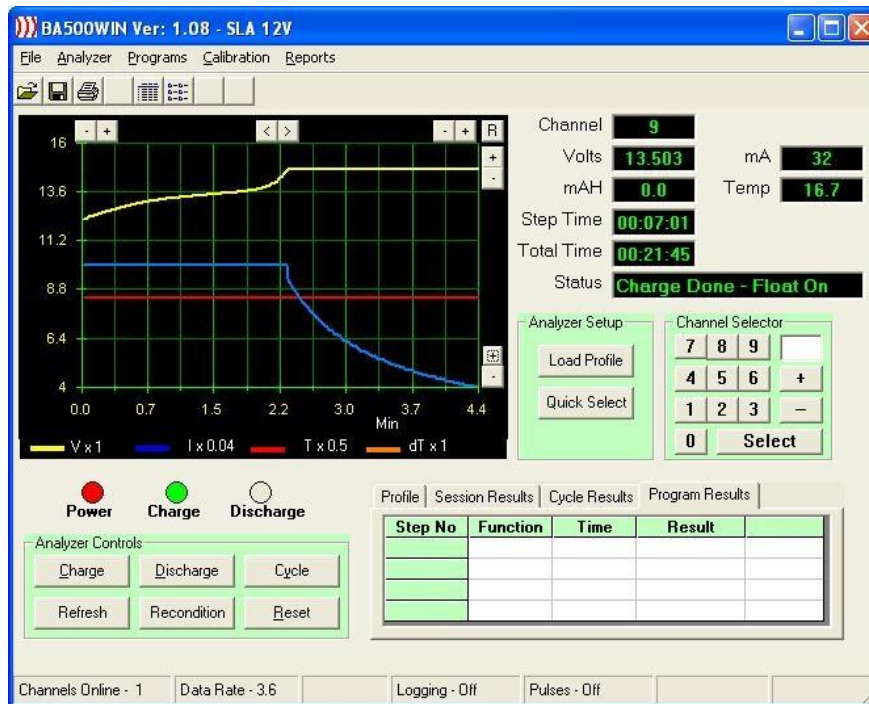
Faradiac efficiency or current efficiency express the portion of electrons that are passed into the cell and take part in the desired reaction. The formula for the current efficiency of zinc electrodeposition is:

$$\text{Mass of the deposited (theory)} = \frac{QM}{NF}$$
$$\% \text{Eff.} = \frac{\text{Mass of deposited}}{\text{Mass of deposited (theory)}} \times 100$$

where M is Molecular weight of zinc, N is 2 for this reaction, F is Faraday's constant (96,487 C/mol) and Q is electric charge passed.

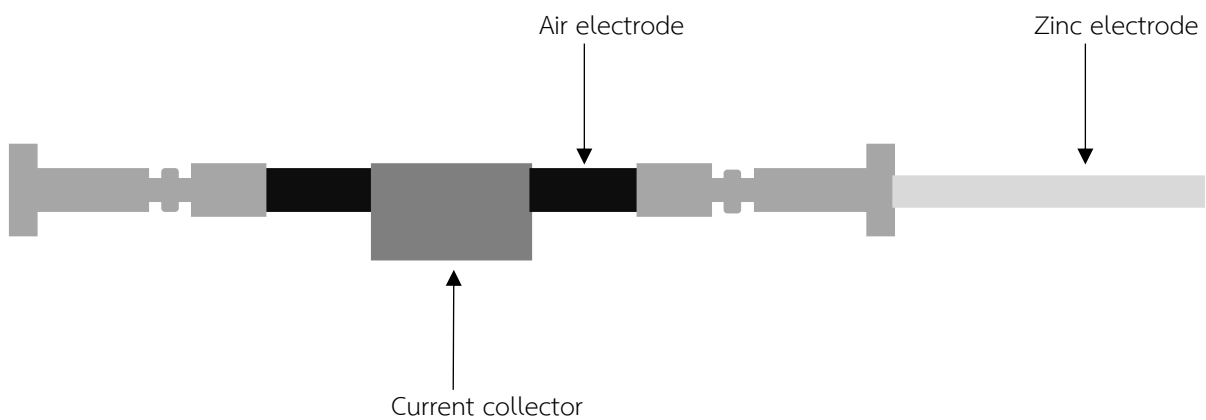
### 3.7 BA500WIN software

BA500WIN is program that can control and monitor a battery test session. You must have battery metric to connect with your computer for using this program during the test session. This program has on screen controls, integrated graph and data reporting and several ways to set up the test parameters to begin a battery test session. This program has many features such as research and laboratory that make it convenient to change the test parameters. There are different charging & discharging scenarios, collect a lot of data and view various reports.



### 3.8 Zinc-air battery

The zinc electrode is regenerated zinc deposits. The air electrode with active area  $14 \text{ cm}^2$  is applied which consist of nickel foam coated with polytetrafluoroethylene (PTFE) binder, glucose, sodium bicarbonate ( $\text{NaHCO}_3$ ) and acetylene black 50 .The catalyst side is composed of nickel foam coated with black pearl 2000, manganese dioxide ( $\text{MnO}_2$ ) and polystyrene binder.



## Chapter 4

### Results and discussion

#### 4.1 Short experiments (varying current densities)

Batch operations were performed for 4 hours by varying current densities that were 10, 20, 30 and 40 mA/cm<sup>2</sup>. The short operations were carried out in order to study performance of cell. Figure 13 showed preliminary experiments that exhibited current efficiencies and cell voltages at various current densities.

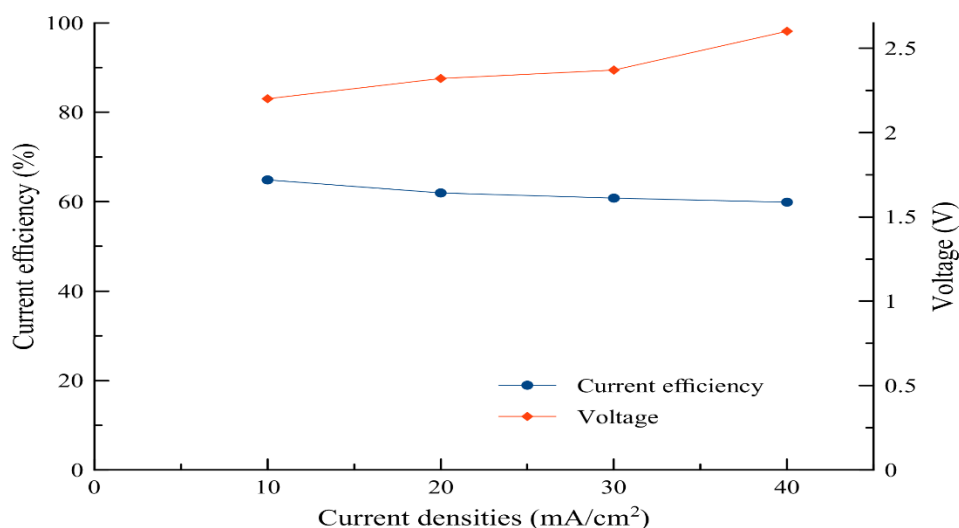


Figure 14 current efficiency versus current densities (blue line) and cell voltage versus current densities (orange line)

