

**THE EFFECT OF MCM-41 ADDITION TO PVA/PAN/PVP
POLYMER ELECTROLYTE FOR ZINC-AIR BATTERIES**



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ผลของการเติม MCM-41 ใน PVA/PAN/PVP พอลิเมอร์อิเล็กโทรไลต์สำหรับ
แบตเตอรี่สังกะสี-อากาศ



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เมมเบรนแผ่นกั้นขั้วอิเล็กโทรด คือหนึ่งในองค์ประกอบที่สำคัญของแบตเตอรี่สังกะสี-อากาศ มีบทบาทสำคัญในการควบคุมการถ่ายโอนมวลสารในปฏิกิริยาไฟฟ้าเคมีของแบตเตอรี่ ซึ่งกำหนดประสิทธิภาพการใช้งานของแบตเตอรี่ งานวิจัยนี้มีเป้าหมายในการพัฒนาเมมเบรนแผ่นกั้นขั้วอิเล็กโทรดชนิดใหม่ โดยการใช้พอลิเมอร์แบบผสม ซึ่งขึ้นรูปจากโพลีไวนิลแอลกอฮอล์ (PVA), โพลีอะคริลาไมด์ (PAN), โพลีไวนิลไพโรลิโดน (PVP) นอกจากนี้มีการใช้สารอนินทรีย์ขนาดอนุภาคระดับนาโน ที่มีองค์ประกอบของกลุ่มไฮดรอกไซด์สูง อย่างเช่น MCM-41 เป็นสารเติมแต่งในพอลิเมอร์ ผลจากการวิจัยพบว่า การเติม PAN ใน PVA สามารถเสริมความสามารถในการดูดซับสารอิเล็กโทรไลต์และการนำไอออนของเมมเบรนได้ อย่างไรก็ตาม การเติม PAN ที่ความเข้มข้นสูง (>30-50 wt.%) ส่งผลให้เมมเบรนทนอัลคาไลน์อิเล็กโทรไลต์ได้แย่ลงทำให้ประสิทธิภาพการใช้งานในแบตเตอรี่มีค่าลดลง แต่ในทางตรงกันข้าม การเติม PVP ใน PVA ไม่ส่งผลต่อคุณสมบัติของเมมเบรนและประสิทธิภาพการใช้งานของแบตเตอรี่อย่างมีนัยสำคัญ เมื่อทำการเติมสารเติมแต่ง MCM-41 ในปริมาณเล็กน้อย (2.5 wt.%) ใน PVA และพอลิเมอร์ผสม PVP/PVA สามารถช่วยปรับปรุงประสิทธิภาพการใช้งานของแบตเตอรี่สังกะสี-อากาศแบบปฐมภูมิได้ โดยได้ประสิทธิภาพความจุพลังงานจำเพาะสูงสุดที่ 49% และมีประสิทธิภาพหนาแน่นทางพลังงานสูงสุดที่ 41% จากการเติม 2.5 wt.% MCM-41 ในเมมเบรนแบบ PVA บริสุทธิ์ แต่ในทางกลับกัน การใช้งานในแบตเตอรี่สังกะสี-อากาศแบบทุติยภูมิ กลับมีจำนวนครั้งในการใช้งานที่ลดลง นอกจากนี้ พบว่าการเติมพอลิเมอร์ PVP ทำให้ในการข้ามผ่านของซิงค์เคตสูงขึ้น ซึ่งนำไปสู่การลดลงของจำนวนครั้งในการใช้งานของแบตเตอรี่ จากงานวิจัยนี้ พบว่าการทำงานของเมมเบรนแผ่นกั้นขั้วอิเล็กโทรดที่มีองค์ประกอบของ PVA บริสุทธิ์ให้ประสิทธิภาพการใช้งานของแบตเตอรี่สังกะสี-อากาศแบบทุติยภูมิสูงสุด ที่จำนวนครั้งในการใช้งาน 163 รอบ



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Sirinuch Nanthapong : THE EFFECT OF MCM-41 ADDITION TO PVA/PAN/PVP POLYMER ELECTROLYTE FOR ZINC-AIR BATTERIES. Advisor: CHALIDA KLAYSOM, Ph.D. Co-advisor: Assoc. Prof. SOORATHEP KHEAWHOM, Ph.D.

A membrane separator is one of the main components in zinc-air batteries playing an important role in controlling the mass transfer for the electrochemical reaction in the battery which determines the battery performance. This work aimed to develop a new membrane separator for the zinc-air battery. Polyvinyl alcohol (PVA), polyacrylonitrile (PAN), polyvinylpyrrolidone (PVP), and their blends were used for the fabrication of separator in this work. In addition, an inorganic nanoparticle with high hydroxide content such as MCM-41 was also applied as the filler for the polymers. The results revealed that the addition of PAN in PVA enhanced the electrolyte uptake and ionic conductivity of the resultant membranes. However, the addition of PAN at high content (>30-50 wt.%) worsened alkaline electrolyte stability of the membrane, leading to a decrease in battery performance. On the other hand, the addition of PVP in PVA had no significant influence on the membrane properties and the zinc-air battery performance. When adding a small amount (2.5 wt.%) of MCM-41 in PVA and PVP/PVA blend, the performance of primary zinc-air batteries was improved. Discharge capacity efficiency at 49% and energy density efficiency at 41% were obtained from using membrane with 2.5 wt.% MCM-41 in PVA. However, its battery cycle in rechargeable battery performance was reduced. In addition, the addition of PVP in PVA could promote zincate crossover, leading to a lower rechargeable cycle. The highest rechargeable zinc-air battery at 163 cycle was obtained from using pure PVA membrane.

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CHAPTER 1

INTRODUCTION

1.1 Introduction

A Battery is one of most important energy storage sources, providing electricity to several electrical devices [1]. Metal-air batteries are gaining increasing interests in recent year [2, 3] due to its high power density [4-6] and low cost in production [7]. In addition, the raw materials for making the metal-air battery are abundant on earth. Examples of metal-air batteries are a zinc-air battery, an iron-air battery, a lithium-air battery, a potassium-air battery [1, 8]. Among above mentioned metal-air batteries, zinc-air batteries are the most popular and promising one [1]. When comparing a zinc-air battery with a lithium-ion battery, the zinc-air battery has proved to be more safe and even has more energy density [1, 5, 8].

The main component of a zinc-air battery includes an air cathode, a zinc anode, a membrane separator and alkaline electrolyte [1]. The zinc-air batteries produce electricity from an electrochemical reaction from an air cathode, a zinc anode, and an alkaline electrolyte. A membrane separator is used to prevent a contact between the cathode and the anode [9] to store electrolyte, and to facilitate the mass transfer of the hydroxide ions through alkaline electrolyte during charge/discharge process. Primary zinc-air batteries have been successfully applied in small devices for a hearing aid [7], navigation, medication, railway signal light, and emerging mobile devices [1, 10]. Whereas, the secondary zinc-air batteries are still under the development and is still far from being commercialized. Therefore, there is

an urgent need for the development of rechargeable zinc-air batteries for use in electric vehicles and portable electronic devices [10]. The main problems of zinc-air rechargeable batteries are related to the electrode and the control of mass transfer through membrane separator. The electrode related problems includes an inadequate bi-functional electrode, dendrite formation, ZnO precipitation, and unwanted by-product formation [11, 12]. In addition, the zinc-air battery has to be constructed in an open system, in which the cathode is opened to an air that leads to an induced evaporation of the liquid electrolyte. The performance of the battery, thus, gradually declines over the operating period. The membrane separator/electrolyte related problems include inadequate membrane material with low electrolyte uptake, low ionic conductivity and high zincate crossover. These problems are, in fact, complex phenomena caused from each component of battery. The improvement of each component in zinc-air battery could lead to an overall improvement of battery performance and lifetime. Many research studies nowadays pay tremendous attention to the development of the zinc anode and the air cathode. However, there are only a few works, focusing on improving membrane separator and electrolyte [13-18]. Therefore, this work aims to fulfill this research gap and focus on the development of a new membrane separator/electrolyte for zinc-air batteries.

There are certain requirements for a good membrane separator/electrolyte.

These include:

- High ability to retain electrolyte
- High ionic conductivity in alkaline electrolyte ($>10^{-2} \text{ ms}^{-1}$)
- Good chemical, thermal and mechanical stability
- Highly selective to hydroxide ions but not zincate

- Proper pore size and porosity
- Processable and economic.

Traditionally a polypropylene (Celgard 3501) membrane separator/electrolyte is the main commercial separator for batteries [13]. The Celgard 3501 membrane separator has microporous structure that can accommodate high liquid electrolyte and facilitate ionic conductivity. However, this porous structure also allows the zincate to crossover easily, the loss of liquid electrolyte from evaporation, and penetration of dendrite through the pores that leads to an unstable performance and short cycle life of the battery [13].

Recently, there were some efforts paying for the development of a new type of separator membrane/electrolyte. To solve the abovementioned problems found in porous membranes, the development of new membranes/electrolyte moves toward new membrane-electrolyte structure so called gel-type polymer electrolyte (GPE). In GPE, electrolyte is absorbed and swollen by highly hydrophilic polymers like polyvinyl alcohol (PVA), polyvinyl acetate (PVAc), polyethylene oxide (PEO), polyvinyl chloride (PVC) and the blends. Among the hydrophilic polymers, PVA is the most widely studied material because of its high hydroxide content in the polymer structure and high electrolyte uptake. However, the main disadvantage of PVA is high zincate crossover and not stable at excess alkaline electrolyte. Thus, the pure PVA separator/electrolyte could not meet all requirements previously mentioned for the good membrane separator/electrolyte. Though these GPEs could provide a better performance compared to the Celgard 3501, they still have several limitations in terms of ionic selectivity and zincate crossover. In addition, the use of pure polymer

will always be limited by its inherent properties, especially low chemical and thermal stability.

Combining some inorganic fillers into a polymer matrix, making composite materials was reported to improve overall properties of the parent polymer in several membrane/electrolyte applications including battery close-related application like fuel cell and ion-exchange membranes. The same strategy could also be effective in the development of membrane separator/electrolyte in zinc-air battery.

Generally, the ionic conductivity of the separator depends on the amount of electrolyte uptake. The addition of inorganic fillers containing high hydroxyl groups could enhance the electrolyte uptake, leading to an increase in ionic conductivity. MCM-41 is one of the promising fillers, containing high porosity with high density of hydroxyl group that could be a good reservoir for electrolyte. In addition, some research paper was found that it can improve the electrochemical stability of the membranes [16].

In this work, MCM-41 was used as the inorganic fillers for highly hydrophilic polymer such as PVA, polyvinylpyrrolidone (PVP), polyacrylonitrile (PAN), and the blends for developing new composite membrane separators/electrolyte for zinc-air batteries. The effects of MCM-41 filler loading on membrane/electrolyte properties and zinc-air battery performance were investigated.

CHAPTER 2

BACKGROUND AND LITERATURE REVIEW

2.1 Fundamentals of electrically rechargeable zinc-air batteries

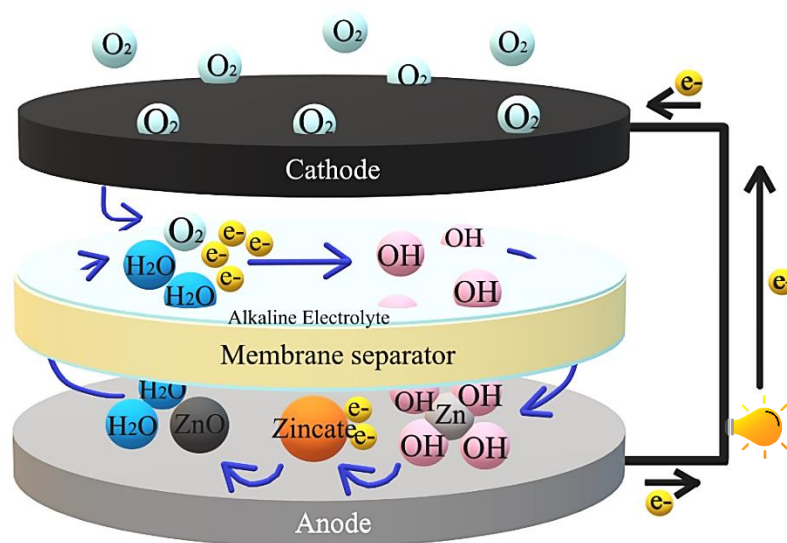


Figure 1. A reaction of a zinc-air battery

The main component of zinc-air battery includes a positive electrode (air cathode), a negative electrode (zinc anode), an alkaline electrolyte and a membrane separator (see Figure 1.) [1]. Each components are equally important and have an impact on the overall performance of the battery.

(1) A positive electrode (air cathode)

The positive electrode (cathode) is mostly made of carbon. At the cathode, oxygen from air in the atmosphere diffuses through the porous cathode to react with water, producing hydroxide ions.

(2) A negative electrode (zinc anode)

The negative electrode (anode) is made of zinc. The zinc reacts with hydroxide ions forming zincate and electrons [1].

(3) Alkaline electrolyte

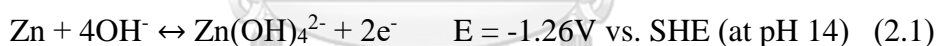
The alkaline electrolyte usually used in a zinc-air battery is potassium hydroxide or sodium hydroxide [1].

(4) A membrane separator

A membrane separator (battery separator) is used for partitioning a positive and a negative electrode [1]. The main functions of a membrane separator are preventing a short circuit between the anode and cathode, enhancing ionic conductivity in alkaline electrolyte, storing electrolyte, and preventing zincate ion crossover from the anode compartment to the cathode.

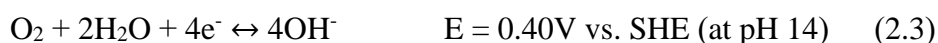
Reactions in zinc-air battery are as follows [1].

At the zinc anode, hydroxide ions react with zinc producing zincate ion and electron (Eq (2.1)). The zincate ion could decompose to zinc oxide, water and hydroxide ions (Eq (2.2)).



The electron moves to a circuit line to the cathode, creating an electrical power. Whereas, water transports from a zinc anode to an air cathode through the membrane separator.

At the air cathode, oxygen diffusing from the air reacts with water and electron, producing hydroxide ions. The hydroxide ions then cross over from the air cathode to the zinc anode through the membrane separator.



The overall reaction is



The reaction of the zinc-air battery continues until the reactants are all used up

Theoretical discharge voltage and power density obtained from the zinc-air battery are summarized in Table 1 [1].

Table 1. A theoretical power generation from a zinc-air battery

Specific Energy (Power density)	1084 Wh kg ⁻¹
Volumetric Energy Density	6136 Wh L ⁻¹
Capacity	820 mAh g ⁻¹
Cell Voltage	1.66 V

In general, the power generation of zinc-air batteries will be thermodynamically favorable. The overall reaction can convert to the overall electromotive force (E_{emf} , V). It can define from the potential difference between two electrodes (a cathode and an anode)

The overall electromotive force (E_{emf} , V) is related to the electrical work done (W) in a cell (Eq 2.5).

$$\text{Electrical work done (W)} = -\text{charge (Q)} \times \text{Voltage (E}_{\text{emf}}) \quad (2.5)$$

$$\text{or} \quad W = nf \times \text{Voltage (E}_{\text{emf}}) \quad (2.6)$$

n = the number of electrons in the chemical reaction

F = the Faraday constant

If, the system does not lose energy, the electrical work can be estimated from Eq 2.7.

$$W = \Delta G_T \text{ (the Gibbs free energy change)} \quad (2.7)$$

However, the obtained cell voltage, capacity, and power density are practically less than the theoretical value. The cell voltage from experiments is usually 1.2 V and the discharge capacity is 350-650 mAh/g [13, 15, 16].

The main factors causing the lose of zinc-air batteries performance are as follows

1) Ohmic losses

Ohmic losses are from the electrical resistance of electrodes, and the resistance of ions motion in the electrolyte. It can obtain from Eq 2.8.

$$V = iR \quad (2.8)$$

V = the amount of voltage drop

I = the current

R = the resistance of component

The prevention of the ohmic lose in the system can be done by using the electrodes with high electrical conductivity and the alkaline electrolyte with high ionic conductivity.

2) Activation losses

Activation losses in the system are due to the slowness of chemical reaction on the surface of the electrodes. Using the cathode with high active

surface area and catalytic with high activity can reduce activation loss of the system [19, 20].

In fact, the zinc-air batteries performance is much lower than the theoretical value due to the combined problems from each component in the battery. Table 2 summarizes the phenomenon occurring in zinc-air battery that cause the performance lost.

Table 2. Problems in zinc-air batteries

Phenomena	Cause	Consequence
Dendrite growth [1, 5]	Dendrite is the reformation of zinc during charging, having a needle-like form that can puncture a membrane separator, if the membrane is too porous or not strong enough.	<ul style="list-style-type: none"> ○ Short circuit ○ Loss of battery capacity
Shape change of electrode [1, 5]	During charging, zinc in alkaline electrolyte deposits randomly at different position on the negative electrode surface.	<ul style="list-style-type: none"> ○ Short discharge time ○ Un-uniform densification of the electrode

Phenomena	Cause	Consequence
Passivation and internal resistance [1, 5, 21]	The precipitation of zinc oxide during the discharge reaction blocks the electrode surface.	<ul style="list-style-type: none"> ○ Low rate of a reaction and short discharge time ○ Loss of available zinc for discharging reaction
Hydrogen evolution [1, 5]	Unwanted competitive side reaction of the hydrogen evolution at the cathode.	<ul style="list-style-type: none"> ○ Loss of capacity ○ Corrosion of cathode and unsteady performance
Formation of carbonate [5]	CO ₂ from the air diffusing through the porous cathode reacts with alkaline electrolyte forming carbonate (CO ₂ + H ₂ O → H ₂ CO ₃).	<ul style="list-style-type: none"> ○ Loss of alkaline electrolyte ○ The carbonate blocks the pore of cathode ○ Shorten the battery life
Cathode flooding [5]	Too high releasing rate of electrolyte from membrane separator to the air cathode leads to an electrolyte flooding at the cathode side.	<ul style="list-style-type: none"> ○ Electrolyte blocks the diffusion of air, leading to low produced electricity
Sluggish oxygen reactions [5]	A sluggish rate of the oxygen reduction reaction (ORR) at the cathode	<ul style="list-style-type: none"> ○ Loss of energy and power density

Phenomena	Cause	Consequence
Low alkaline electrolyte storage [5]	One side of cathode is open to the air, leading to the evaporation of alkaline electrolyte and carbonation reaction that reduce the amount of electrolyte in the system.	<ul style="list-style-type: none"> ○ Short discharge time
Low ionic conductivity [17]	High ionic resistance of membrane separator	<ul style="list-style-type: none"> ○ Short discharge time
High zincate crossover [13, 14]	High porous structure of a membrane separator enables zincate ions crossover from anode to cathode compartment.	<ul style="list-style-type: none"> ○ The zincate can undergo a side reaction, forming ZnO resistive layer on the air cathode that leads to the loss of battery capacity and cycle life.