From figure 14, current efficiencies were about 60-65% which they tended to decrease at higher current densities. As reported by Alias and Azmin Mohamad [38], the current efficiency was about 90% because their research set low current density. Low current density caused high current efficiency, but mass of zinc deposits was obtained low which was 0.0276 grams per 1 hour at 0.1 mA/cm<sup>2</sup>. In this research, mass of zinc deposits was obtained about 0.7 grams per 4 hours at 1 A/cm<sup>2</sup> that was shown in table 3 for other current densities. The calculation of current efficiency was displayed in Appendix A1. It was found that if it was required high current efficiency,

low mass of zinc deposits was gained, and it took long time to get adequate mass of zinc deposits for application in zinc-air battery.

Table 3 Efficiency of Zn electrodeposition at different current densities for 4 hours

Current density (mA/cm <sup>2</sup> )	Mass gain (g)	Efficiency (%)
10	0.225	64.87
20	0.44	63.36
30	0.62	60.8
40	0.71	59.9

At higher current density, there was charge more than lower density. There was hydrogen evolution reaction that hydrogen was produced on zinc surfaces during electrodeposition process. The reaction occurred adsorption of hydrogen ion ( $H^+ + e^- + Zn \longrightarrow ZnH_{ad}$ ) which take placed at active sites via weak Vann der Waals bonds and the desorption of hydrogen gas from zinc surfaces ( $ZnH_{ad} + H^+ + e^- \longrightarrow Zn + H_2$ ) according to Baik and Fray [39]. High current density had more electron charge than low current density that tended to occur reaction with hydrogen ion in order to produce hydrogen gas. The high rate of hydrogen evolution led to low current efficiency. Cell voltage increased when current density increased, since voltage was direct proportional with current accordingly Ohm's law. The voltages had 2.2-2.6 volt range that was consistent with Jirichy [35].

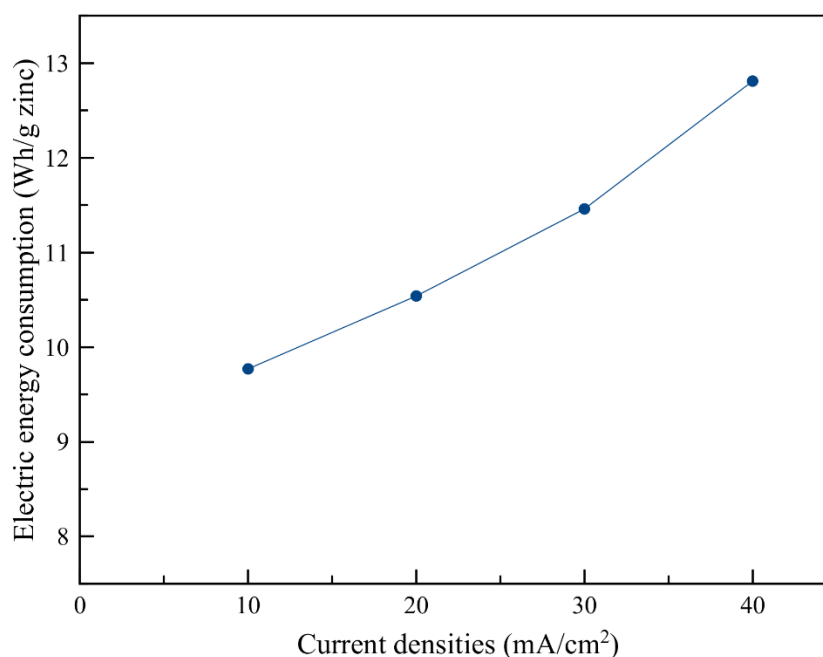
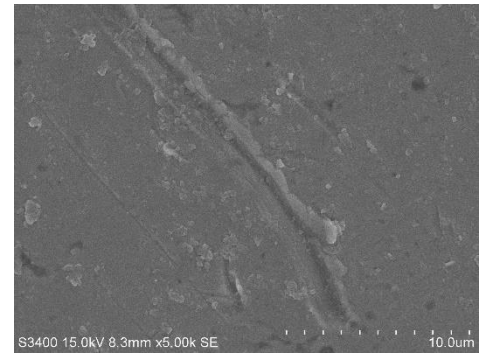
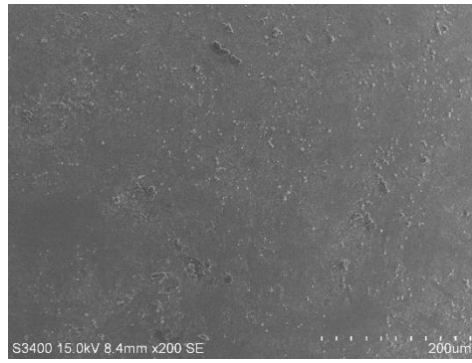
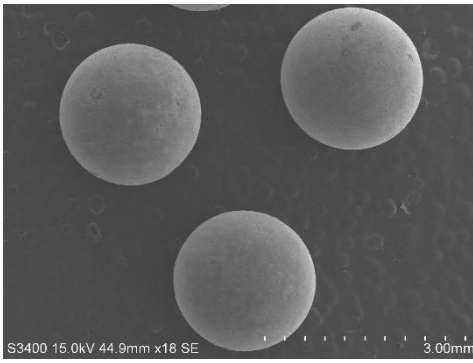


Figure 15 Current densities versus electric energy consumption

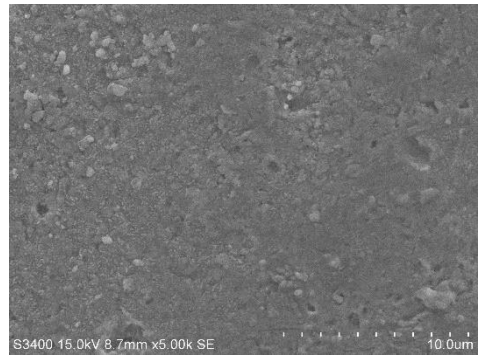
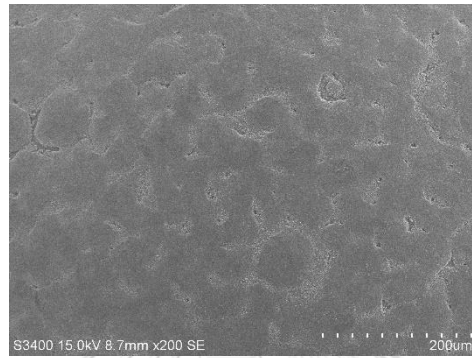
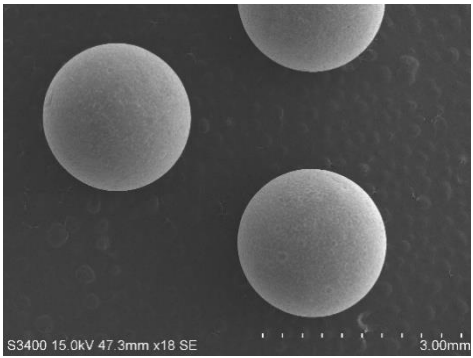
From figure 15, electric energy consumption increased with increased current density because power was direct proportional with current and cell voltage. Hence, higher current and cell voltage caused higher electric energy consumption. The range of electric energy consumption was about 9-15 Wh/g zinc for 4 hours at 10, 20, 30 and 40 mA/cm<sup>2</sup>. Roy and Evans [40] explained that, at higher current density, gas was produced at anode. There was entrapment of bubble on separator that caused loss conductivity and increasing cell voltage. Currents and cell voltages increased so, electric energy consumption increased.

#### 4.2 Morphology study of zinc deposits

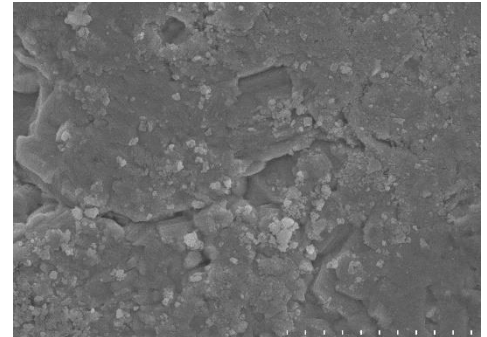
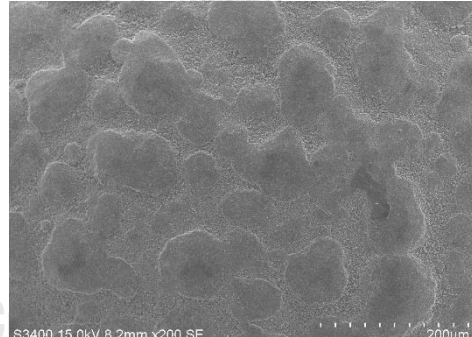
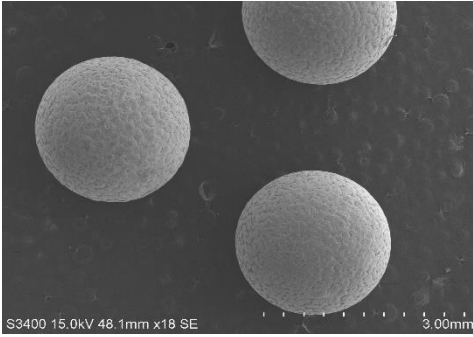
In short term experiments, there was study morphology of zinc deposits at 10, 20, 30 and 40 mA/cm<sup>2</sup> and EDX was used for elemental analysis which indicated that zinc could electrodeposit on stainless steel surfaces.



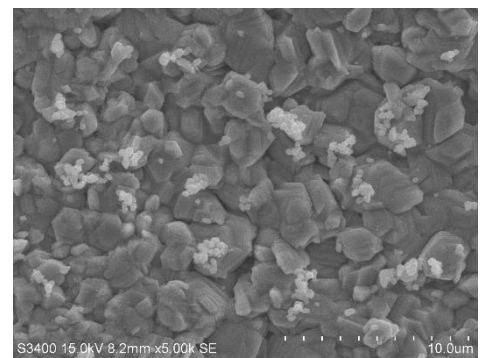
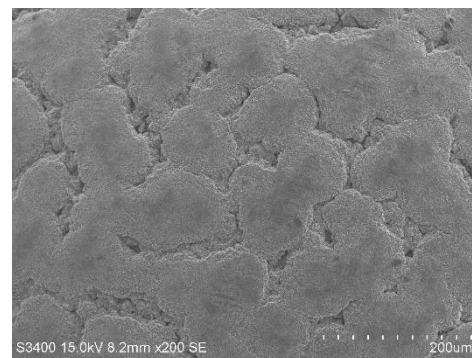
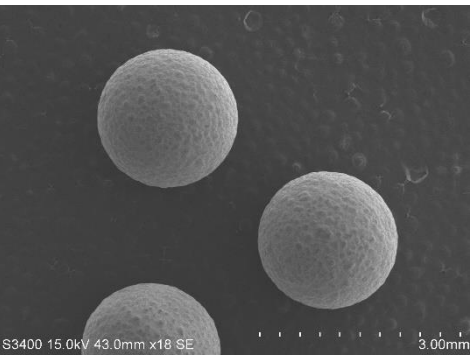
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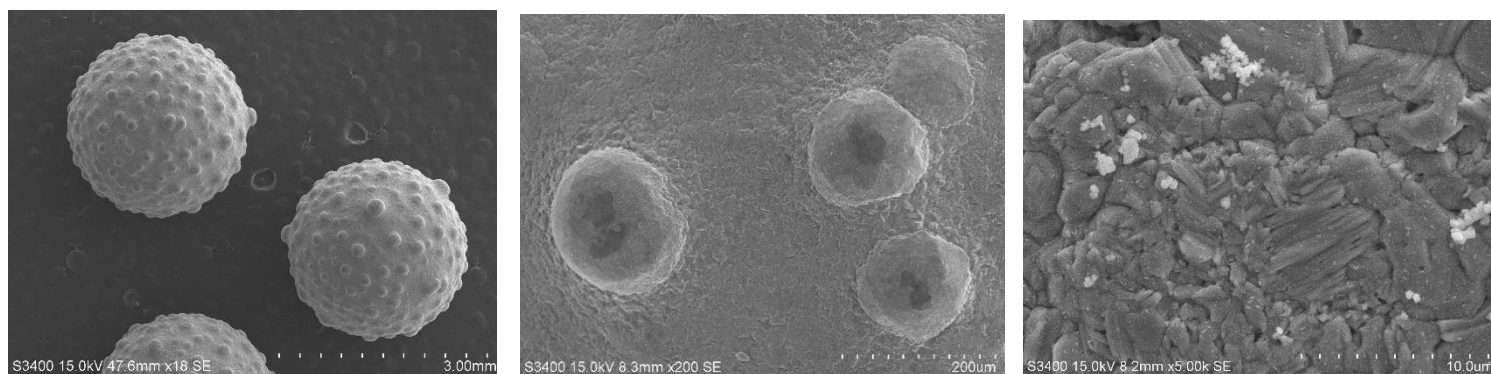
b)



c)



d)



e)