The improvement in each components of zinc-air batteries is thus crucial for obtaining optimum properties and performance of the zinc-air batteries. This work is interested in the development of a membrane separator/electrolyte for enhancing zinc-air batteries performance. Therefore, the literature review (section 2.2) only

covers the development of membrane separators/electrolyte specifically designed for the zinc-air batteries.

2.2 Literature Review

Battery separator or membrane separator is one of the main components of all batteries. It is placed between a positive and a negative electrode for preventing the direct contact of both electrodes that may lead to electrical short circuits [9]. In addition, a membrane separator also controls the mass transfer of ionic electrolyte between the two electrodes for a continuation of the reaction and electrolyte storage for using in the reaction of a zinc-air battery.

Properties of a good membrane separator for using in zinc-air batteries include: [9]

- High electrical resistance and ionic conductance
- High electrolyte and chemical resistance
- Good mechanical properties
- High electrolyte storage

Material for making membrane separators can be inorganic (inorganic polymer) [9], organics (polymer) and composite (organic combined with inorganic). The widely used materials for forming membrane separators are polymers such as polypropylene (Celgard 3501) [13], cellulosic polymer, polyvinyl acetate (PVAc), polyvinyl alcohol (PVA), and polyethylene oxide (PEO) [13, 14, 17]. Among the above motioned polymers, PVA was the most studied material because of its high hydrophilic and high electrolyte uptake [17].

Usually, a membrane separator for zinc-air batteries is in a dense or microporous structure formed from one or several materials. For instance, a commercial separator namely Celgard 3501 is a microporous separator (see Figure 2) [22]. The main advantage of this polymer is high electrolyte uptake and ionic conductivity. However, due to its high porosity, zincate can cross over easily that leads to a short discharge time.

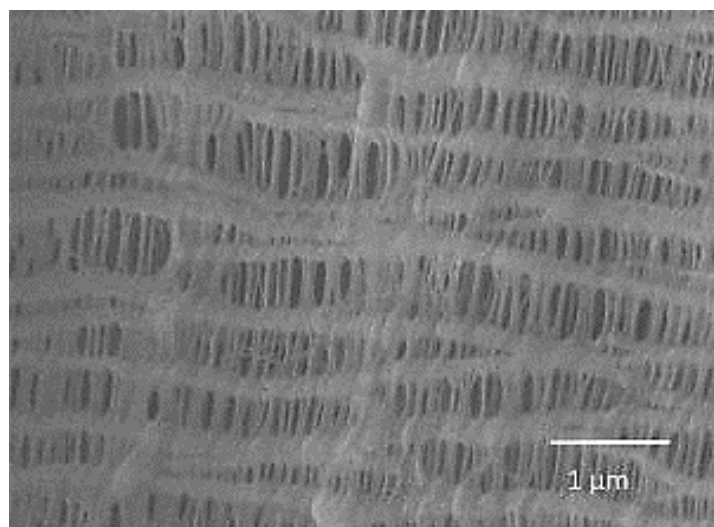


Figure 2. SEM image of Celgard-3501

There are several techniques for preparing membrane separators such as a solution casting method, an electrospinning technique, and a dip-coating method [23]. These methods result in different membrane structures. For instance, the solution casting method is the process, in which a polymer solution is first prepared, then cast into a film and dried to a solid film [17]. This technique usually results in a dense membrane. On the other hand, electrospinning technique uses electric force to draw polymer solution to deposit on the target plate, forming polymer fibers and nanomat [13]. Membranes from the electrospinning technique are normally highly porous. Therefore, the fiber mat is generally used as the support for more hydrophilic polymer

[13, 14]. The common techniques to fill the pores of the support or to coat another materials on the support are impregnation and dip-coating method. Table 3 compares the properties of membranes separators/electrolyte prepared from various materials and techniques.



Table 3. The development of membrane separators/electrolyte for a zinc-air battery

A membrane separator/electrolyte character		A membrane separator/electrolyte performance					Zinc-air battery performance				Ref
Support	Poly-electrolyte	Electrolyte uptake (%)	Ionic conductivity ($S\text{ cm}^{-1}$)	Zincate crossover ($\text{cm}^2\text{ min}^{-1}$)	Mechanical strength	Voltage discharge	Discharge capacity	Discharge time ($>1\text{ V}$)	Cycle number		
MCM-41	3M and 6M KOH	-	-	-	-	1.2 V (at 1 and 5 mA) [stable]	15 mAh /cell volume	37 min (at 5 mA) 312 min (at 1 mA)	-	[16]	
PEI nanomat	PVA – GPE (KOH) liquid electrolyte – swollen PVA)	87	0.0131	5.0×10^{-6}	High [tensile]	1.0 -1.1 V [stable]	645 mAh/g [1 st discharge], 213mAh/g [2 nd discharge]	81 min at 2 nd discharging	7	[13]	
Polypropylene (Celgard 3501)	KOH	52	0.0137	19.2×10^{-6}	Lower than PEI nanomat + PVA membrane [tensile modulus]	1.0 -1.1 V	563 mAh/g [1 st discharge], 34 mAh/g [2 nd discharge]	18 min [2 nd discharge]	-		
-	PVA - GPE	118	0.0135	10.5×10^{-6}	-	-	-	-	-		

A membrane separator/electrolyte character		A membrane separator/electrolyte performance					Zinc-air battery performance				Ref	
Support	Poly-electrolyte	Electrolyte uptake (%)	Ionic conductivity ($S\text{ cm}^{-1}$)	Zincate crossover ($\text{cm}^2\text{ min}^{-1}$)	Mechanical strength	Voltage discharge	Discharge capacity	Discharge time ($>1\text{ V}$)	Cycle number			
PVA/PAA nanomat	7 wt% Nafion	31.2	0.0066	0.41×10^{-6}	High [tensile]	1.2 V	-	-	2500 min [at 20 mA cm^{-2} , 10 min cycle]			[14]
Polypropylene (Celgard 3501)	KOH	80.1	0.0128	23.24×10^{-6}	Lower than PVA/PAA nanomat + 7 wt% Nafion	1.1 V	-	-	900 min [at 20 mA cm^{-2} , 10 min cycle]			
-	PVA/PAA	61.1	0.0112	11.02×10^{-6}	-	1.1 V	-	-	750 min [at 20 mA cm^{-2} , 10 min cycle]			
Nafion film	-	2.6	0.0008	0.04×10^{-6}	-	-	No discharge					
PEO + PVA	Micro-crystalline cellulose dissolved in 5% LiCl/DMAc	Solid electrolyte (7 g KOH)	0.153	-	0.76 MPa	Start at 1.35 V [non-stable-Decreasing Function]	1339.5 mAh/g	80 min (still to 535 min at lower 1V - Decreasing Function)	-			[17]
			0.055	-	0.28 MPa	-	-	-	-			
			-	-	-	-	190.95 mAh/g	12 Hour				

A membrane separator/electrolyte character		A membrane separator/electrolyte performance					Zinc-air battery performance				Ref
Support	Poly-electrolyte	Electrolyte uptake (%)	Ionic conductivity (S cm ⁻¹)	Zincate crossover (cm ² min ⁻¹)	Mechanical strength	Voltage discharge	Discharge capacity	Discharge time (>1 V)	Cycle number	Ref	
PP	Coat with EBIH + BMA	-	-	0.5 x 10 ⁻⁶	-	1.0 – 1.1 V	-	-	107		[18]
	-	-	-	10.8 x 10 ⁻⁶	-	-	-	-	37	[18]	
Filter paper	PAA 80% neutralized + PVA	Increase (compare with filter paper)	Increase (compare with filter paper)	-	Increase (compare with filter paper)	Start at 1.5 V	344.7 mAh/g	23.5 Hour	-	[15]	
	PAA pure	-	-	-	-	-	190.95 mAh/g	12 Hour	-	[15]	

The approaches for improving the properties of membrane separators/electrolyte are explained in details as follows.

1) Increasing of electrolyte uptake and ion exchange capacity

Electrolyte uptake is one of the main factors, determining the zinc-air batteries performance. Membranes with high electrolyte uptake can provide large amount of electrolyte for electrochemical reaction at the electrodes, leading to high discharging time of the zinc-air batteries. Polypropylene and filter paper are normally used as the separator for zinc-air batteries. These separators have highly porous structure that can uptake large amount of electrolyte. Therefore, they possess high ionic conductivity. But the main disadvantage of these porous membranes is the migration of other ions besides the electrolyte. In addition, the zinc-air battery is an open air system, the evaporation of liquid electrolyte from the pores of these highly porous membrane is significant. The use of these porous membrane usually resulted in unstable battery performance and short rechargeable cycle. Some research studies have tried to solve the problem of these porous membranes by filling their pores or coating other materials on their surface. Wang et al., coated PVA and PAA on a filler paper and found that the electrolyte uptake was enhanced [15]. This was due to high concentration of PAA salt led to an increased osmotic pressure that promoted the absorption of electrolyte. In addition, the coating polymer on the support membrane can decrease of the evaporation of liquid electrolyte. The formation of gel-type polymer electrolyte (GPE) can also decrease the evaporation of liquid electrolyte and migration of other ions. The most widely used material for forming gel polymer electrolyte is PVA because of its high hydrophilicity, high adsorption capacity for alkaline electrolyte and high ionic conductivity [24-26]. However, using

PVA-gel electrolyte was not enough for enhancing electrolyte uptake and ionic conductivity for using in zinc-air batteries. So, the development polymer electrolyte by other methods such as blending the PVA with other polymer and applying some fillers were explored. Zhang et al., developed a composite membrane separator/electrolyte for enhance ionic conductivity by the addition of microcrystalline cellulose [17]. The microcrystalline cellulose was dissolved with dimethylacetamide solution (LD-MCC) in a blend polymer of PVA/PEO to provide extra hydroxyl groups to the separator. Hydrogen bonding between hydroxyl group of MCC and alkaline electrolyte help supporting the interaction between the membrane and electrolyte, leading to high electrolyte uptake and ionic conductivity. The addition of 5%wt LD-MCC can increase ionic conductivity of the membrane/electrolyte from 0.018 S cm^{-1} to 0.153 S cm^{-1} that lead to a long discharge time in the zinc-air batteries. Saputra et al., used MCM-41 as separator for zinc-air batteries [16]. MCM-41 has nano-channels and hydrophilic nature from high hydroxyl group in the structure that can promote the transport of the alkaline electrolyte, leading to an increased ion exchange capacity in the battery [27]. That can help voltage discharge of zinc-air batteries on stable at 1.2V.

In addition, many researches paper interest about the effect of polymer type and the concentration ratio to ionic conductivity. In example, the research paper of Choi et al, they were developed of PEO/PAN blend polymer membrane on the ionic conductivity. From the result revealed that high PAN concentration ratio can increase ionic conductivity [28, 29]. Qiao, J. and et.al. investigated the effects of the blend polymer PVA/PVP on alkali stability and ionic conductivity of the membrane. The results revealed that at blending mass ratio of 1:0.5 between polyvinyl alcohol

(PVA) and polyvinylpyrrolidone (PVP) membrane provided highest ionic conductivity at 0.53 S cm^{-1} [30].

2) Reducing zincate crossover

As mentioned earlier, the zinc anode reacts with hydroxide ions, producing zincate ions that can further decompose and form zinc oxide and water. However, if the zincate ions cross the membrane separator/electrolyte to the air cathode, it can convert to zinc oxide and form a resistance layer on the air cathode. This resistant layer blocks the effective area for the reduction reaction at the cathode, leading to the loss of battery capacity [13]. The zincate crossover can be prevented by tuning the porosity of the membrane separator. Wang et al., coated polymerized ionic liquids from 1-[(4-ethenylphenyl)methyl]-3-butylimidazolium hydroxide (EBIH) and butylmethacrylate (BMA) on a polypropylene (PP) porous membrane [18]. The ionic liquids filled the pores of PP membrane and limited the crossover of zincate ions. The improvement of membrane separator/electrolyte by this method can enhance a cyclic stability of secondary zinc-air batteries [18]. Similar approach by impregnation of polyvinyl alcohol (PVA) into pores of electrospun polyetherimide (PEI) nanofiber mat was applied by Hyeon-Ji Lee and his team [13]. Due to impregnation of PVA into PEI nanofiber mat, nonporous structure was formed. Bulky zincate cannot cross the separator from the anode to cathode but smaller ions like hydroxide ions can easily transport through the membrane/electrolyte. In addition, Hyun-Woo Kim et al impregnated 7% Nafion into electrospun polyvinyl alcohol (PVA) /polyacrylic acid (PAA) nanofiber mat forming a membrane separator/electrolyte for zinc-air batteries. The result revealed the success in prevention of zincate crossover [14].

3) Enhancing of membrane separator stability

Zinc-air battery contains strong alkaline electrolyte (4-6 molar of KOH) that cause the stability problem in the battery. Materials for a membrane separator/electrolyte should possess high chemical and mechanical stability, especially high tensile and compression properties for a prolong operation of zinc-air battery. Most polymers are not stable in strong alkaline electrolyte and high temperature. Many research studies tried to improve mechanical properties of membrane separators/electrolyte by using chemically stable polymers or by adding some filler to strengthen the matrix polymer. For instance, Zhang et al found that the addition of 5wt% microcrystalline cellulose in the blend of PVA/PEO polymer can also enhance mechanical properties of the membrane in term of tensile properties from 0.28 MPa to 0.76 MPa [17].

As the control of mass transfer across the membrane/electrolyte is of crucial to the electrochemical reaction in battery, the development of good membrane separator/electrolyte should not be neglected. More research attentions should be paid to the optimization of membrane properties in terms of chemical and mechanical stability, electrolyte uptake and hydroxide ion conductivity.

CHAPTER 3

OBJECTIVE AND SCOPE OF WORK

3.1 Objective

To investigate of the effects of additives used in polymer electrolyte on the structure, electrochemical properties, and performance of the separator electrolyte in zinc-air batteries.

3.2 Scope of work

The experiment was divided in three main parts. Firstly, a MCM-41 and membrane separator/electrolyte were synthesized. Secondly, various characterization techniques were applied to investigate the properties of the prepared separators/electrolyte. Lastly, zinc-air battery was fabricated and its battery performance was evaluated.

The studied parameters and their variables are summarized as follows

3.2.1 Membrane separator/electrolyte preparation

Studied parameter	Variable
(1) Type of polymer	Polyvinyl alcohol, Polyacrylonitrile, Polyvinylpyrrolidone
(2) Total polymer concentration	13 wt.%
(3) Blending ratio	0 – 50 wt.% of PAN or PVP in the blend polymer
(4) Solvent	N,N-Dimethylformamide (DMF,99.8%) DI water
(5) Filler	MCM-41
(6) Filler loading	0-7.5 wt.% of the blend polymer
(7) Thickness	1.8-2.0 mm
(8) Electrolyte	Potassium hydroxide (6M KOH)

3.2.2 Characterization of membrane separator/electrolyte

Property	Characterization technique
(1) Morphology and structure	Scanning electron microscope (SEM)
(2) The chemical structure	Fourier-transform infrared spectroscopy (FT-IR)
(3) The electrolyte uptake	Measuring the weight difference of a membrane separator before and after immersing in 6M KOH electrolyte solution
(4) Zincate crossover	Measurement of zinc concentration in electrolyte solution (by an inductively coupled plasma (ICP-OES))
(5) Ionic conductivity	AC impedance analysis by Electrochemical Impedance Spectroscopy (EIS)

3.2.3 Performance evaluation of zinc-air battery

Zinc-air battery was fabricated in a coin cell (CR 2032) for primary zinc-air batteries testing and a box cell for rechargeable zinc-air batteries testing. The battery was used zinc as the anode and carbon/MnO as the cathode. The battery performance was evaluated by using galvanostatic technique (constant current method) [31, 32] with following condition;

For primary zinc-air batteries testing

- Current : 5 mA
- Discharge voltage cut off : 0.19 V

For rechargeable zinc-air batteries testing

- Current : 5 mA
- Discharge voltage cut off : 0.9 V
- Charge voltage cut off : 5 V

Zinc-air batteries performance was reported in term of voltage discharge, discharge capacity, power density, and cycle number (for rechargeable zinc-air batteries testing).

CHAPTER 4

RESEARCH METHODOLOGY

4.1 Materials

Polyacrylonitrile (PAN, MW 150,000 Da), polyvinylpyrrolidone (PVP, MW 40,000 Da), tetraethylorthosilicate (TEOS, 99%+), were purchased from Sigma-Aldrich. Polyvinyl alcohol (PVA, MW 100,000 Da) was purchased from Chem-supply. Cetyltrimethylammonium Bromide (C₁₆TAB, 98%) and Potassium hydroxide (KOH, Pellets) were obtained from Asia Pacific Specialty Chemical Limited. Ammonia solution (NH₃, 25%) and N,N-Dimethylformamide (DMF, 99.8%) were purchased from QREC.

4.2 Synthesis of MCM-41

Mixture solution of C₁₆TAB, NH₃, and TEOS was prepared at the weight ratio of 0.3: 11: 1. The mixture solution was stirred at room temperature for 2 hours. After that, the precipitated MCM-41 was filtered out and washed with deionized water. The obtain powders were dried at 100°C overnight in an oven and calcined at 550°C for 6 hours by use heating rate at 10°C per min in the air [33].

4.3 Preparation of a membrane separator/electrolyte

13 wt.% of the blended polymer with different blending ratios was dissolved in a solvent (DMF for PAN, and DI water for PVP) under a heating conditions at 80-110°C and stirring until homogeneous solution was obtained. A desired amount of MCM-41 was added in the blended polymer solution.

The composite polymer solution was poured into a petri dish with a control thickness at 1.8-2.0 mm and air dried at a room temperature overnight. The prepared membrane was immersed in 6M KOH (alkaline electrolyte) for 24 hours at the room temperature [34-36]

4.4 Characterizations

4.4.1 Morphology and chemical structure

Morphology of a membrane separator/electrolyte was observed by scanning electron microscope (SEM) (JEOL, JSM-IT500HR). Chemical functional groups of the prepared membrane separator/electrolyte were identified by Fourier-transform infrared spectroscopy (FTIR) (Scientific, Nicolet 6700).

4.4.2 Electrolyte uptake

The weight of the membrane separator/electrolyte before and after immersing in 6M KOH for 24 h at room temperature was recorded [13]. Electrolyte uptake was thus estimated by Eq (4.1).

$$\text{Electrolyte uptake (\%)} = \left[\frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \right] \times 100 \quad (4.1)$$

W_{wet} = The weight of a membrane separator/electrolyte after being immersed with electrolyte (6M KOH) at room temperature for 24 h

W_{dry} = The weight of a membrane separator/electrolyte before immersed with electrolyte (6M KOH) at room temperature

4.4.3 Ionic conductivity

The ionic conductivity of a membrane separator/electrolyte can be measured by an electrical impedance spectroscopy (EIS). The impedance can be estimated from the relation of a complex number of a real component and an imaginary component in the Nyquist plot. The sample was prepared by immersing membrane in 6M KOH for 24 h at room temperature before the test with Electrochemical Impedance Spectroscopy (EIS) at a frequency range of 0.15-150,000 Hz at room temperature. A membrane/electrolyte sample is placed between two stainless electrodes. The calculation of ionic conductivity is expressed in Eq (4.2).

$$\sigma = \frac{L}{(R_b \times A)} \quad (4.2)$$

L = The membrane sample thickness (cm)

R_b = The bulk resistance (ohm). The bulk resistance can be analyzed from the x-cross point of the Nyquist curve (graph between Z_{im} and Z_{re}).

A = Area of the stainless electrode (cm²)

4.4.4 Zincate crossover

The zincate crossover through a membrane separator/electrolyte was measured in a two compartments cell illustrated in Figure 3. The membrane sample was placed between the two chambers, containing 6M KOH (electrolyte) in one chamber and 0.5M zinc oxide in the other chamber. The testing solution was stirred at room temperature. The solution from right

chamber (containing 6M KOH) is collected at 150 h to measure zinc oxide concentration (specifically, Zn element) by an inductively coupled plasma (ICP-OES) (Agilent, ICP-OES 5100) [13, 37].

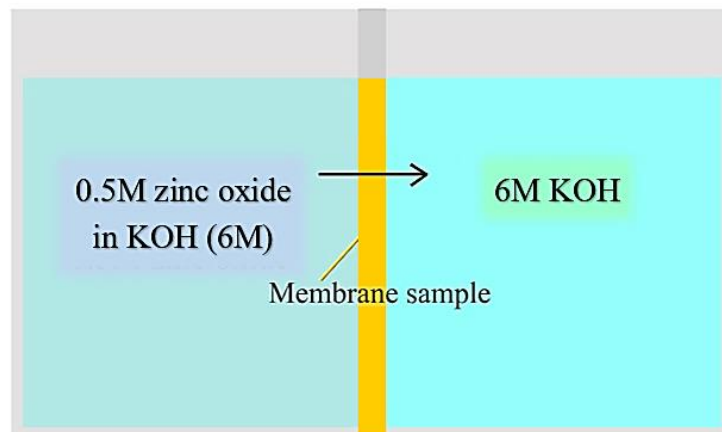
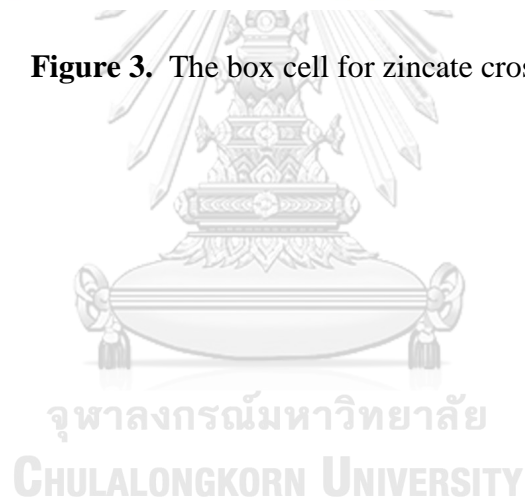


Figure 3. The box cell for zincate crossover testing



4.5 Battery performance test

Zinc-air battery is fabricated in a coin cell battery (CR2032) for primary zinc-air battery testing and the box cell for rechargeable zinc-air battery testing, composing of an air cathode, a zinc anode and a membrane separator/electrolyte. Before being formed into a battery, the membrane separator is immersed in 6M KOH for 24 h.

- **The preparation of a zinc anode**

A zinc anode was prepared by using electroplating technique, illustrated in Figure 4.

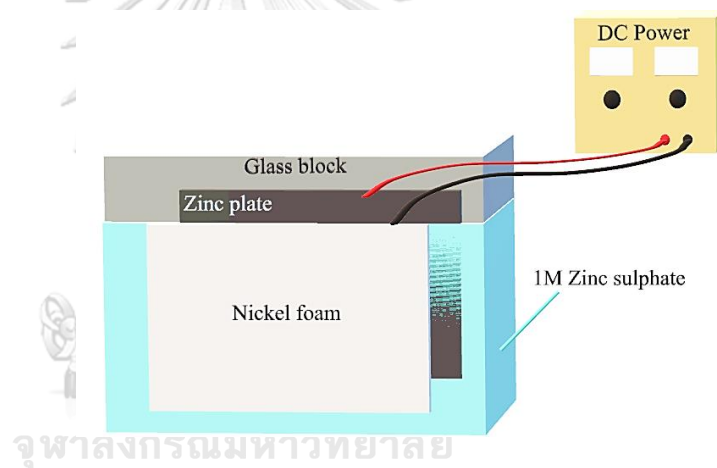


Figure 4. The electroplating technique used for making a zinc anode

The fabrication of a zinc anode was prepared by electroplating on a nickel foam with thickness at 1 mm (7 x 7 cm). To make the zinc anode, the nickel foam was electrodeposited in 1M zinc sulfate solution at a current density of 350-450 mA for 5-6 h and dried at 60-70 °C for 15-20 min. Fixed thickness of a zinc anode at 0.5 mm by using a rolling mill stand [38].

- **The preparation of an air cathode**

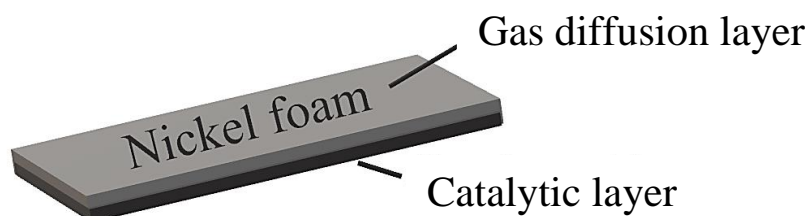


Figure 5. An air cathode for a zinc-air battery

An air cathode comprising two parts, a gas diffusion layer and a catalytic layer as shown in Figure 5 was prepared via the following procedure;

The gas diffusion layer of an air cathode was prepared by coating the mixture solution of PTFE, carbon, glucose and NaHCO_3 at 1:1:0.25:0.25 concentration ratio (dissolve in Ethanol) on one side of the nickel foam. Then, it was heated at 350-400 °C until dried [26].

The other side of the nickel foam was then coated with the mixture solution of carbon and MnO at 1:1 concentration ratio (dissolve in 3wt% PVDF). After that, it was dried at 60-70 °C for 15-20 min and compressed with a rolling mill stand at a fixed thickness of 0.8 mm [34, 35, 39].

○ **The preparation of a zinc-air coin cell battery**

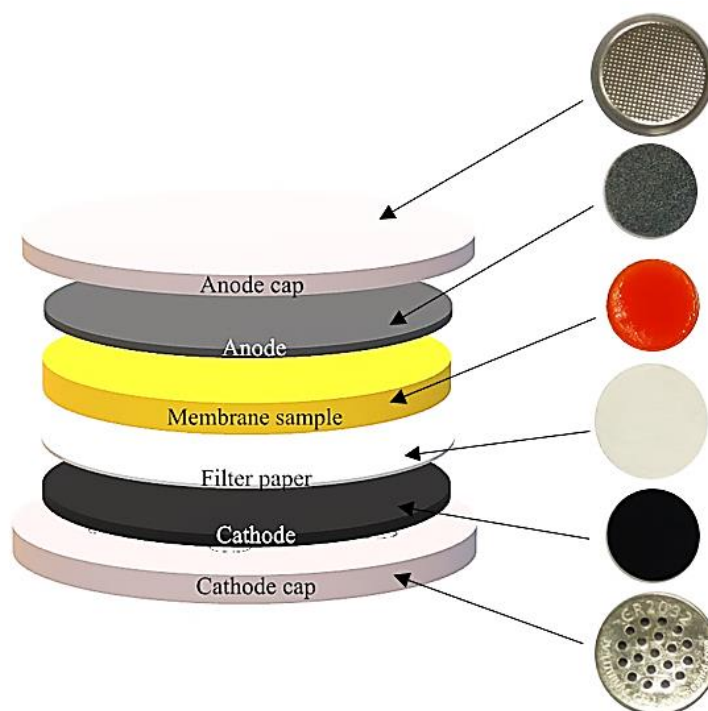


Figure 6. A zinc-air coin cell battery

The zinc-air coin cell battery with several components shown in Figure 6 was prepared. The membrane separator after immersing in 6M KOH for 24 h was placed between the air cathode and the zinc anode. The caps were placed on top and bottom of battery, covering the cathode and anode. Finally, the whole stacking component was compressed forming a coin cell battery.

The zinc-air batteries performance was tested by using the galvanostatic technique. The primary zinc-air battery was tested under a controlled discharge current at 5 mA. The voltage discharge was recorded and the discharge capacity, and power density were estimated using Eq 4.3 and 4.4, respectively.

$$\text{Discharge capacity (mAh/g)} = \frac{\text{capacity (mAh)}}{\text{the weight of zinc as the anode (gram)}} \quad (4.3)$$

$$\text{Energy density (Wh/kg)} = \frac{\text{energy (Wh)}}{\text{the weight of zinc as the anode (gram)}} \quad (4.4)$$

○ **The setup of a cell battery for testing rechargeable zinc-air battery**

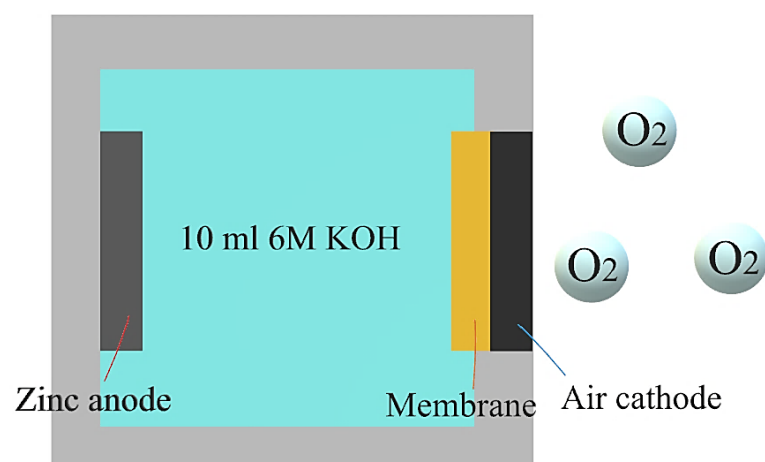


Figure 7. A zinc-air box cell battery for rechargeable zinc-air battery testing

The box cell battery for rechargeable zinc-air battery testing shown in Figure 7 was prepared. The membrane separator after immersing in 6M KOH for 24 h was placed between the air cathode and the zinc anode (with a chamber filled with 10 ml of 6M KOH in between). The zinc plate was used as the anode for an excess supply of zinc. The performance of rechargeable zinc-air batteries was tested at charge-discharge current at 5 mA and charge-discharge capacity at 2.5 mAh/g. The cycle number of the battery was recorded.

CHAPTER 5

RESULTS AND DISCUSSION

This chapter is divided into three parts based on types of polymer used

5.1 PAN/PVA membrane

5.1.1 PAN/PVA membrane characterization

The blended polymer of PAN and PVA at different blending ratios was used for preparing membrane separator for zinc-air battery. The effects of PAN addition in PVA on electrolyte uptake, ionic conductivity, and membrane structure were investigated.

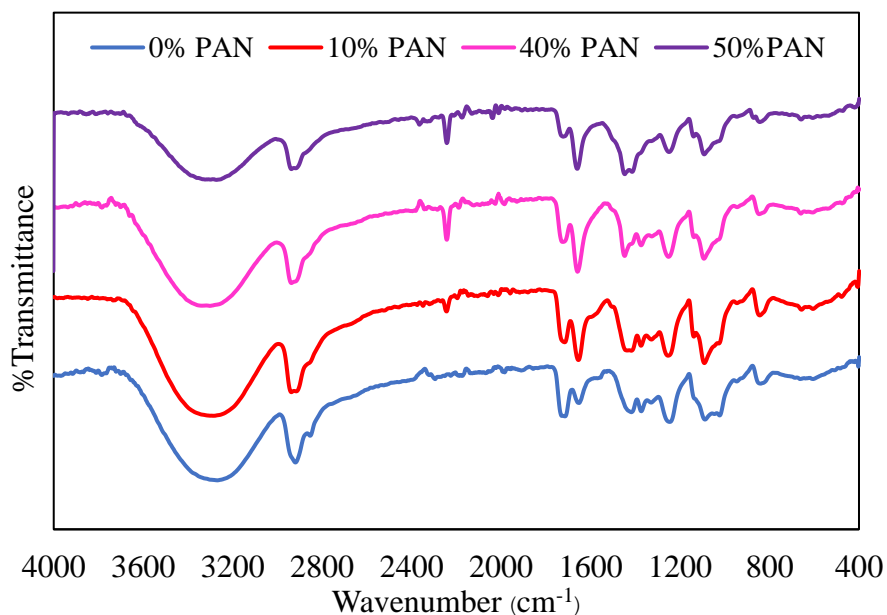


Figure 8. The ATR-FTIR spectra of the PAN/PVA membrane with different PAN contents

The ATR-FTIR was used to identify the presence of PAN in the final membranes. The functional group of the blend PAN/PVA membrane at different PAN content was shown in Figure 8. The absorption peaks of the nitrile group at around

2240 cm^{-1} which is the characteristic peak for PAN appeared in all blended-polymeric membranes, confirming the presence of the PAN polymer in the blend PAN/PVA membrane [40, 41].

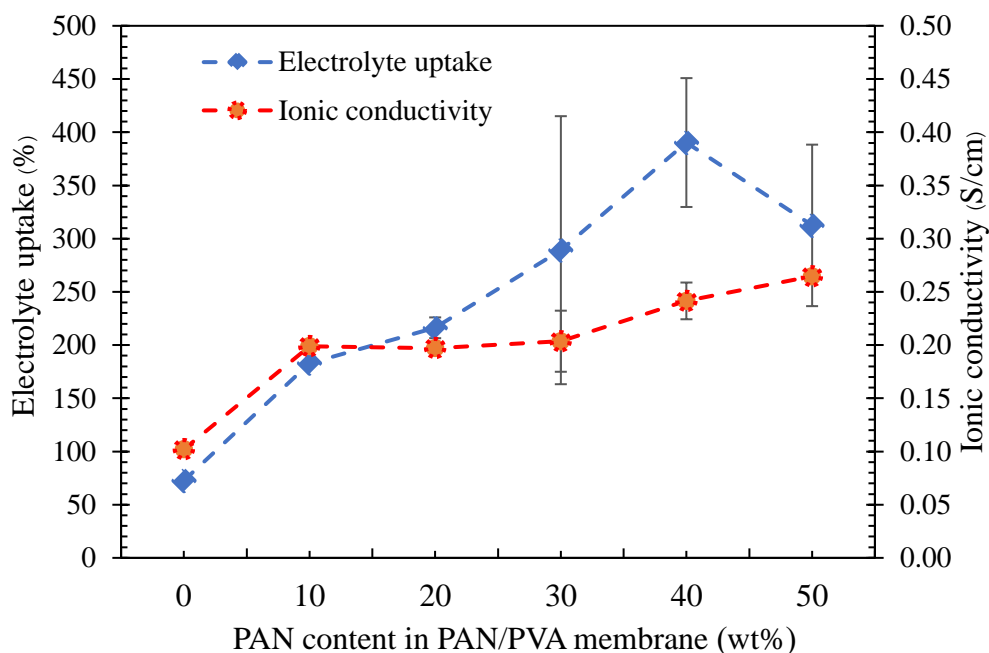


Figure 9. The electrolyte uptake and ionic conductivity of the prepared membranes with different PAN content

The effects of polymer blending ratio on electrolyte uptake and ionic conductivity of the membrane separator were investigated and illustrated in Figure 9. It was found that increasing PAN concentration in the blend PAN/PVA membrane, the electrolyte uptake and ionic conductivity were increased. This was mainly due to the hydrophilicity of PAN polymer [42]. The ionic conductivity showed a similar trend as the electrolyte uptake. However, the membrane obtained the highest electrolyte uptake when it contained 40% PAN. The drop of electrolyte uptake in the membrane with high PAN concentration (>40%) might be because of its worsen alkaline stability. The alkaline stability of the prepared PAN/PVA membranes after soaking in 6M KOH for 24 hours was observed (Figure 10).