Figure 16 SEM micrographs of zinc deposits a) bare stainless steel b)  $10 \text{ mA/cm}^2$  c)  $20 \text{ mA/cm}^2$  d)  $30 \text{ mA/cm}^2$  e)  $40 \text{ mA/cm}^2$

From figure 16a-e), showed the surface morphology of stainless steel substrate and zinc electrodeposited on steel substrate at different current densities. Smooth surfaces can be noticed for stainless steel (Fig 16a) before electrodeposition processes. At  $10 \text{ mA/cm}^2$  (Fig 16b), a rough surface started to appear on surface of Zn deposited on stainless steel. At  $20 \text{ mA/cm}^2$  (Fig 16c), there was appeared irregular growth of zinc deposits and rate of electrodeposition slowly increased. Microporosity emerged on zinc surface and nucleation was observed on the stainless steel surface. When current density was increased to  $30 \text{ mA/cm}^2$  (Fig 16d), the morphology of zinc deposits began to transform hexagonal-like crystalline structure with flake-like-layer on stainless steel surface. In addition, macroporosity expanded while microporosity decreased. In this case, dense nucleation was identified when zinc was deposited that current densities were more than  $30 \text{ mA/cm}^2$ . Finally, A very rough surface of zinc deposits was noticed at high current density  $40 \text{ mA/cm}^2$  (Fig 16e) and zinc agglomerated which deposited on zinc surface on substrate. Hexagonal-like crystalline structure diminished, layer-by-layer structure grew with decreased flake-layers and the stainless steel surface was fully concealed by zinc deposits. It was found that the rate of zinc deposition and morphology of zinc deposits depended on current.

When current was input to the process, electrons moved to the negative electrode. Then, the negative electrode was encircled by  $Zn^{2+}$  and  $H^+$  ions that the ions were adsorbed onto the substrate surface by way of a feeble Van der Waals bond. This bond caused diffusion on the surface which reduction of ions occurred at favorable sites. The reduction of  $Zn^{2+}$  for deposition zinc metal on substrate was receiving two electrons to create zero-valent zinc metal. The clarified equation reaction was shown as follows:



Indeed, hydrogen ( $H_2$ ) gas was produced from the reduction of  $H^+$  which contest with reduction reaction of Zn. The equation of hydrogen evolution was illustrated as follow:



Because low electrons transferred to negative electrode, the rate of electrodeposition process was low at current density  $10 \text{ mA/cm}^2$ . Hence, a few  $Zn^{2+}$  were reduced and deposited on the substrate. Nevertheless, the rate of electrodeposition rose with increasing current density. At high current density, a enormous amount of  $Zn^{2+}$  was reduced to form dense and layer structure of the nucleuses which many nucleuses were created close together on substrate in nucleation step then, zinc deposits grew and held together formed rough surface in growth step whereas a few nucleuses were formed far away in nucleation step at a low current density so the surface of zinc deposits in growth step was smoother than high current density. The adsorption of hydrogen bubbles from hydrogen evolution that was shown in equation 18 were related to the irregular growth of zinc deposits. Goodarzi [41] described that a change of morphology of zinc occurred owing to the increased in current density. Moreover, a hexagonal-like crystalline structure was a general of morphology zinc deposits for no additives in electrolyte solution that was



reported by Ponce-De-Leon [42] and Gomes [43]. The morphology was transformed from smooth to irregular structure and continued to rough and layer-by-layer structure at high current density. Based on morphology for these results, zinc deposits at current density  $40 \text{ mA/cm}^2$  was chosen for usage in long term experiment because of the maximum rate of electrodeposition process and acceptable morphology of zinc deposits which zinc deposits at current density  $40 \text{ mA/cm}^2$  were used as anode electrode for zinc-air battery.