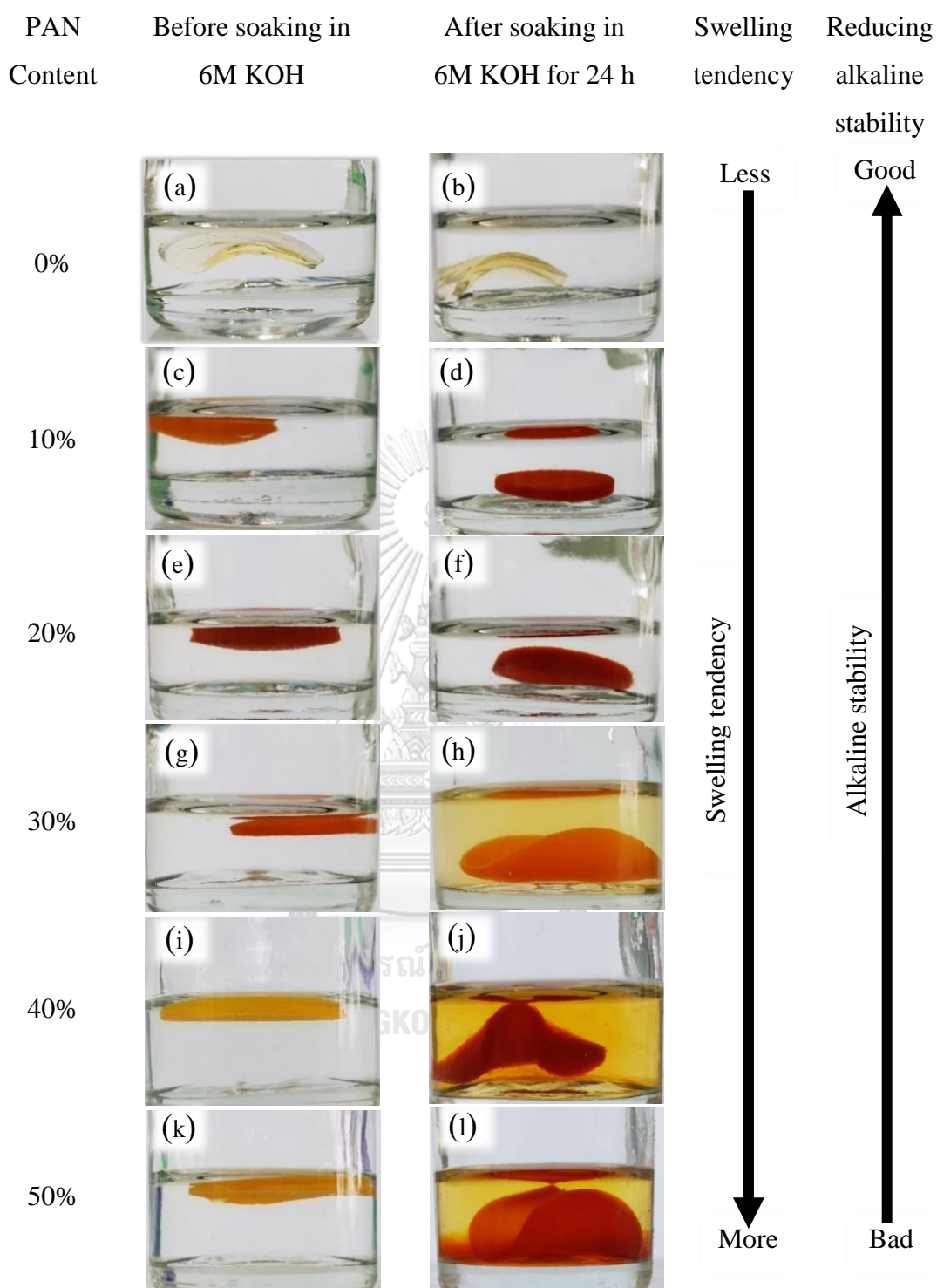
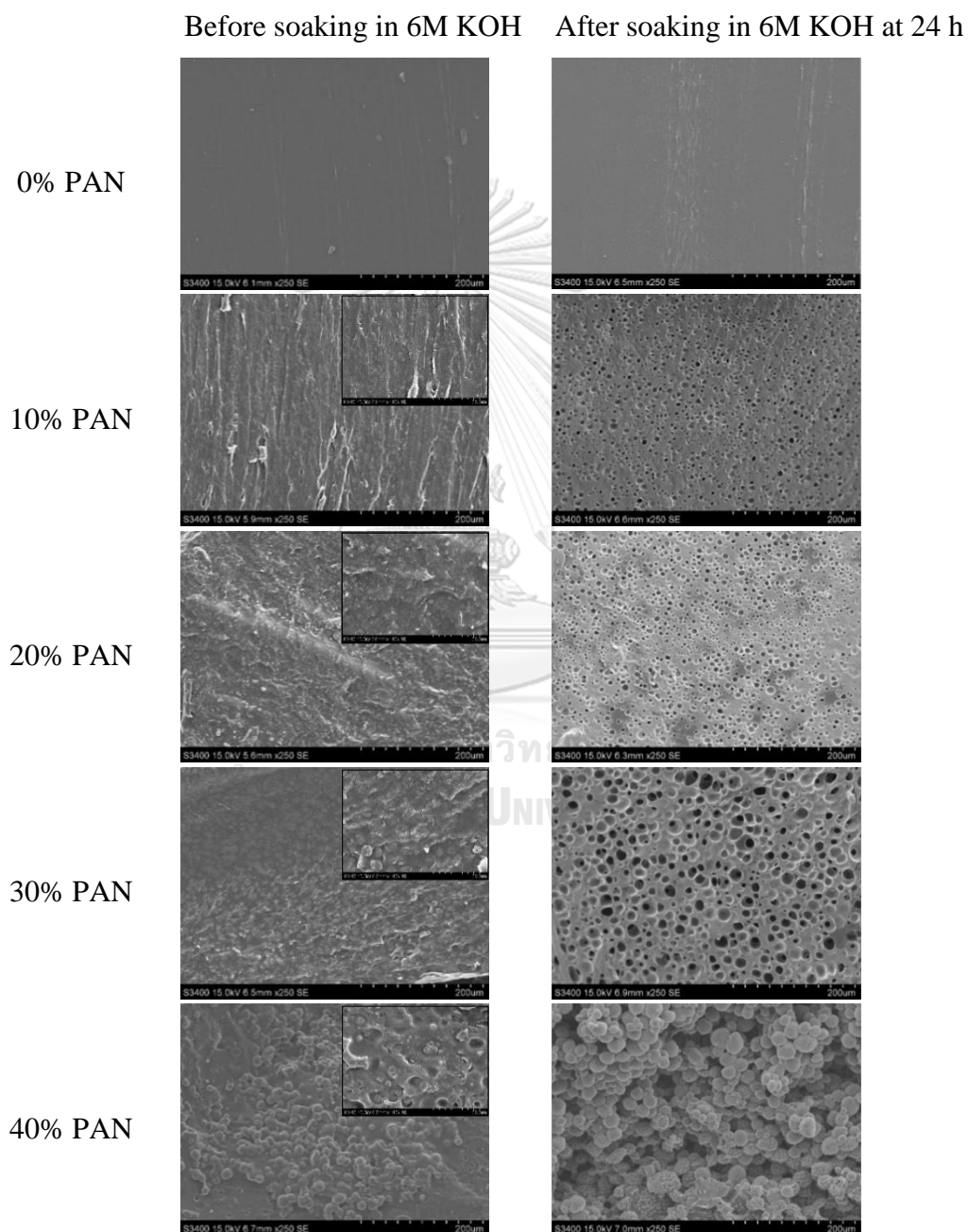


Figure 10. The observation of alkaline electrolyte stability of PAN/PVA membrane with different PAN concentration at 0% (a, b), 10% (c, d), 20% (e, f), 30% (g, h), 40% (i, j) and 50% (k, l) after immersing in 6M KOH for 24 hours at room temperature

It was clear that increasing PAN/PVA blending ratio leads to the worsen chemical stability of the membrane as the polymer started bleeding into the electrolyte solution after 24 h of soaking time, leading to structure change from a dense non-porous to the porous structure (see SEM images in Figure 11).



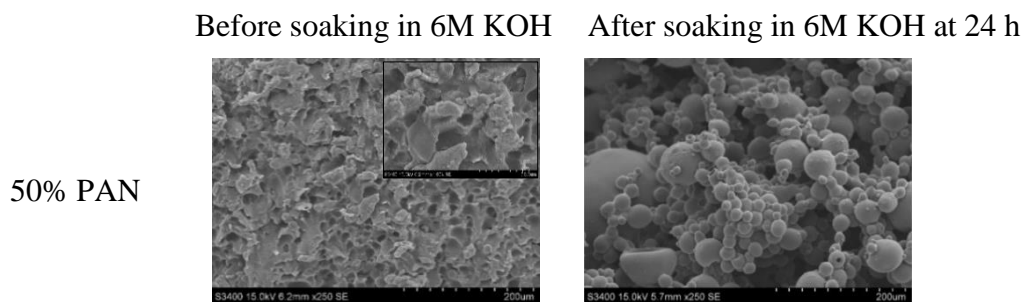


Figure 11. The structure of the blend PAN/PVA membrane from cross-section SEM (250x and 400x from small figure) with 0%, 10%, 20%, 30%, 40% and 50% PAN concentration after immersing in 6M KOH for 24 hours at room temperature

These structural changes can lead to the loss of alkaline electrolyte to air cathode easily and reduce battery performance

5.1.2 The performance of zinc-air battery using PAN/PVA membrane

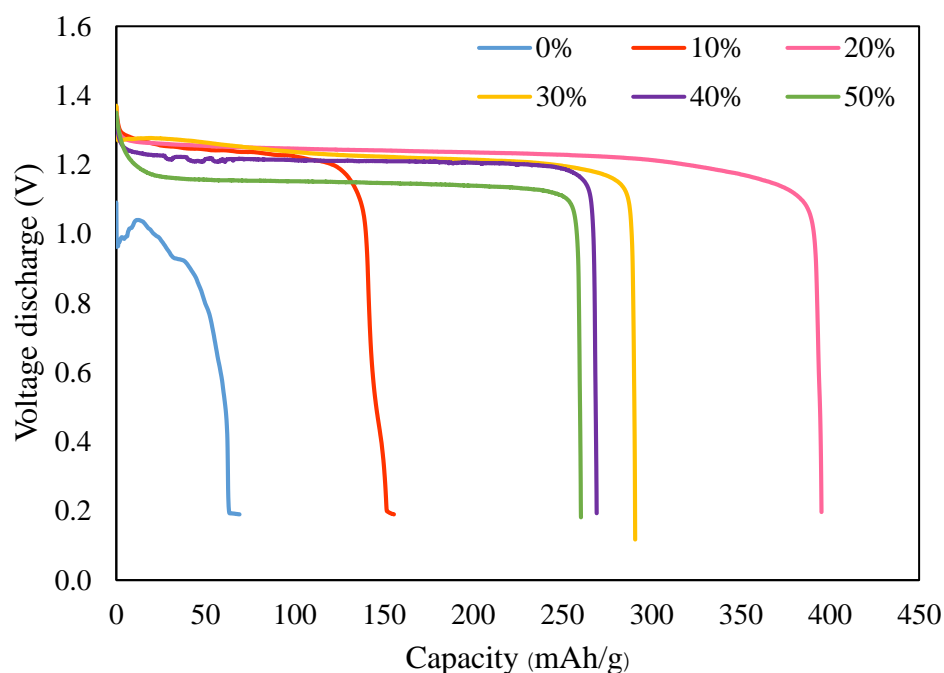


Figure 12. Discharge capacity of zinc-air battery by using PAN/PVA membrane at different PAN concentration

Voltage discharge and discharge capacity of the zinc-air coin cell battery (CR 2032), using PAN/PVA membrane as the separator, was investigated and shown

in Figure 12. Increasing PAN concentration in the blend PAN/PVA membrane has an effect on the voltage discharge and discharge capacity of the zinc-air battery. The voltage discharge of the prepared battery with all membrane containing PAN reached a stable value at around 1.1 – 1.3 V. On the other hand, the battery with pure PVA membrane could not provide a stable discharge voltage. This was mainly due to the addition of PAN in PVA enhanced the adhesion between the membrane/electrolyte and the zinc anode, resulting in a lower resistance compared to when pure PVA membrane was used. The highest discharge capacity obtained from the battery with blended polymer with 20 wt.% PAN content was 391 mAh/g. When increasing PAN addition to 30-50%, the voltage discharge and discharge capacity reduced. This may be due to the low alkaline electrolyte stability of the high PAN-contained membranes explained previously.

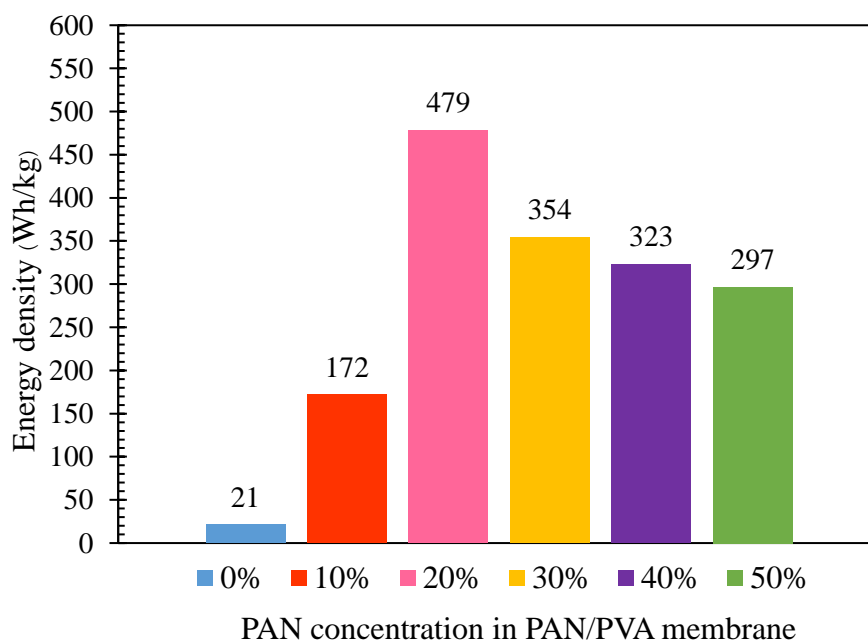


Figure 13. Energy density of zinc-air battery by using PAN/PVA membrane with different PAN concentration

The energy density of the prepared zinc-air coin cell battery, using PAN/PVA membrane with different blending ratios was estimated as shown in Figure 13. The results of the energy density showed a similar trend as the discharge capacity (from Figure 12). The highest energy density was 479 Wh/kg, obtained from using the blend PAN/PVA membrane with 20% PAN concentration. The energy density of zinc-air batteries was dropped when using high PAN concentration in the blend PAN/PVA membrane. The addition of PAN at 20% was found to be the optimum blending ratio to provide the highest discharge capacity and energy density (see Figure 14).

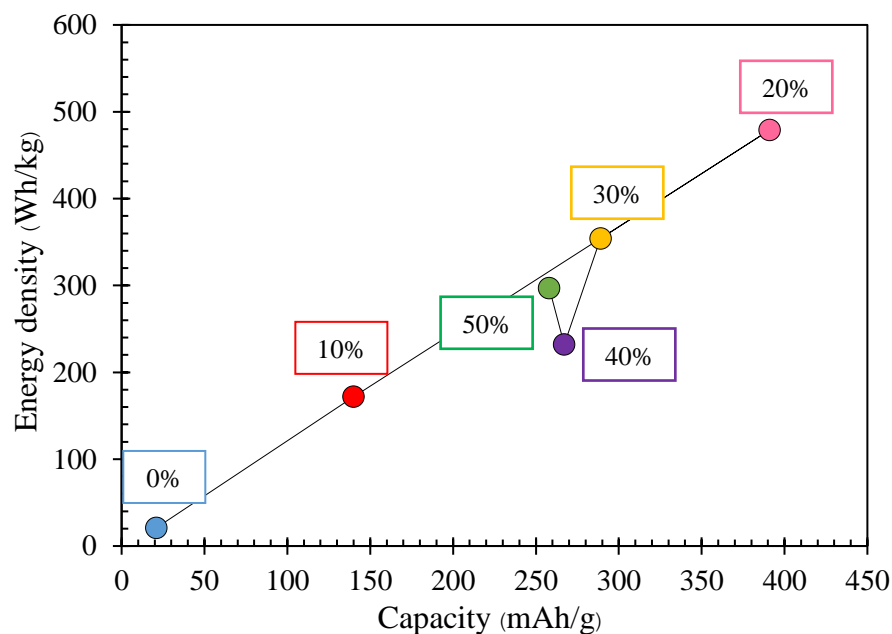


Figure 14. The relation between capacity and energy density of zinc-air battery by using PAN/PVA membrane at different PAN concentration

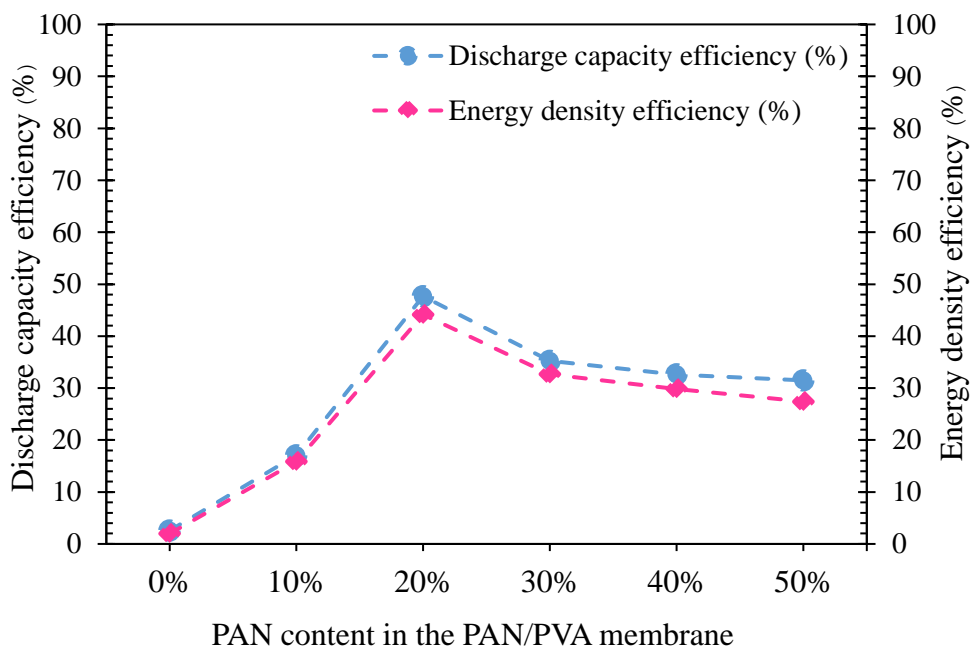


Figure 15. The performance of the prepared zinc-air batteries (discharge capacity and energy density performance) from using a PAN/PVA membrane at different PAN concentration (0-50%)

The efficiency of discharge capacity and energy density of the zinc-air batteries with different blended membranes is illustrated in Figure 15. The battery, showing the highest performance at 47.67% for discharge capacity and 44.15% for energy density, was the one prepared with the 20/80 PAN/PVA membrane. Although, increasing PAN concentration in the blend membrane led to high electrolyte uptake and good ionic conductivity, its zinc-air battery performance reduced. This might be due to the porous structure of these membranes, promoting the evaporation of the alkaline electrolyte on primary zinc-air battery testing [5].

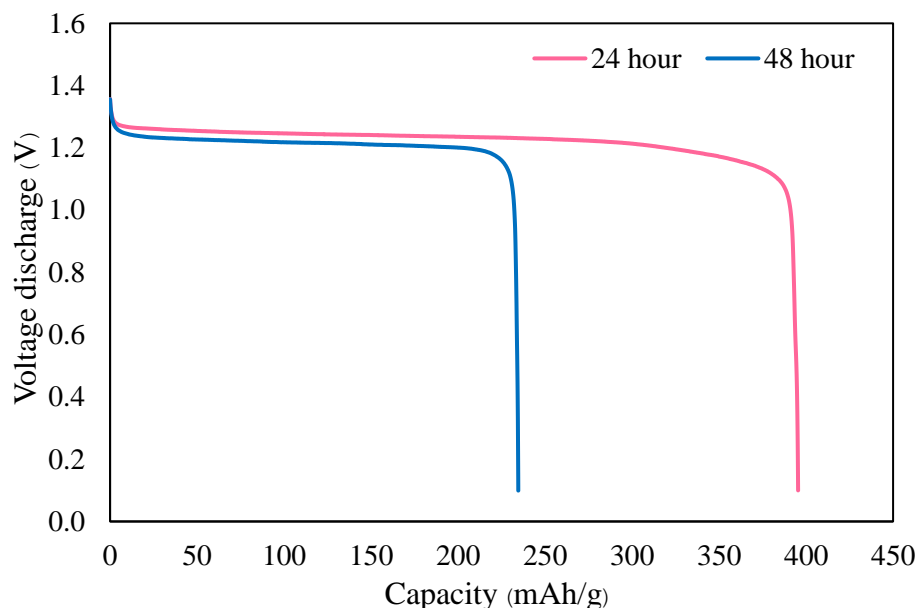


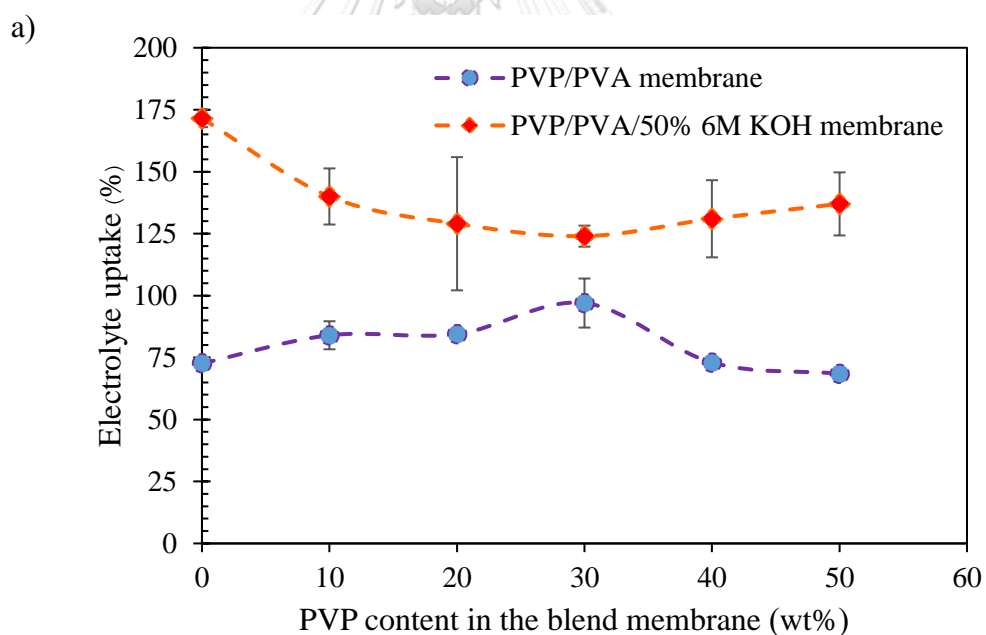
Figure 16. Discharge capacity of zinc-air battery with the membrane containing 20wt% PAN in a blend PAN/PVA membrane after immersing in 6M KOH for 24 h. and 48 h.

The discharge capacity of the prepared batteries from using a blend PAN/PVA membrane at 20% PAN concentration after immersing in 6M KOH at 24 h and 48 h is shown in Figure 16. Increasing immersion time (from 24 h to 48 h) caused a reduction in the discharge capacity of zinc-air batteries from 391 to 232 mAh/g. The zinc-air battery has lost around 19.36% of its capacity. In addition, the energy density of the membrane has dropped from 479 to 282 Wh/kg. The cause of these declined properties was because of the low alkaline stability of the blend PAN/PVA membrane leading to the membrane structure changes, that can lose alkaline electrolyte from the batteries to air via the evaporation more easily [5].

Although the addition of PAN in PVA can improve zinc-air battery performance in term of voltage discharge, discharge capacity and energy density, the membrane became unstable to the exposure of alkaline electrolyte and long term operation.

5.2 PVP/PVA/KOH membrane

It is worth to mention here that the formation of the membrane separator from PVP/PVA blended polymer was slightly different from the PAN/PVA blended polymer. In order to increase the electrolyte uptake and ionic conductivity, 50 wt.% of 6M KOH was added into polymer solution before casting [43-45]. Without the addition of KOH in polymer solution during the formation of the membranes, the resultant membrane was so dense and rigid that make it difficult to adsorb electrolyte. As the consequence, the electrolyte uptake and ionic conductivity of the membrane prepared without KOH priming step were much lower than those prepared with the KOH priming as can be seen in Figure 17.



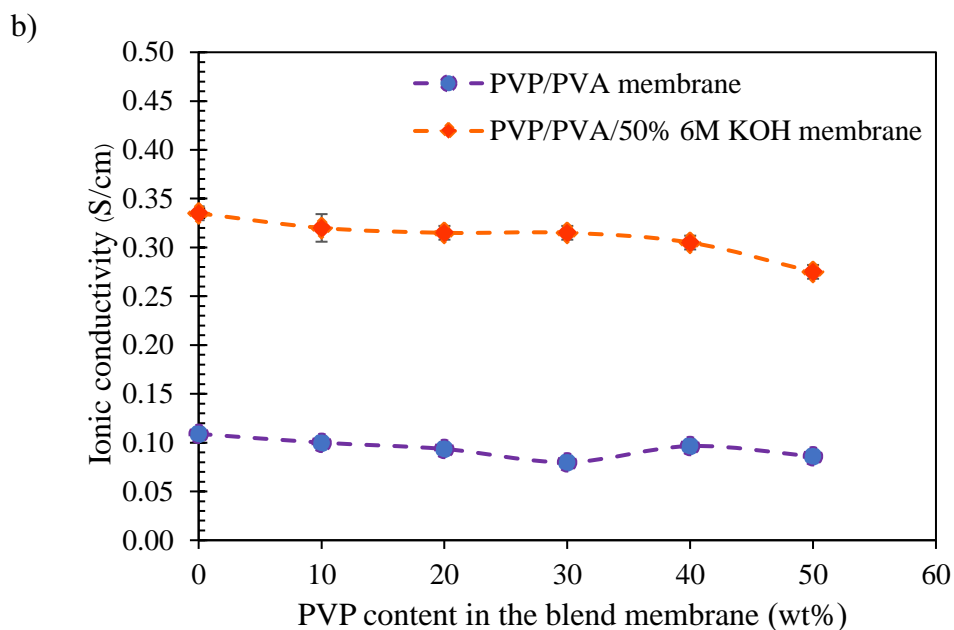


Figure 17. The electrolyte uptake (a) and ionic conductivity (b) of PVP/PVA/50% 6M KOH membranes with different PVP concentration

The effects of blending ratio of PVP/PVA with the present of KOH were investigated.

5.2.1 PVP/PVA/KOH membranes characterization

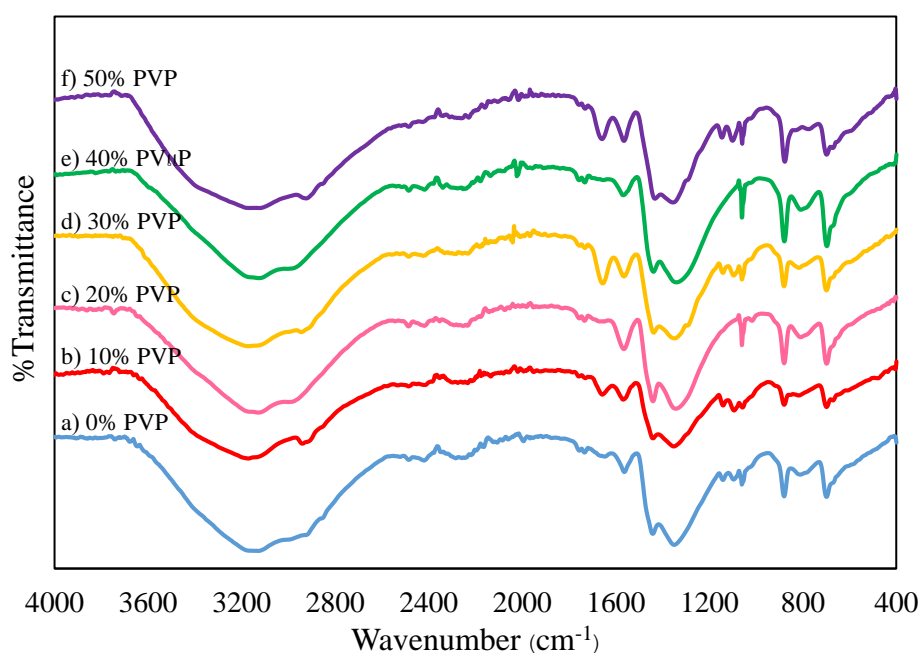


Figure 18. The ATR-FTIR spectra of the PVP/PVA/KOH membrane with different PVP contents at (a) 0, (b)10, (c) 20, (d) 30, (e) 40, and (f) and 50%

Figure 18 shows ATR-FTIR spectra of the prepared membrane. All PVP/PVA/KOH membrane showed similar FTIR spectra. The PVP polymer in the blend membrane could be identified from the shift of OH groups from 3200 cm^{-1} to 3100 cm^{-1} due to the interaction between C=O groups of PVP and OH bond of PVA polymer. The presence of these functional groups can confirm that there was PVP polymer in the blend PVP/PVA/KOH membrane [46-49].

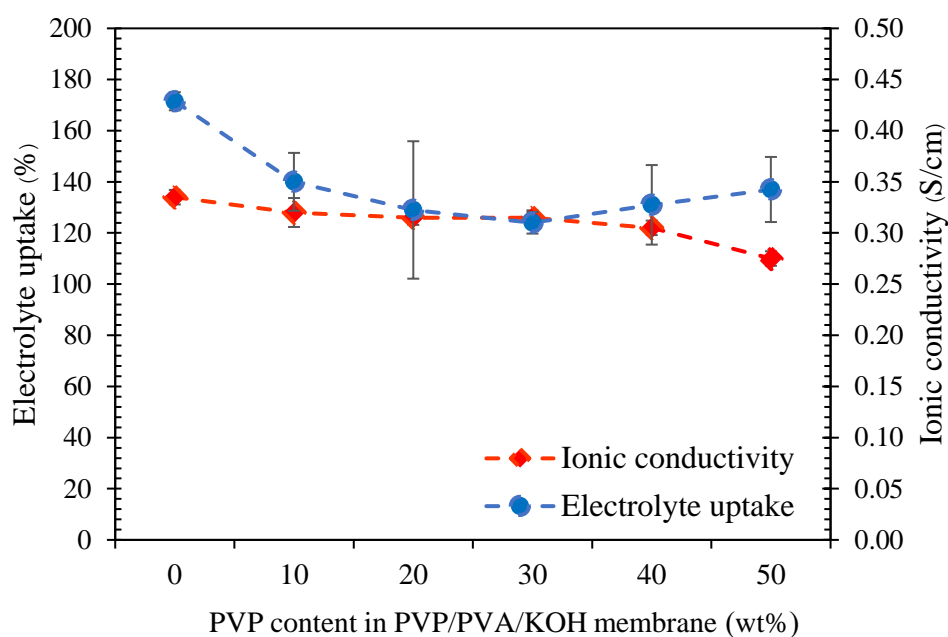
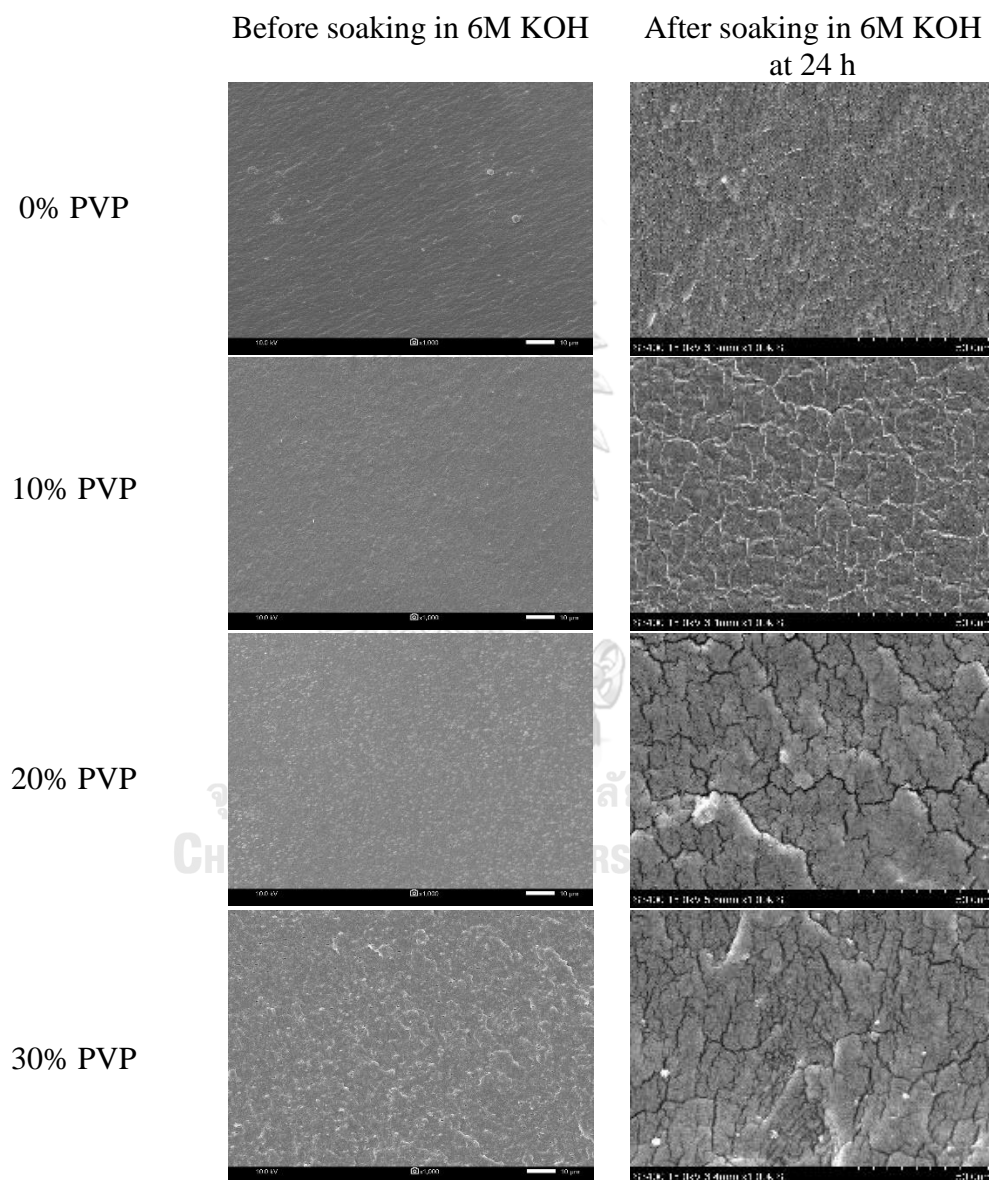


Figure 19. The electrolyte uptake and ionic conductivity of the prepared membranes with different PVP content

The electrolyte uptake and the ionic conductivity of the PVP/PVA/KOH membrane separator/electrolyte at different PVP concentration are shown in Figure 19. Increasing PVP concentration reduced the electrolyte uptake and the ionic conductivity. Pure PVA membrane showed the highest electrolyte uptake and ionic conductivity at 172% and 0.34 S/cm, respectively. The addition of PVP did not have a positive influence on the electrolyte uptake and the ionic conductivity of the blended polymeric membrane. This might be due to the inhomogeneous dissolution of PVP

in KOH solution (see in appendix C). The mixture solution showed a phase separation while drying in a petri dish. Using high PVP content of the membrane led to a lower KOH in the resultant membranes; as the consequence, the electrolyte uptake and ionic conductivity were decreased.



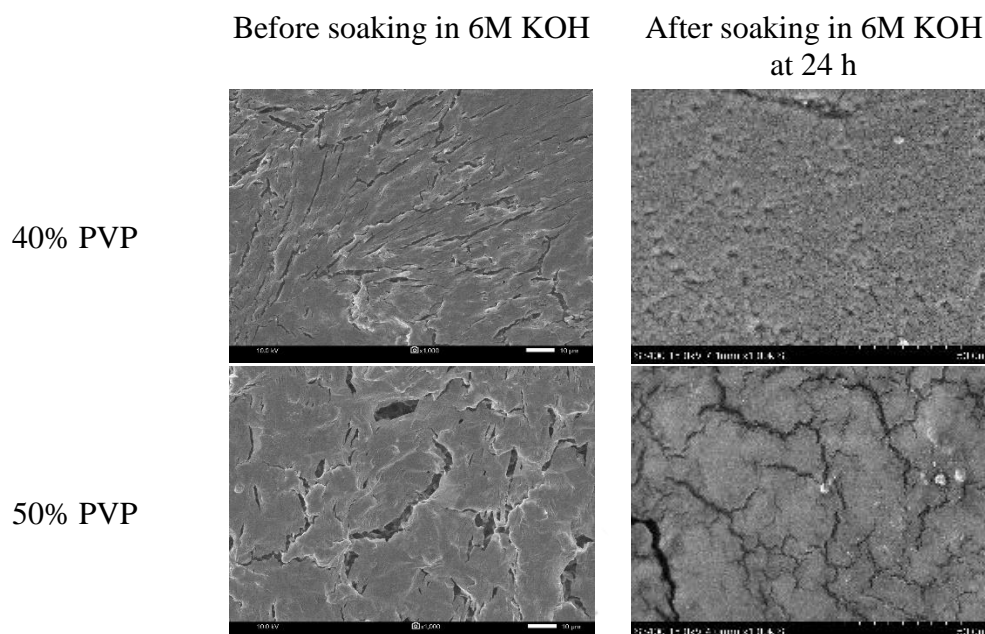


Figure 20. The structure of the blend PVP/PVA/KOH membrane from cross-section SEM (1000x) with 0%, 10%, 20%, 30%, 40% and 50% PVP concentration after immersing in 6M KOH for 24 hours at room temperature

The structure of PVP/PVA/KOH membrane at different PVP concentration at 0-50% was shown in Figure 20. The incompatibility of PVP polymer and KOH lead to the porous structure of the membrane when using high PVP content (40-50%). After immersing in 6M KOH, the crack of a membrane was increased at high PVP content (see from the cross-section with SEM). So, increasing PVP concentration leads to the low alkaline stability of a blend membrane.

5.2.2 The performance of zinc-air battery using PVP/PVA/KOH membrane/electrolyte

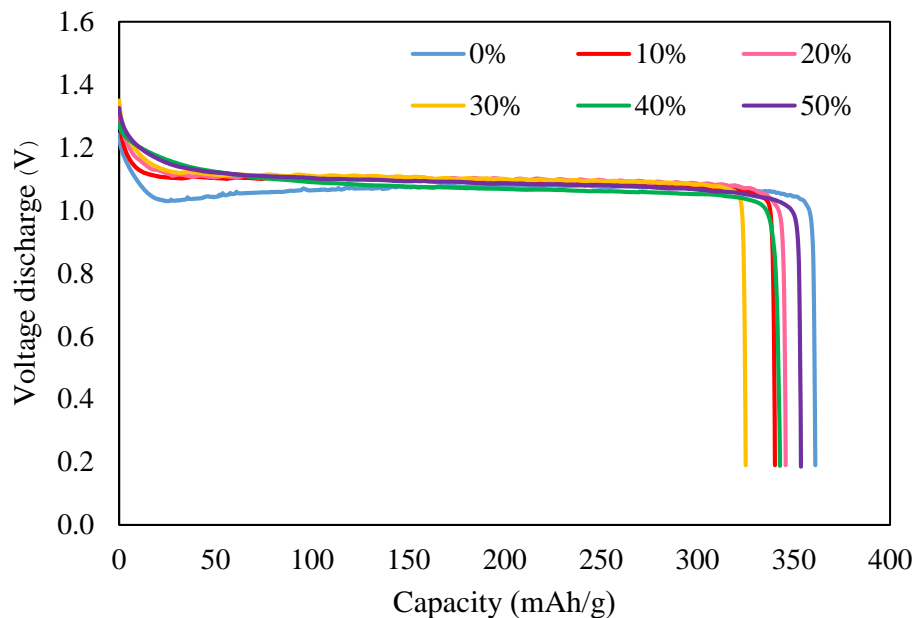


Figure 21. Discharge capacity of zinc-air battery by using PVP/PVA/KOH membrane at different PVP concentration

The zinc-air battery performance from the prepared battery by using PVA/PVP/KOH membrane separator/electrolyte at different PVP concentration was shown in Figure 21. The voltage discharge of all the prepared batteries at around 1.1 V was obtained. The addition of PVP polymer from 0% to 50% PVP concentration of the prepared membranes could slightly increase voltage discharge in the beginning of the discharge test. Similar to the case of PAN addition, the addition of PVP softened the structure of PVA film and improved the adhesion and the contact between the membrane/electrolyte and the zinc anode. However, all PVP/PVA/KOH membranes with different PVP contents provided similar discharge capacity around 323-358 mA/g/h.