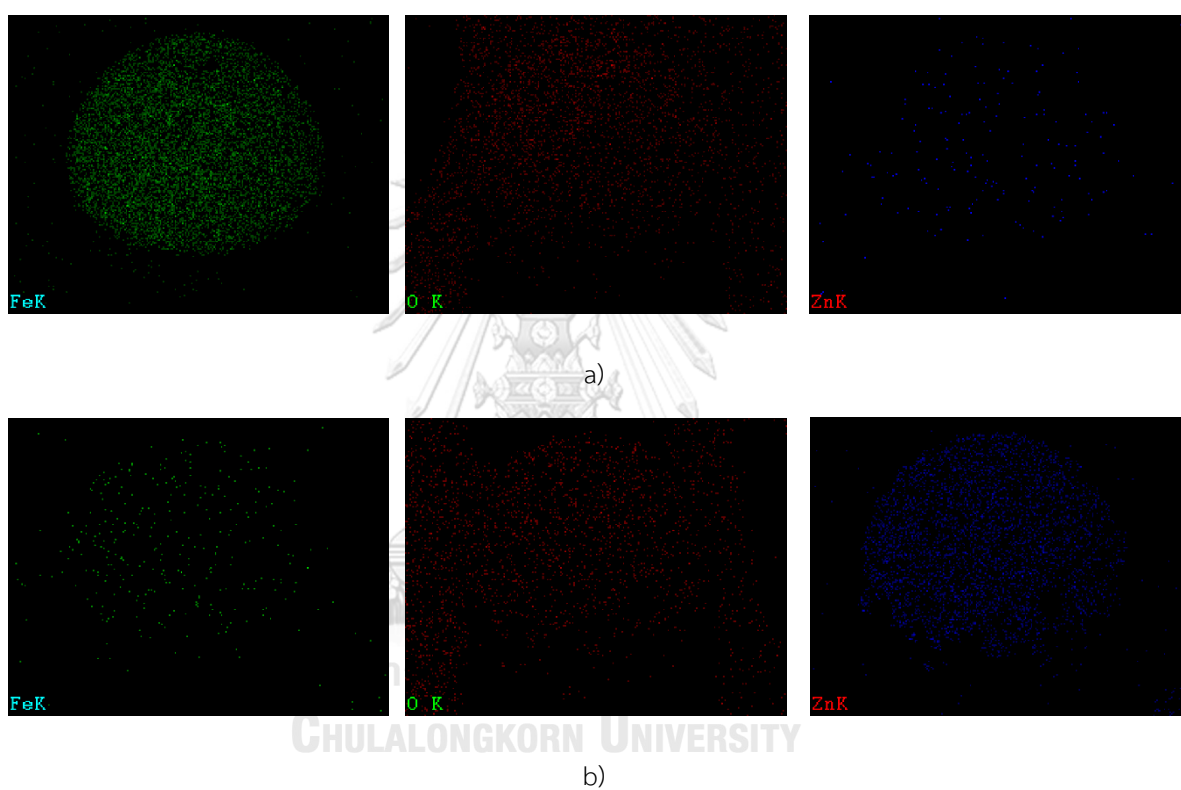


Figure 17 EDX analysis for bare stainless steel and zinc deposits at current density  $40 \text{ mA/cm}^2$  a) bare stainless steel b)  $40 \text{ mA/cm}^2$

From figure 17, elements mapping revealed that percent weight of bare stainless steel (Fig17a) showed 90.56 wt% of Fe (left), 8.54 wt% of  $\text{O}_2$  (middle) and 0.89 wt% of Zn (right). Percent weight of zinc deposits at current density  $40 \text{ mA/cm}^2$  (Fig16b) exhibited 1.97 wt% of Fe (left), 4.29 wt% of  $\text{O}_2$  (middle) and 93.74 wt% of Zn (right). Compared with figure16a and figure16b, it was proved that zinc can be deposited on stainless steel substrate because the element points at current density  $40 \text{ mA/cm}^2$  of

zinc were more dense and packed than bare stainless steel which had few point and sparse and percent weight of zinc increased at current density 40 mA/cm<sup>2</sup>.

#### 4.3 Long term experiments

Long term experiments were fulfilled as part of investigation. For the first run, electrodeposition was operated with total time 16 hours at current density 40 mA/cm<sup>2</sup> that the largest single run time was 5.3 hours. Another run was operated with total time 32 hours at current density 20 mA/cm<sup>2</sup> that the largest single run time was 5.8 hours.

Table 4 Long term experiment at current density 40 mA/cm<sup>2</sup> for 16 hours

No.	Time (h)	Cell voltage (V)	Zinc deposited (g)	Current efficiency (%)	Electric energy consumption (Wh/g)	Charged passed (mAH)
1	3	2.6	0.6	59.06	13	2999
2	4	2.65	0.82	62.89	12.93	3849
3	5.3	2.8	1	56.64	14.84	5211
4	4	2.89	0.9	66.78	12.84	3978
summary	16.3	2.735	3.32	61.35	13.4	16037

From table 4, it was concluded that seed particles increased from initial size about 0.4 mm with 16 hours for electrodeposition at current density 40 mA/cm<sup>2</sup>. The average cell voltage was 2.735 volts, masses of zinc can be regenerated from electrolyte about 3.32 grams, average current efficiency was about 61.35 %, overall of charged passed was 16037 mAH, an average and total electric energy consumption were 13.4 Wh/g and 53.62 Wh/g respectively.

Table 5 Long term experiment at current density 20 mA/cm<sup>2</sup> for 32 hours

No.	Time (h)	Cell voltage (V)	Zinc deposited (g)	Current efficiency (%)	Electric energy consumption (Wh/g)	Charged passed (mAH)
1	4.1	2.32	0.44	63.36	10.81	2050
2	6	2.6	0.61	62.46	12.79	2883
3	4.2	2.46	0.43	60.42	12.01	2101
4	4.17	2.4	0.43	60.76	11.64	2089
5	5.5	2.47	0.49	52.40	13.86	2760
6	5.8	2.6	0.53	54.17	14.22	2888
7	2.3	2	0.23	57.44	10	1182
summary	32.07	2.4	3.16	58.72	12.19	15953

From table 5, it was shown that the average cell voltage was 2.4 volts, the masses of zinc that can be regenerated were 3.16 grams, the average current efficiency was 58.72 %, overall charged passed was 15953 mAH, an average and total electric energy consumption were 12.19 Wh/g and 85.34 Wh/g respectively. From the results of long term experiments, the average electric energy consumption of both runs was close to short term experiment. Current density was varied 2 times which was from 20 mA/cm<sup>2</sup> to 40 mA/cm<sup>2</sup> and time of electrodeposition was varied 2 times that were 16 hours and 32 hours. It was indicated that the overall charged passed and the number of zinc deposited at current density 40 mA/cm<sup>2</sup> and 20 mA/cm<sup>2</sup> were similar values. Therefore, these results accorded with definition of current which there was 1 coulomb of charge passing through cross sectional area every 1 second. The total electric energy consumption at current density 40 mA/cm<sup>2</sup> was lower than approximately 1.6 times at current density 20 mA/cm<sup>2</sup> and the average current efficiency at current density 40 mA/cm<sup>2</sup> was higher than at current efficiency 20 mA/cm<sup>2</sup>. Consequently, the condition at current density 40 mA/cm<sup>2</sup> was suitable

than at current density  $20 \text{ mA/cm}^2$  for long term experiment that regenerated zinc deposits was used in zinc air battery in the next section.