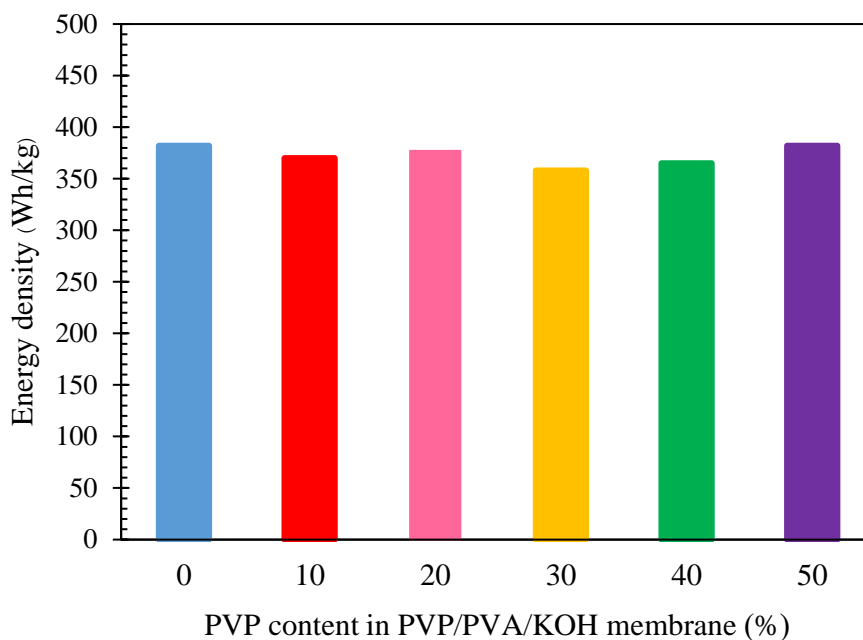


Figure 22. Energy density of zinc-air battery by using PVP/PVA/KOH membrane with different PVP concentration

The zinc-air battery performance in term of energy density from using PVP/PVA/KOH membranes at different PVP concentration is shown in Figure 22. The energy density of the battery using membrane with different PVP contents was relatively constant at around 358-382 mAh/g. It can imply that the addition of PVP in the blend PVP/PVA/KOH has no effect on the energy density of zinc-air batteries.

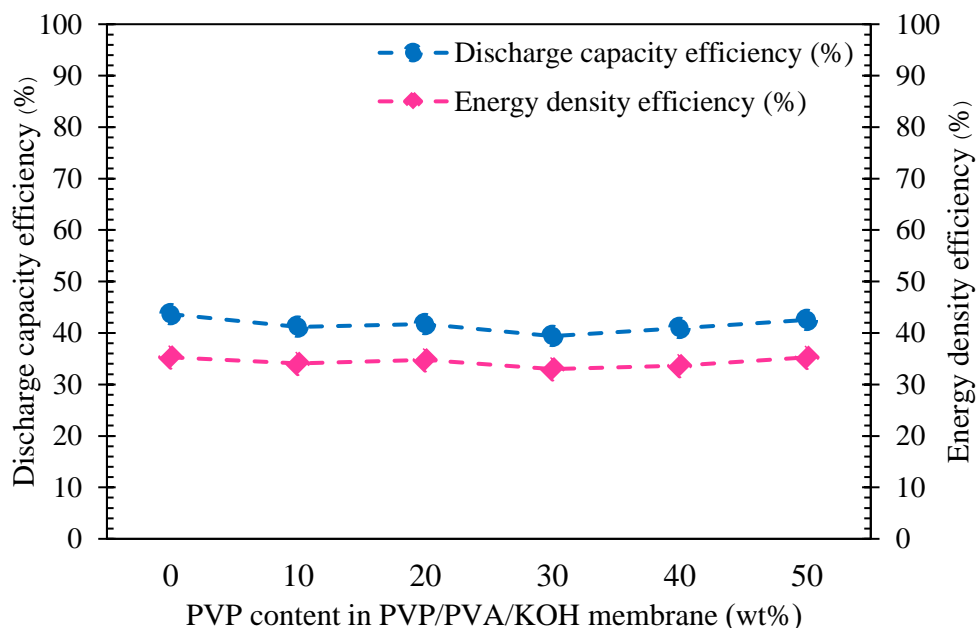


Figure 23. The performance of the prepared zinc-air batteries (discharge capacity and energy density performance) from using a PVP/PVA/KOH membrane at different PVP concentration (0-50%)

The efficiency of discharge capacity and power density of the prepared zinc-air batteries with different PVP/PVA/KOH membranes was estimated and shown in Figure 23. The efficiency of discharge capacity and power density of battery with all PVP/PVA/KOH membranes was constant at around 39-44% and 33-35%, respectively. The similar of the electrolyte uptake and ionic conductivity in all PVP concentration of a blend membrane led to the two constant battery efficiency. When comparing the effect of PVP addition to the PAN addition, the addition of PVP in PVA resulted in a more stable membrane.

5.3 The effect of MCM-41 addition

This section studies the effect of inorganic filler addition (MCM-41) in the blend PVP/PVA/KOH. The characteristics of the synthesized filler shown in Appendix D confirmed that the fillers were mesoporous MCM-41.

5.3.1 Characterization of the composite membrane

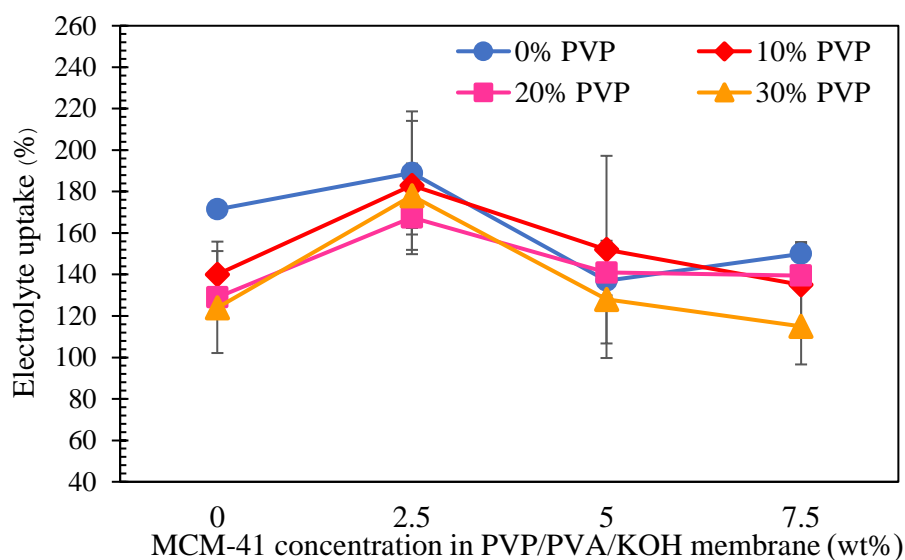


Figure 24. The electrolyte uptake of the prepared membrane at 0, 10, 20 and 30% PVP content with different MCM-41 concentration

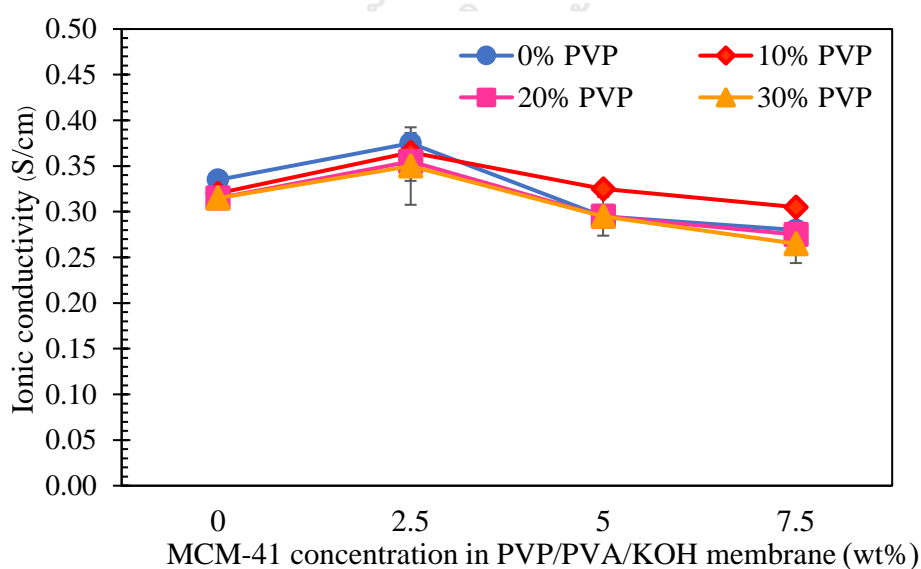
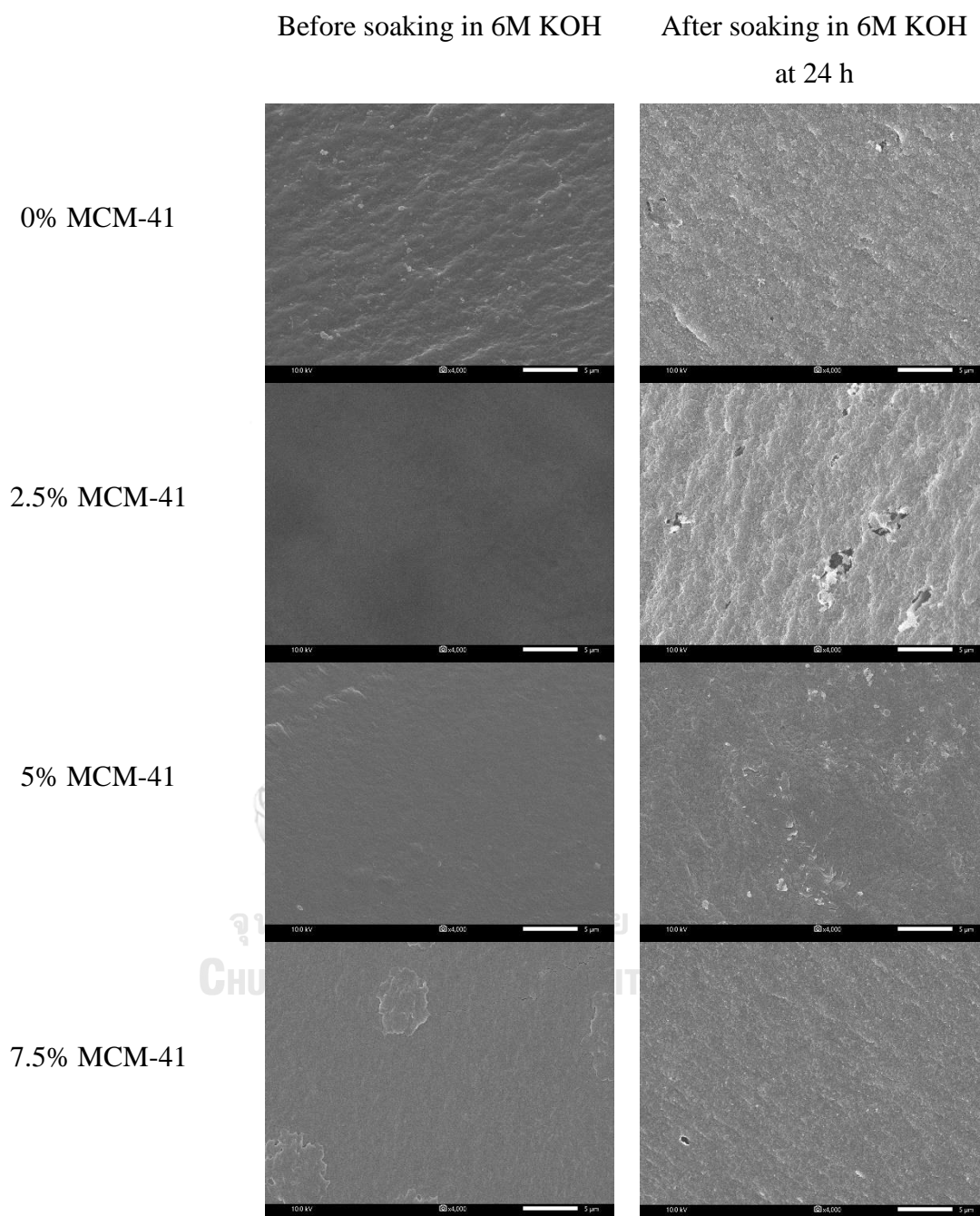


Figure 25. The ionic conductivity of the prepared membrane at 0, 10, 20 and 30% PVP content with different MCM-41 concentration

The electrolyte uptake and ionic conductivity of the composite MCM-41/PVP/PVA/KOH membrane at different PVP and MCM-41 concentration were illustrated in Figure 24 and 25, respectively. The small addition of MCM-41 (2.5 wt.%) resulted in an enhancement of the electrolyte uptake and ionic conductivity in the composite membrane; however, when increasing the addition amount ($>2.5\%$) the electrolyte uptake and ionic conductivity gradually reduced. The low KOH adsorption capacity of the composite membrane at high MCM-41 content (shown in Appendix C) led to a decrease in both electrolyte uptake and ionic conductivity. So, using small MCM-41 content was found to increase the electrolyte uptake and ionic conductivity.



a) The addition of MCM-41 in pure PVA polymer electrolyte



b) The addition of MCM-41 in 30% PVP of the composite polymer electrolyte

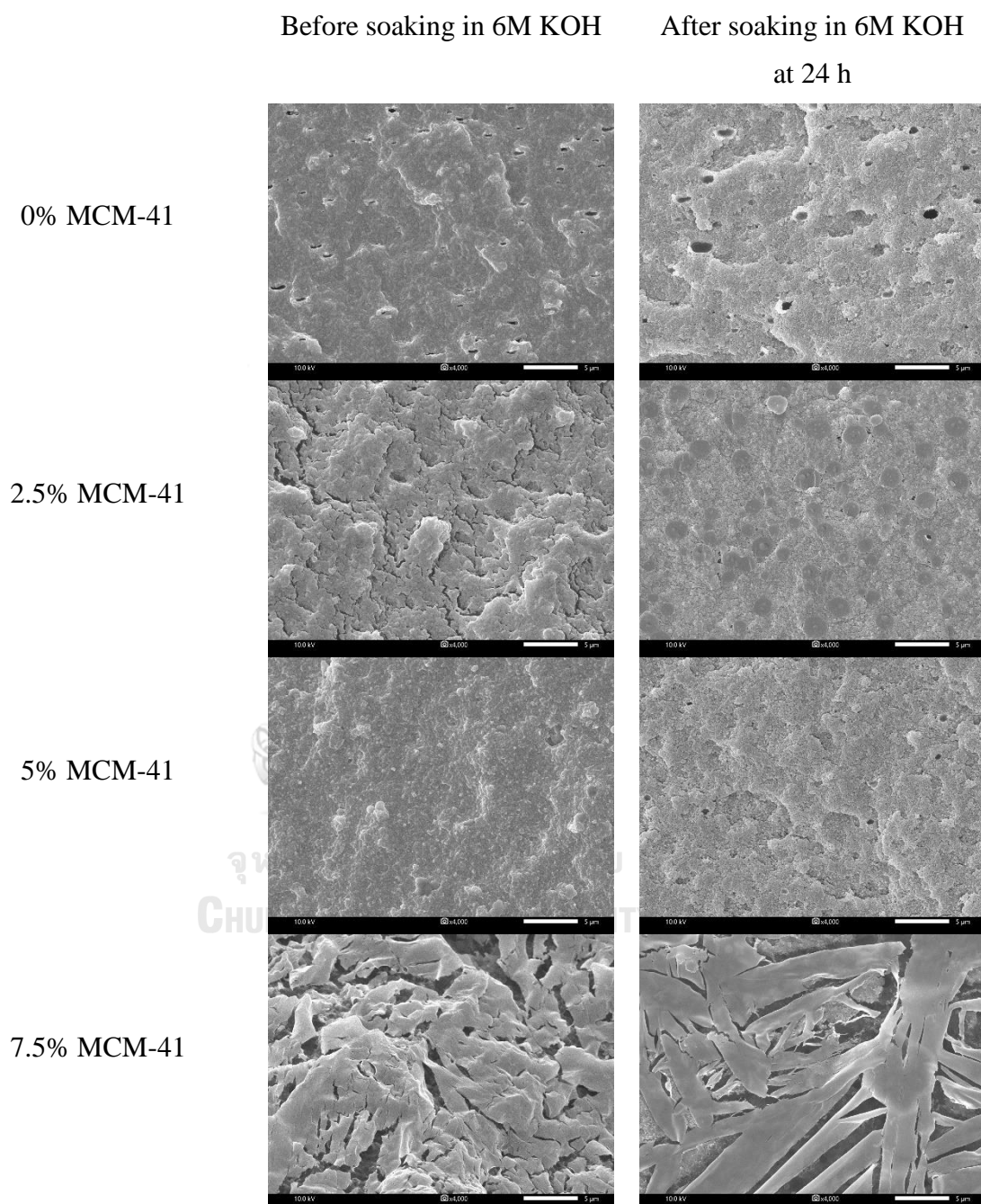


Figure 26. The structure of the composite MCM-41/PVP/PVA/KOH membrane from cross-section SEM (4000x) with 0% and 30% PVP concentration after immersing in 6M KOH for 24 hours at room temperature

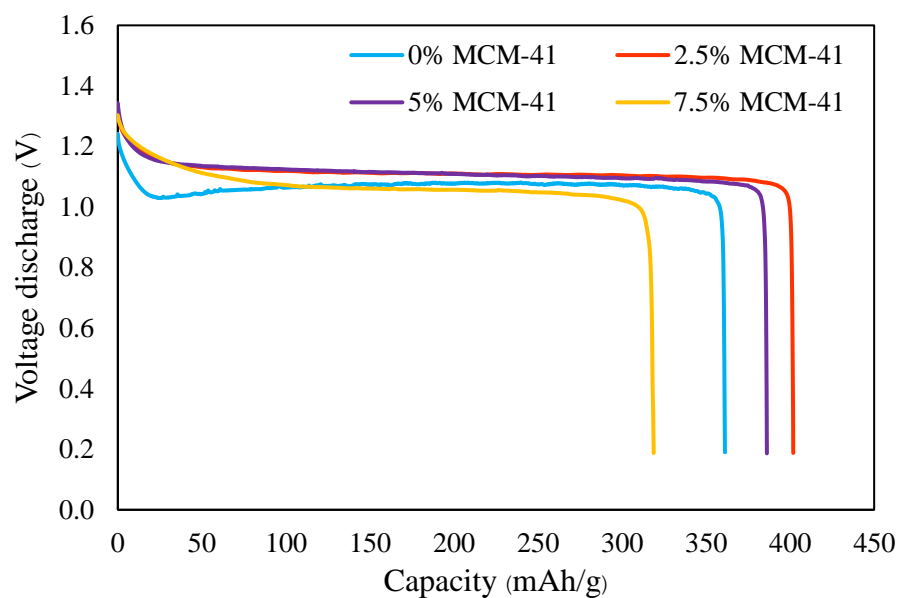
The structure of MCM-41/PVP/PVA/KOH membrane at 0 and 30% PVP content with different MCM-41 concentration at 0-7.5% was shown in Figure 26. Increasing PVP combine with MCM-41 content led to a rougher surface and more porous structure. After immersing the membrane containing MCM-41 in 6M KOH, no membrane structure change was observed.