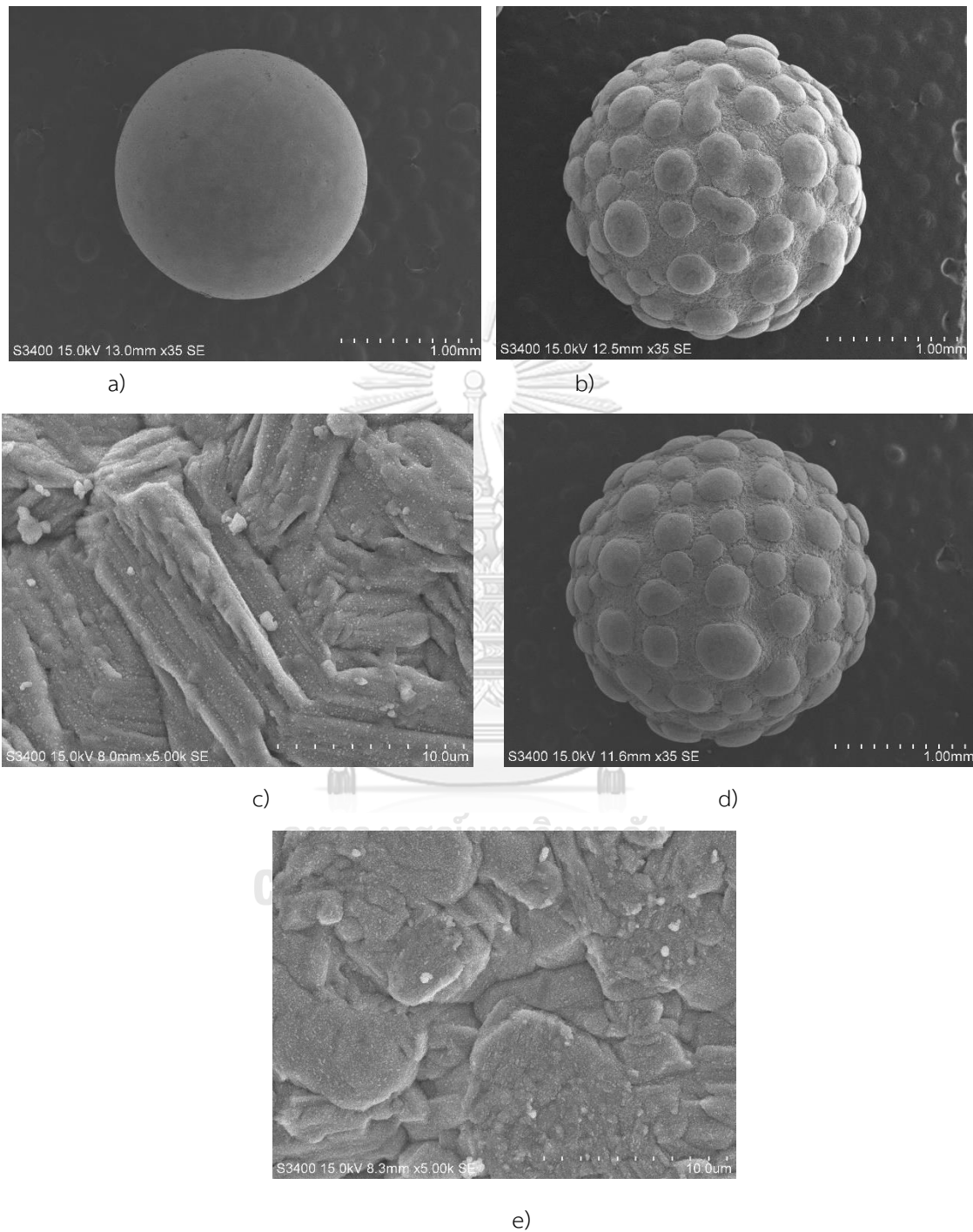


Figure 18 SEM micrographs for long term experiments a) bare stainless steel b,c)  $40 \text{ mA/cm}^2$  d,e)  $20 \text{ mA/cm}^2$

From figure 18, the current was applied to the system that caused the change of morphologies from smooth surface to rough surface. In eye view, the morphologies of regenerated zinc deposits at current density  $40 \text{ mA/cm}^2$  were not much different with current density  $20 \text{ mA/cm}^2$  because the surfaces of both looked rough, many enormous grains which they looked like custard apple, noticeable porosities, approximately equal size after deposition process and fully covered zinc metal. Because there was porosity on zinc deposits that the electrolyte can be trapped in the pores, it was speculated that minor white points on these micrographs at higher magnification may be contaminating the zinc with potassium hydroxide as referred to [35]. From the micrographs, the potassium hydroxide level was conjectured low. It was observed that the current was applied for a long time caused larger grains size. At higher current density, the nucleation rate was higher than the grain growth rate. The regenerated zinc deposits were received that the surfaces ought to be fine grained. Nevertheless, the expansion of grain size at higher current density can be ascribed the increase of hydrogen evolution. Therefore, the rate of electrodeposition decreased but the grain size increased [44]. According to Martyak [45], the addition of additives decreased grains size and obtained fine grained size. In high magnification, the morphologies at current densities  $20 \text{ mA/cm}^2$  and  $40 \text{ mA/cm}^2$  were boulder-like layer which was consistent with Neybour [27]. The low current density (lower than  $4 \text{ mA/cm}^2$ ) showed mossy structure, moderate current density (between  $4$  and  $60 \text{ mA/cm}^2$ ) appeared layer-mixed with granule and high current density (higher than  $100 \text{ mA/cm}^2$ ) exhibited dendritic formation that the current densities of this research were  $20 \text{ mA/cm}^2$  and  $40 \text{ mA/cm}^2$  appeared layer-mixed with granule as referred to earlier. The boulder-like layer can be applied on zinc air battery which dendrite and mossy cannot be used on zinc air battery due to brittleness, fracture, poor conducting and easy to cause short circuit. From figure 18c) and e), the current density  $40 \text{ mA/cm}^2$  had the layer of rock dense and tight than current density  $20 \text{ mA/cm}^2$ .

#### 4.4 Battery performance

In this part, the regenerated zinc electrodeposits were applied as anode in zinc air battery to test the discharged characteristics. From the observation, a polarization curve was detected in figure 19.

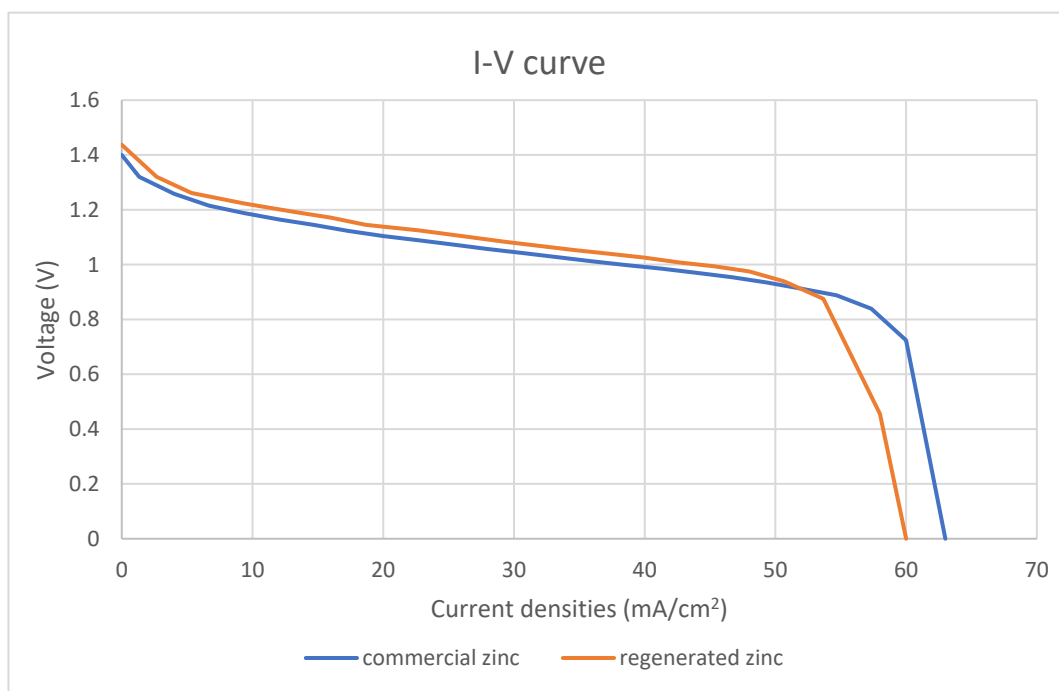


Figure 19 the polarization curve of zinc air battery that regenerated zinc (orange line) and commercial zinc (blue line) were used as anode

Figure 19 showed the comparison polarization curve between regenerated zinc and commercial zinc. The limiting current density for commercial zinc was higher than regenerated zinc that were  $63.3 \text{ mA/cm}^2$  and  $60 \text{ mA/cm}^2$  respectively. The potentials of both conditions were close which were 1.437 and 1.4 V. At low current density, there was activation loss that voltage overpotential required to overcome the activation energy of electrochemical reaction on surface of catalyst. A loss of voltage depended on slowness of oxygen reduction reaction (ORR). From this graph, zinc air battery that used commercial zinc as anode had more activation loss than regenerated zinc. At moderate current density, ohmic loss that the graph had linear part was resistance in the cell battery. Ohmic loss had 2 parts that were electrical resistance and ionic resistance. The electrical resistances were catalyst layer, the gas

diffusion layer and contact. The ionic resistances were electrolyte, ion mobility and electrode surface area. From this graph, it was found that zinc air battery used commercial zinc as anode had lower ohmic loss than regenerated zinc because the quality of regenerated zinc was lower than commercial zinc for ion conductivity and ion transport. At high current density, the relationships of voltage with current density diverged from linear that was called concentration loss. The concentration loss was a result of the decrease in reactant concentration at the surface of electrode as fuel was used. For regenerated zinc deposit, it was decreased faster than commercial zinc because mass transport of regenerated zinc was inferior and maximum limiting current density was lower because the reactants were promptly consumed at surface caused concentration at catalytic surface was zero.

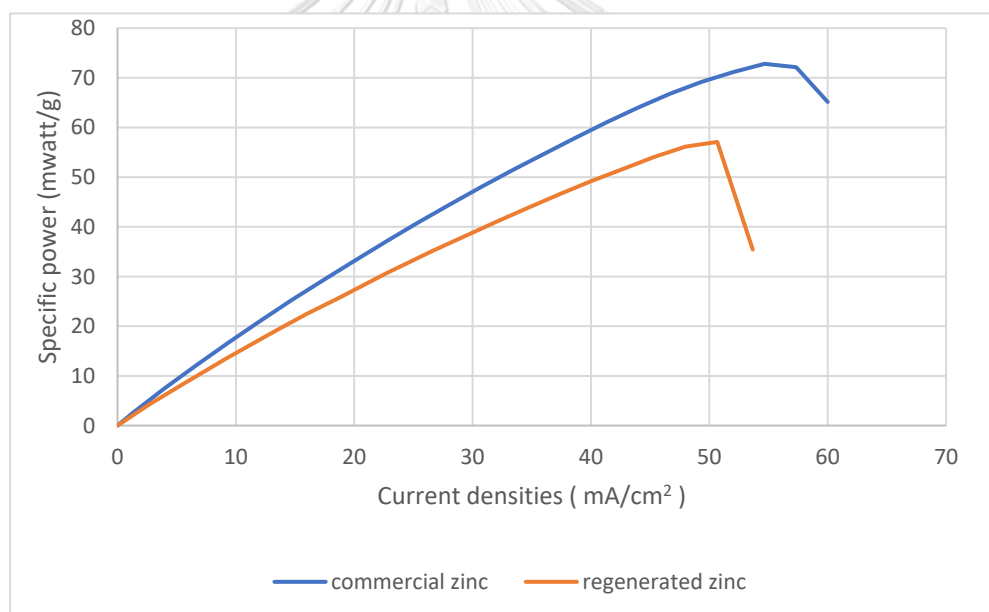


Figure 20 The relationships between specific power and current densities of commercial zinc (blue line) and regenerated zinc (orange line)

From figure 20, it showed that the highest specific powers of commercial zinc and regenerated zinc were 72.8 and 57.1 mWatt/g respectively. In this graph, the specific power of regenerated zinc was lower than commercial zinc because the surface area of commercial zinc was more than regenerated zinc and the surface had smoother than it that made to easily occur the electrochemical reaction. However, the

regenerated zinc can be applied on zinc air battery like commercial zinc. From other researches [7], the specific power of zinc air battery was 100 Watt/kg which this result was comparable and acceptable with it.

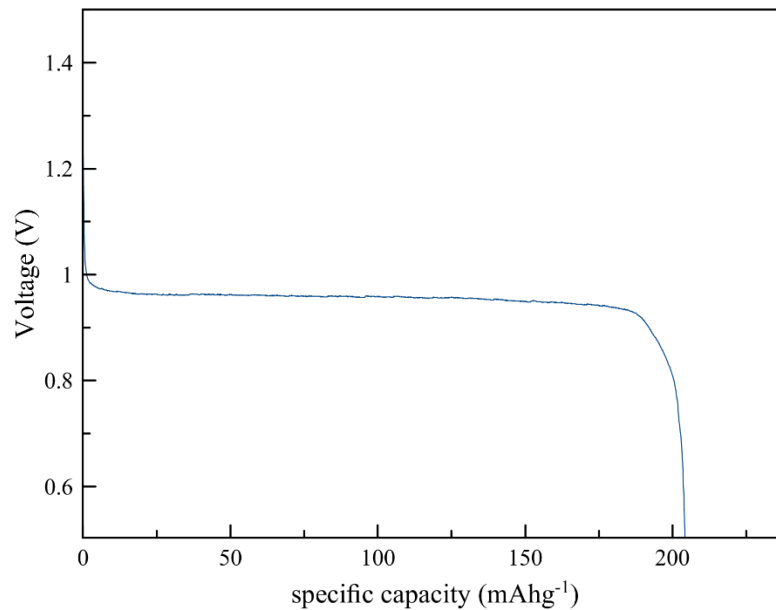


Figure 21 Discharged curve for Zinc air battery at a constant discharge rate of 250 mA