5.3.2 The performance of zinc-air battery using the composite membranes

5.3.2.1 Full discharge zinc-air batteries testing

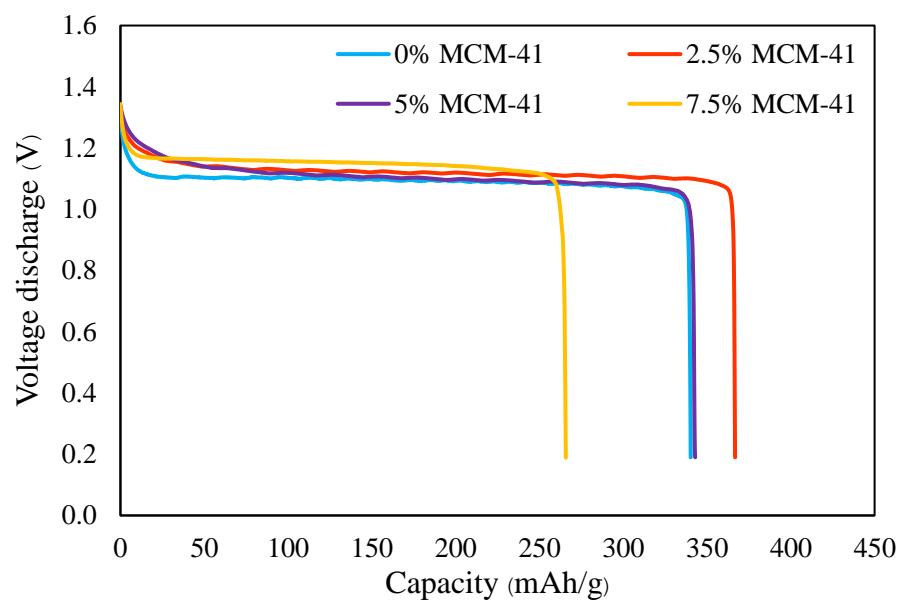
The voltage discharge and discharge capacity of the prepared zinc-air batteries from using different composite membranes are shown in Figure 27.

a) The addition of MCM-41 in pure PVA of the composite polymer electrolyte



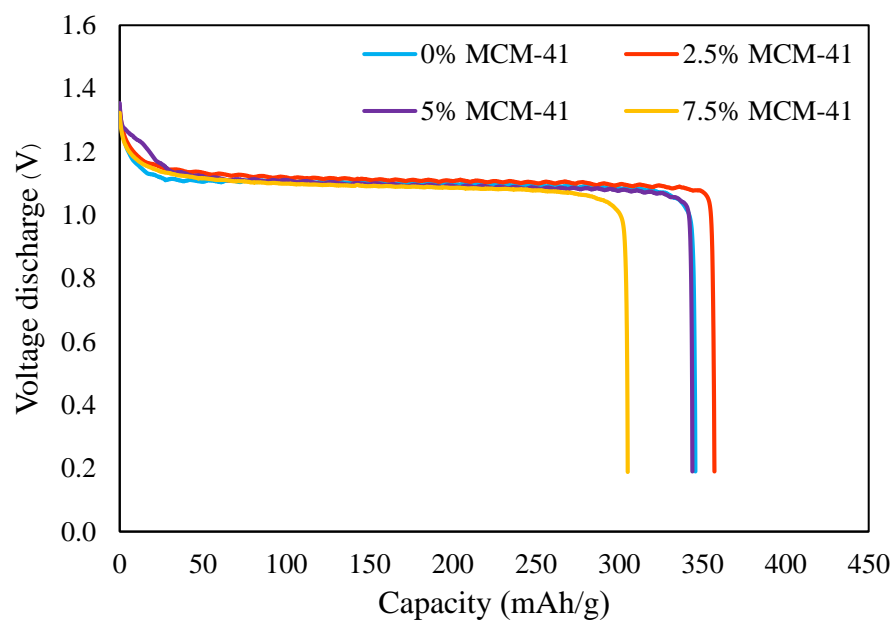
b) The addition of MCM-41 in 10% PVP of the composite polymer

electrolyte



c) The addition of MCM-41 in 20% PVP of the composite polymer

electrolyte



d) The addition of MCM-41 in 30% PVP of the composite polymer electrolyte

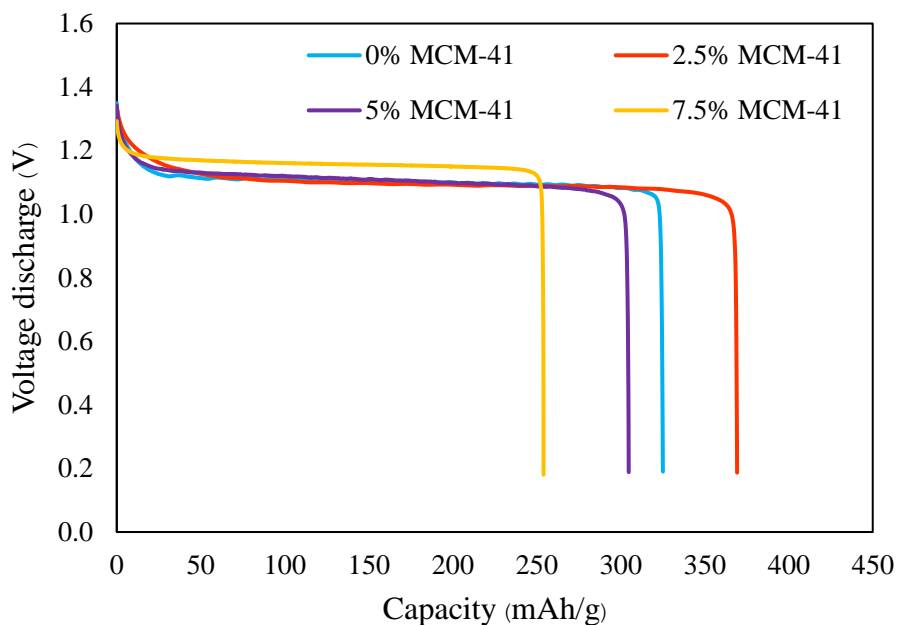
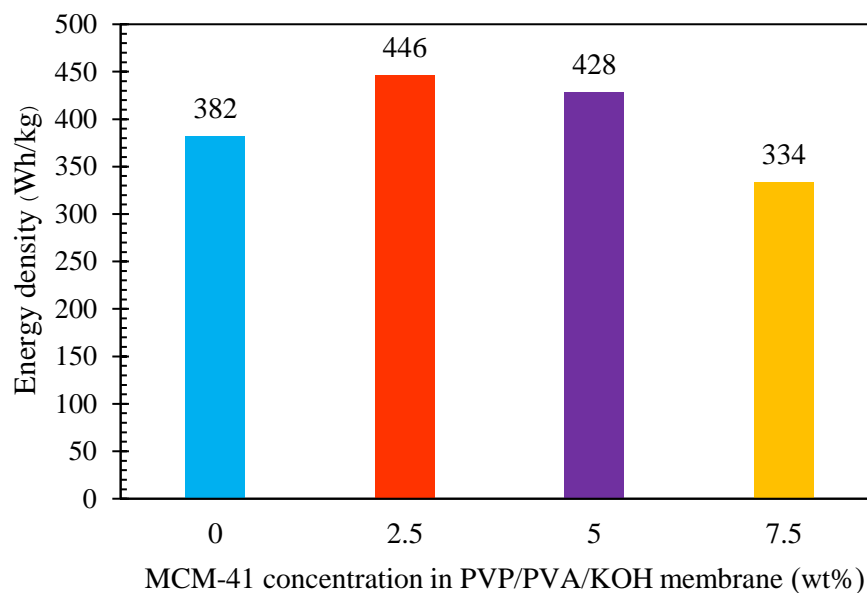


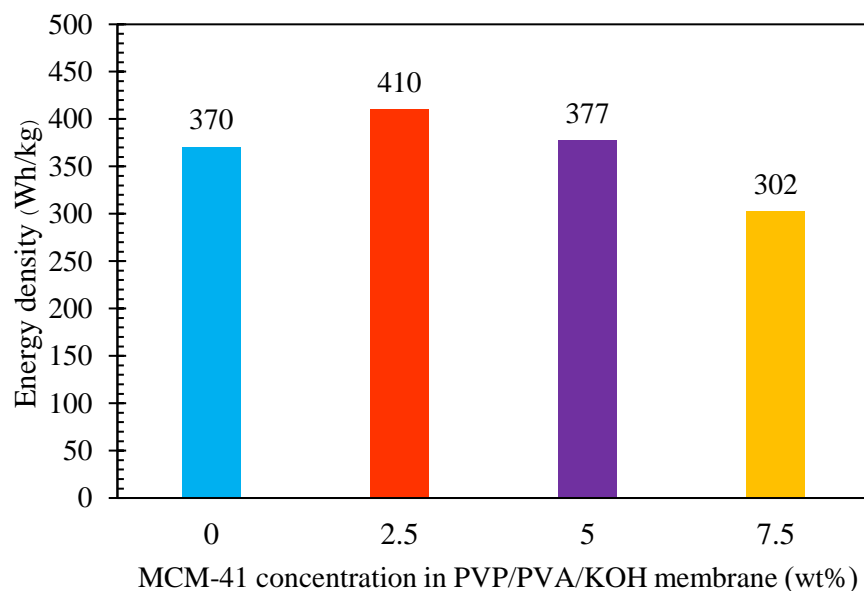
Figure 27. Discharge capacity of zinc-air battery by using MCM-41/PVP/PVA/KOH membrane at different MCM-41 loading

Increasing PVP concentration help stabilizing the voltage discharge of the zinc-air batteries. In addition, the small addition of MCM-41 (2.5-7.5%) in the polymer to gel-like polymer can further improve the voltage discharge of the battery. However, using high PVP and MCM-41 content in the membranes could reduce the discharge capacity of the battery. The pure PVA combine with 2.5% MCM-41 composite membrane showed the highest discharge capacity at 400 mAh/g.

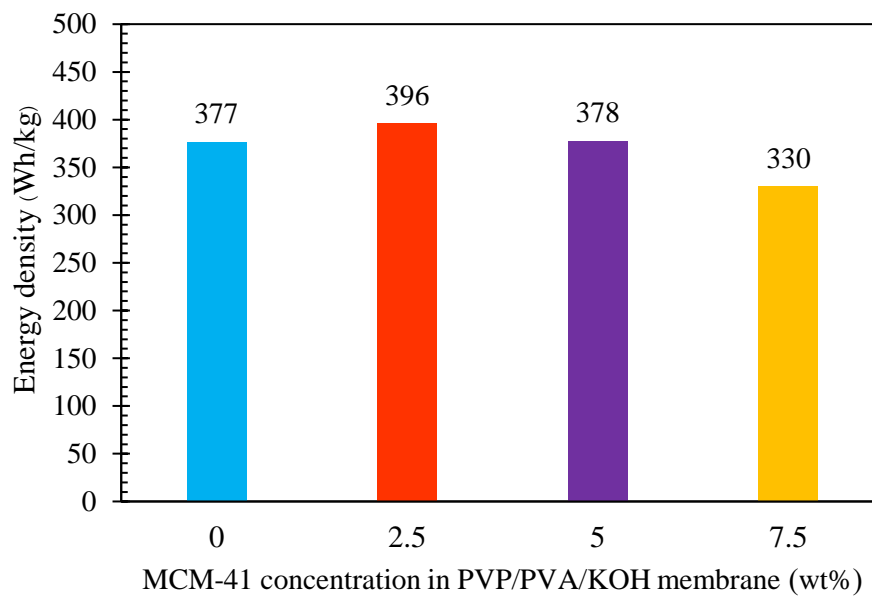
a) The addition of MCM-41 in pure PVA of the composite polymer electrolyte



b) The addition of MCM-41 in 10% PVP of the composite polymer electrolyte



c) The addition of MCM-41 in 20% PVP of the composite polymer electrolyte



d) The addition of MCM-41 in 30% PVP of the composite polymer electrolyte

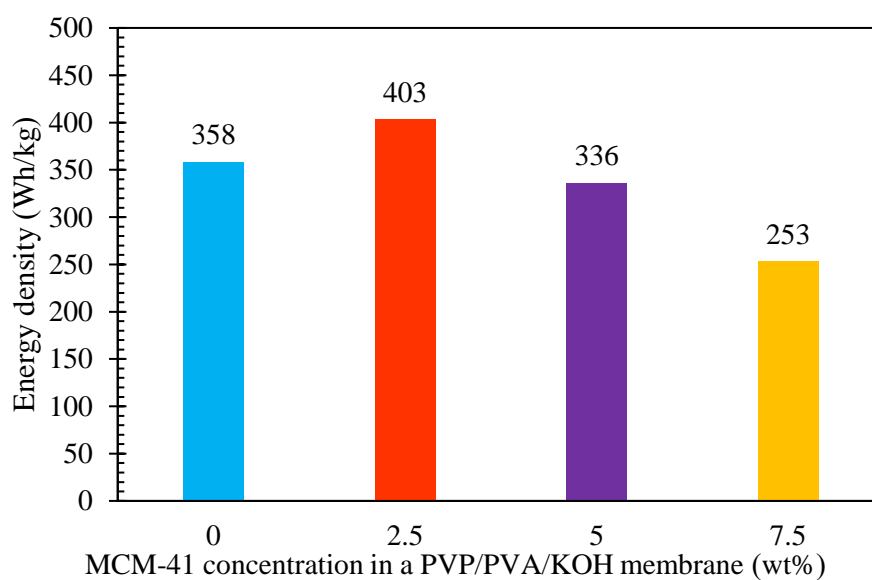
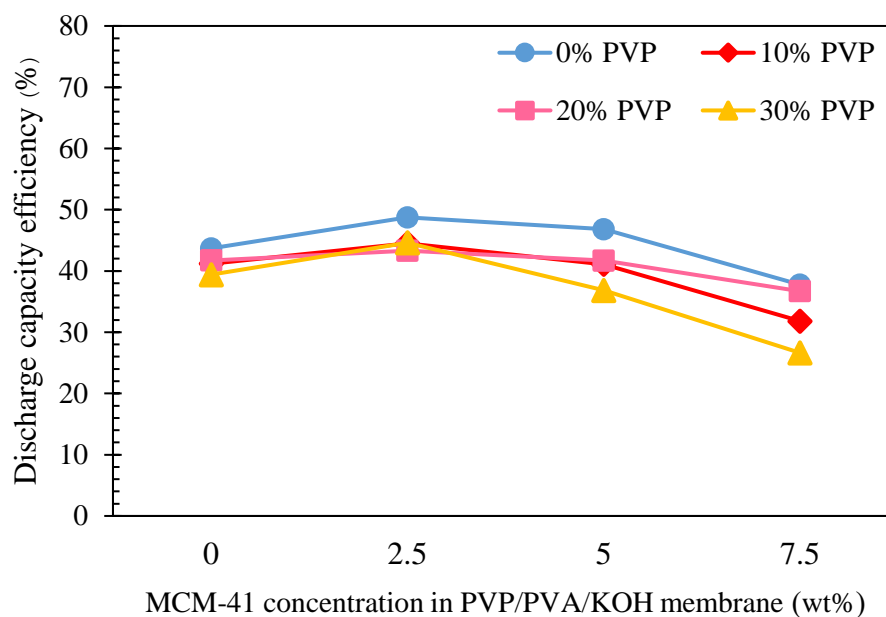


Figure 28. Energy density of zinc-air battery by using MCM-41/PVP/PVA/KOH membrane at MCM-41 loading

The energy density of the prepared zinc-air batteries using different composite membrane is shown in Figure 28. The addition of small amount of MCM-41 up to 2.5 wt.% in all PVP concentration of the blend membrane improved the energy density of the battery. However, further addition of MCM-41 resulted in a decline of energy density. The membrane at 0% PVP concentration with 2.5% MCM-41 content provided the highest energy density at 446 Wh/kg.

a) Discharge capacity efficiency by using MCM-41/PVP/PVA/KOH membrane



b) Energy density efficiency by using MCM-41/PVP/PVA/KOH membrane

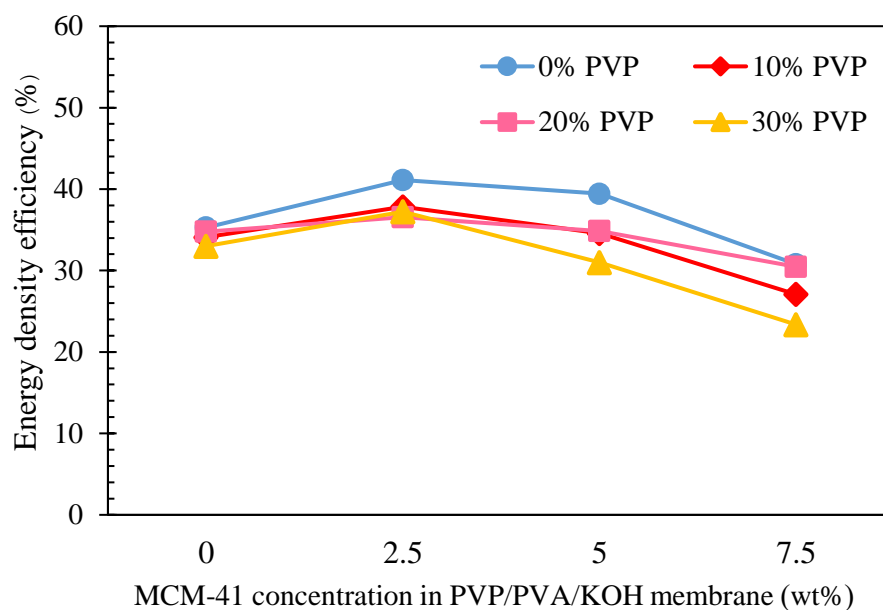
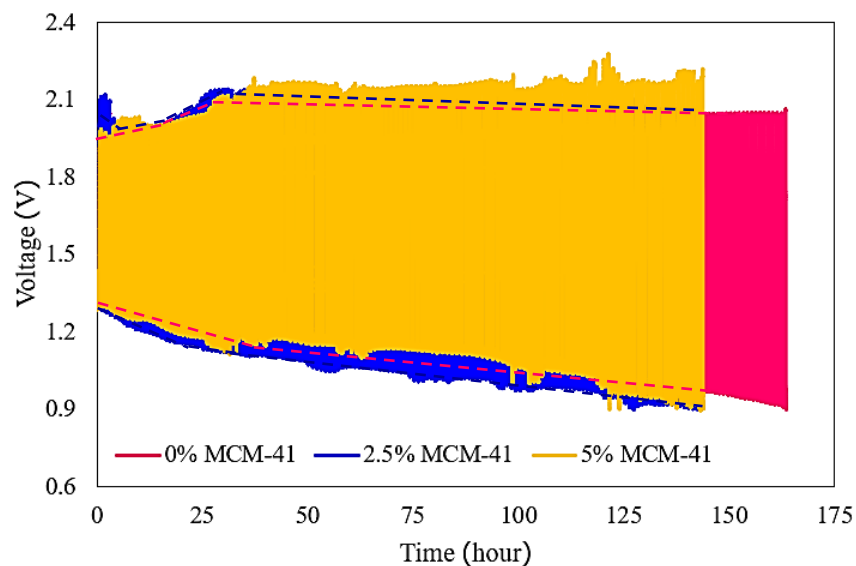


Figure 29. The performance of the prepared zinc-air batteries (discharge capacity and energy density performance) from using a MCM-41/PVP/PVA/KOH membrane at different PVP and MCM-41 concentration

Discharge capacity and energy density efficiency of a zinc-air battery from using MCM-41/PVP/PVA/KOH membrane are shown in Figure 29. In the next section, the life cycle of battery using promising composite membranes containing 0 - 10 wt.% PVP and 0 - 5 wt.% MCM-41 was further investigated.