It was shown that the highest specific power for using regenerated zinc as electrode was at current density about 50 mA/cm<sup>2</sup> in figure 20. Therefore, current density at 50 mA/cm<sup>2</sup> was selected to make discharge curve for zinc air battery. The zinc electrode was regenerated zinc deposits at charged condition 40 mA/cm<sup>2</sup> for 16 hours. The zinc air battery demonstrated good specific capacity at about 212 mAhg<sup>-1</sup>. Compared with Alias [38], the specific capacity of zinc air battery in this research was lower than his research. Nevertheless, his research discharged at lower current density. The efficiency of zinc air battery was calculated about 20 % which was the ratio of practically specific capacity to theoretical specific capacity [2]. It was acceptable because the zinc electrode of theoretical specific capacity was commercial zinc. Hence, usage of regenerated zinc deposits was satisfied despite 20 % effective specific capacity. Indeed, the energy storage of battery was dependent on various characteristics that were temperature of operation, the concentration of



chemical in cell, the sort of cell, the component of electrode and the materials of cell. As reported by Linden [46], the capacity of zinc air battery was mainly influential on the cathode electrode or air electrode which the materials of air electrode must be an efficient oxidizing agent, occupy advantageous working electrode and durable while in contact with the electrolyte. For the zinc air battery system, the equations electrochemical reactions for discharge were shown as followed:

Anode:



Cathode:



Overall



Oxygen ( $\text{O}_2$ ) was directly diffused from ambient air into the cell which generated hydroxyl ions and transported from air electrode to zinc electrode to complete the battery reaction. In zinc electrode, the zinc anodes got oxidized and reacted with  $\text{OH}^-$  to produce soluble zincate ions ( $\text{Zn(OH)}_4^-$ ). When zincate solution became supersaturated in electrolyte, they had unprompted decay to form an insoluble zinc oxide. This result exhibited that the regenerated zinc deposits can be applied in zinc air battery and directly used oxygen from the atmosphere.

## Chapter 5

### Conclusion

#### 5.1 The regeneration of zinc particles by spouted-bed electrochemical reactor

Zinc can be successfully deposited on stainless steel particles by spouted-bed electrochemical reactor in potassium hydroxide electrolyte without addition of additives. Electrodeposition of regenerated zinc at  $40 \text{ mA/cm}^2$  showed acceptable morphology. When current densities increased, the current efficiency decreased. On the other hand, voltage and electric energy consumption increased. In long term runs, the current density at  $40 \text{ mA/cm}^2$  created fine morphology without dendrite and the particles grew from initial about 0.4 mm. The final particles showed porous and boulder layer.

#### 5.2 Battery performance

Regenerated zinc deposited at  $40 \text{ mA/cm}^2$  was used as anode in zinc air battery. The specific power and limiting current densities of regenerated zinc in battery was lower than commercial zinc which was reasonable due to higher surface area of commercial zinc. The discharged curve showed regenerated zinc deposits acceptable specific capacity that was  $212 \text{ mAhg}^{-1}$  and about 20 % compared with theoretical specific capacity and good stability in zinc air battery. Finally, the regeneration of zinc can be deposited on substrate by spouted-bed reactor and applied in zinc air battery.

#### 5.3 Recommendation

1. It should purge nitrogen gas ( $\text{N}_2$ ) to prevent oxygen oxidized on zinc to form zinc oxide formation.
2. Electrolyte should be added additives to improve morphology of zinc deposits.



In the following additional information, the equation and example of calculation in this thesis are shown.

### A.1 Current efficiency equation

$$\text{Mass of the deposited (theory)} = \frac{QM}{NF}$$

$$\% \text{Eff.} = \frac{\text{Mass of deposited}}{\text{Mass of deposited (theory)}} \times 100$$

where M is Molecular weight of zinc,

N is 2 for this reaction,

F is Faraday's constant (96,487 C/mol)

Q is electric charge passed.

**Example** mass gain 0.71 grams at current 1 A charged passed 3499 mAh time of deposition 4 hours

$$\text{Mass of deposits} = (3499 \times 65.38) / (2 \times 96487) = 1.185 \text{ grams}$$

$$\% \text{ eff.} = (0.71 / 1.185) \times 100 = 59.9 \%$$

### A.2 Electric energy consumption

$$\text{Energy consumption} = \frac{I \times V \times t}{M}$$

Where

I is current (A)

V is voltage (V)

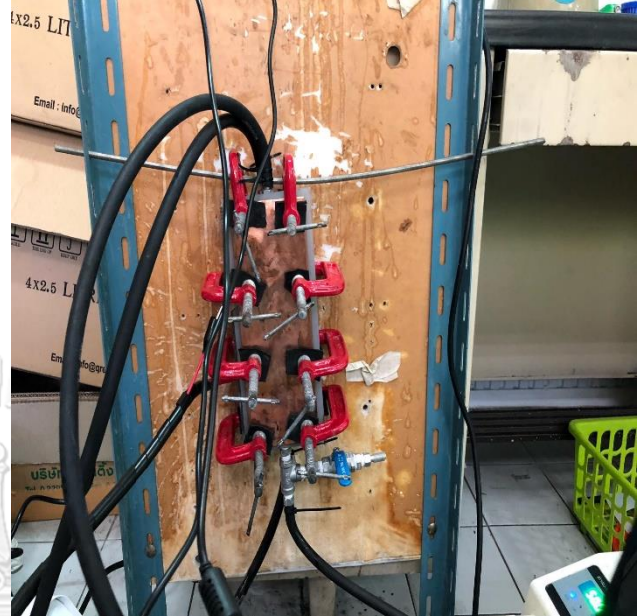
t is time of deposition (hour)

M is mass of deposition (gram)

**Example** mass gain 0.71 grams at current 1 A 2.6 V time of deposition 4 hours

$$\text{Energy consumption} = (1 \times 2.6 \times 4) / 0.71 = 14.64 \text{ Wh/g}$$

### A.3 The experiment of spouted-bed electrochemical reactor system



Particles were spouted.

#### A.4 The operation of zinc-air battery cell



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