5.3.2.2. Discharge-charge zinc-air batteries testing (cycle testing)

(a) MCM-41/PVA/6M KOH membrane



(b) MCM-41/PVP/PVA/6M KOH membrane with 10 wt.% PVP

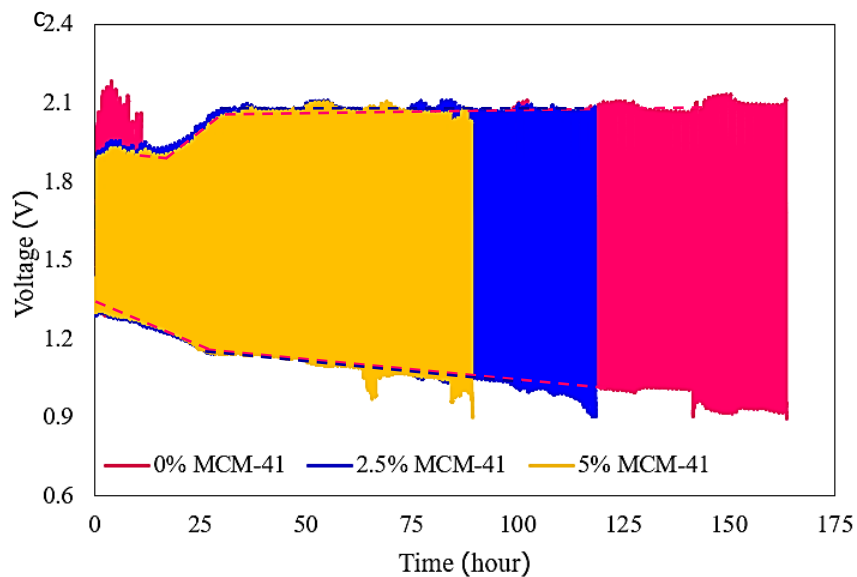
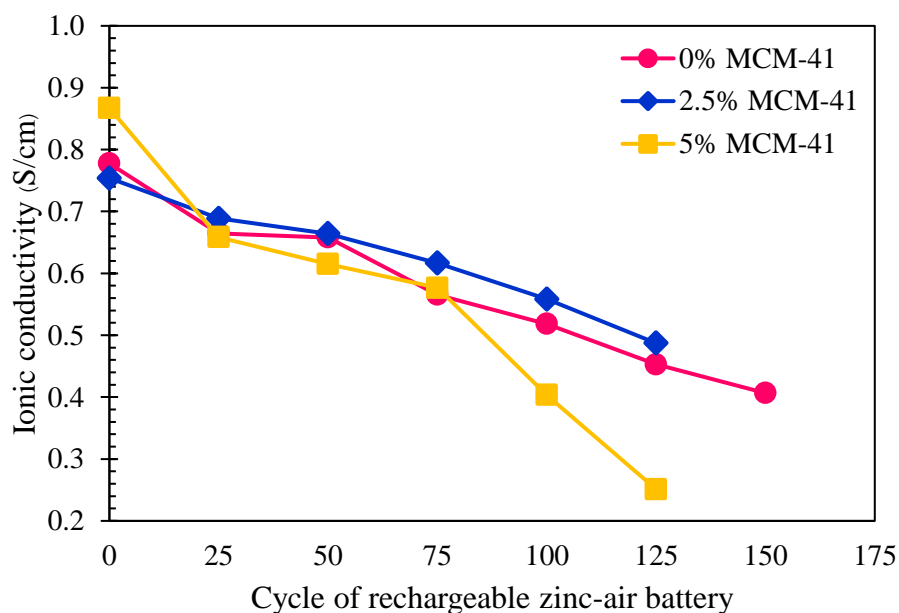


Figure 30. The relation between charge-discharge voltage (V) and time (hour) of rechargeable zinc-air batteries from using (a) MCM-41/PVA/6M KOH membrane with 0 – 5 % of MCM-41 and (b) MCM-41/PVP/PVA/6M KOH membrane with 10 wt.% PVP and 0 – 5 % of MCM-41

The life cycle of rechargeable zinc-air battery by using the selected promising membranes is shown in Figure 30. The addition of MCM-41 led to a lower voltage discharge in each cycle and shorten the life cycle of the battery. The pure PVA membrane has the highest cycle of rechargeable battery at 163 cycles (163 hours). This might be because with the presence of PVP polymer and MCM-41, zinc can more easily cross the membranes (due to the porous structure of a membrane, see Figure 35) from zinc anode to an air cathode and forming zinc oxide resistant layer close the surface of a cathode as can be noticed from the decline of the ionic conductivity of the membrane over the time (see Figure 31) [50]. The zincate crossover from each membrane was also measured and compared in Figure 32.

(a) MCM-41/PVA/6M KOH membrane



(b) MCM-41/PVP/PVA/6M KOH membrane with 10 wt.% PVP

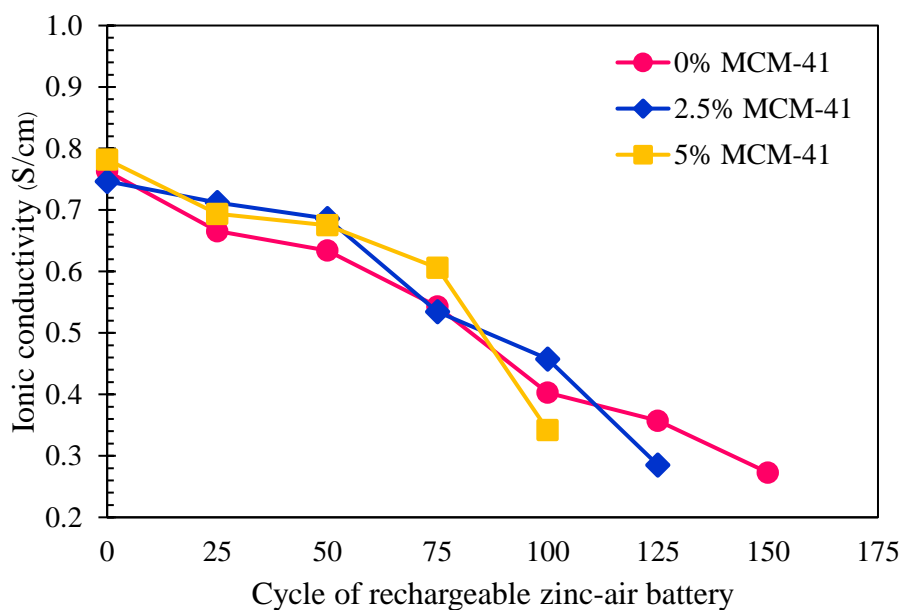


Figure 31. Ionic conductivity of rechargeable zinc-air batteries at 0 - 150 cycle from using (a) MCM-41/PVA/KOH membrane at with 0 – 5 % of MCM-41 and (b) MCM-41/PVP/PVA/KOH membrane with 10 wt.% PVP and 0 – 5 % of MCM-41

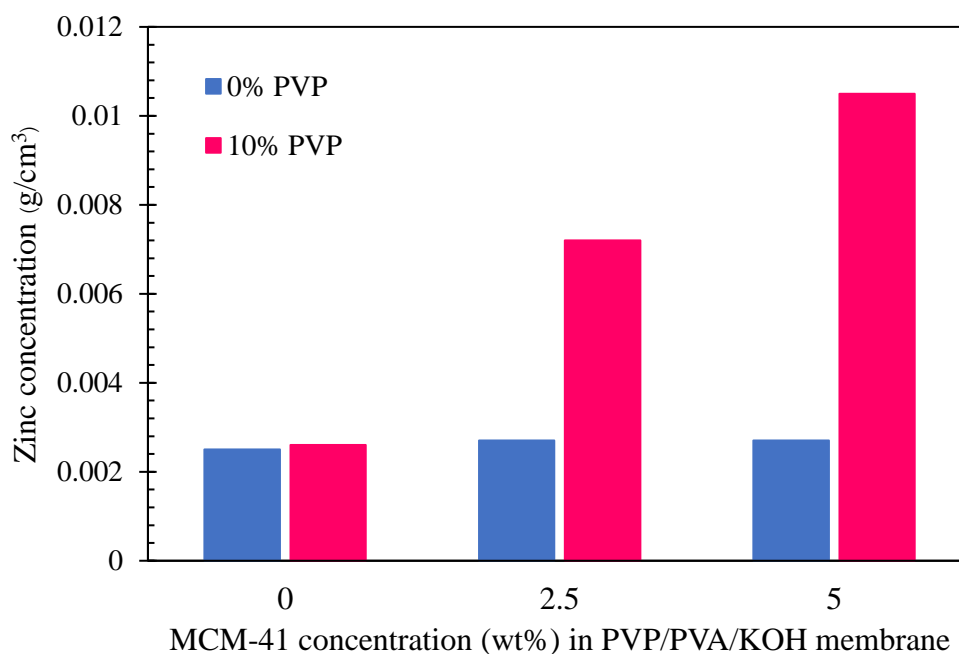


Figure 32. A zincate crossover through MCM-41/PVA/KOH membrane with 0 – 5 % of MCM-41 and MCM-41/PVP/PVA/KOH membrane with 10 wt.% PVP and 0 – 5 % of MCM-41 for 150 hours

However, the addition of 2.5 - 5 wt.% of MCM-41 in the PVA/KOH membrane had no influence on the zincate crossover. On the other hand, it promote the zincate crossover in MCM-41/PVP/PVA/KOH membrane in which the more MCM-41, the more zincate crossover.

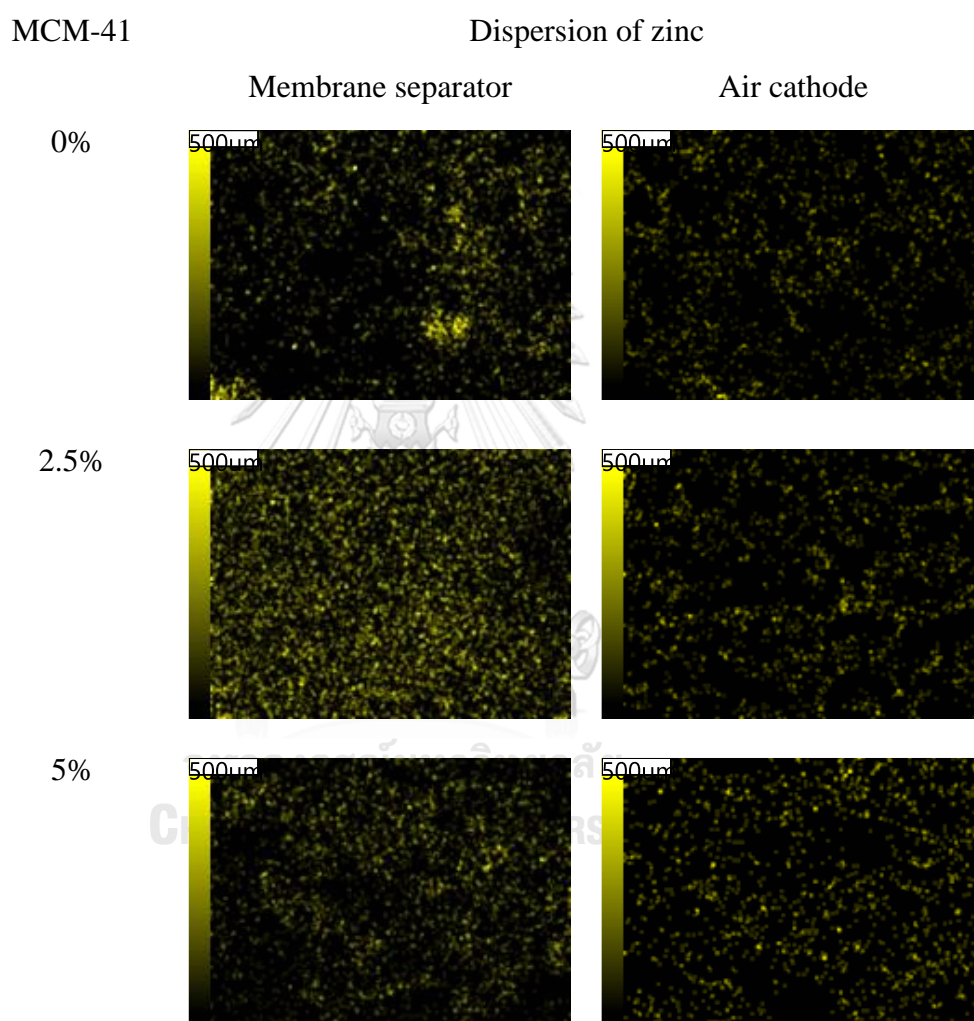


Figure 33. Dispersion of zinc on the surface of MCM-41/PVA/KOH membrane (contact with air cathode side) and air cathode after rechargeable zinc-air battery test

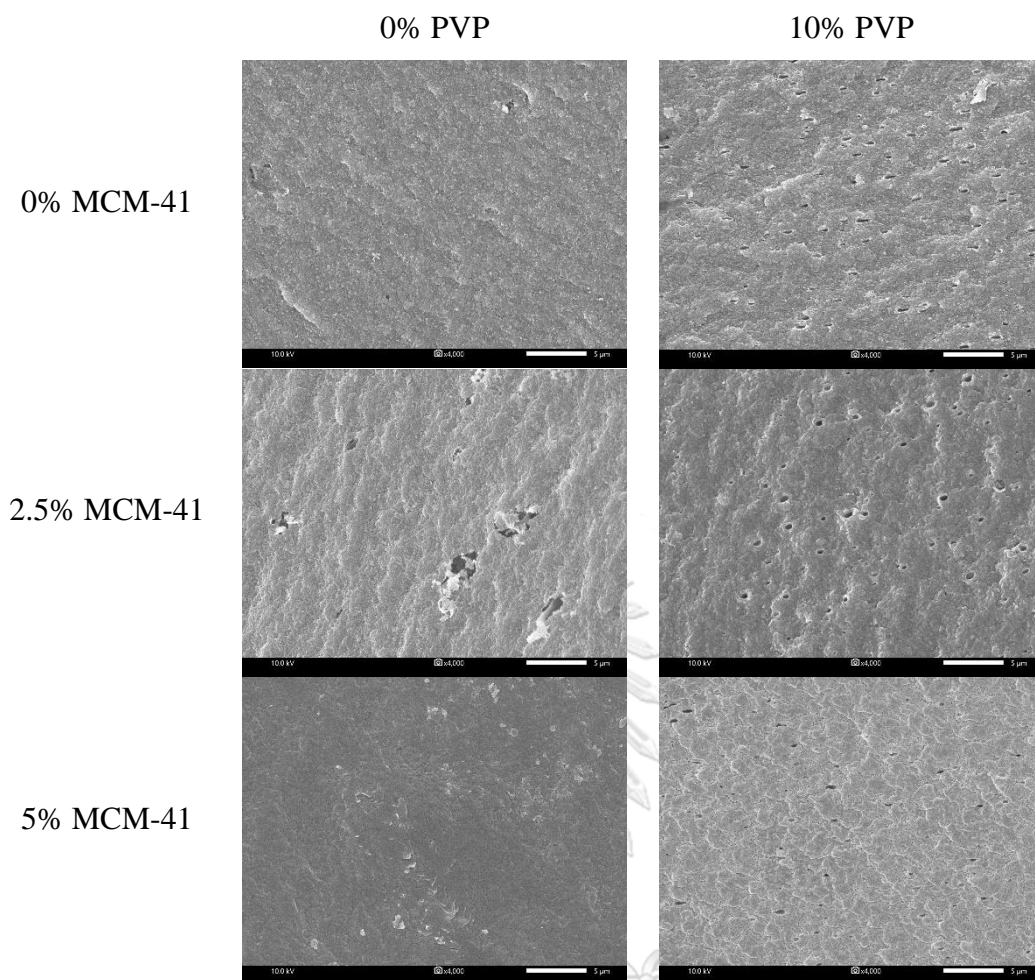


Figure 35. The structure of the composite MCM-41/PVP/PVA/KOH membrane from cross-section SEM (4000x) with 0% and 10% PVP concentration after immersing in 6M KOH for 24 hours at room temperature

The structure of MCM-41/PVP/PVA/KOH membrane with 0, 10% PVP content at different MCM-41 concentration after immersing in 6M KOH for 24 hours is shown in Figure 35. All membrane with MCM-41 addition ratio in both pure PVA and 10% PVP/PVA/KOH blend showed considerably similar morphology. On the other hand, increasing PVP content has an effect on the structure of a membrane, it shows the dense structure for pure PVA membrane and the porous structure for 10% PVP content.

CHAPTER 6

CONCLUSION

This project aimed to develop a membrane separator for using in a zinc-air battery. The effects of additives, polyacrylonitrile (PAN), polyvinylpyrrolidone (PVP) and MCM-41, used in polymer electrolyte (Polyvinyl alcohol (PVA) based polymer) on the structure, electrochemical properties, and performance of the separator electrolyte in zinc-air batteries were investigated. The high addition of PAN into PVA can enhance the electrolyte uptake and ionic conductivity of the membranes. 20% PAN content in the blend PAN/PVA membrane leads to the highest primary zinc-air battery performance in term of voltage discharge, discharge capacity and energy density. However, using high PAN content in the blend membrane led to a lower resistance to alkaline electrolyte and the structure change from dense to porous structure.

For PVP/PVA/KOH blended membrane, it was found that the addition of PVP polymer had no effect on the electrolyte uptake and ionic conductivity. Therefore, there was no improvement in the zinc-air battery performance.

The addition of 2.5% MCM-41 in the blend PVP/PVA/KOH membrane can enhance the electrolyte uptake and ionic conductivity, leading to an increased performance of the primary zinc-air battery in term of discharge capacity and energy density. The highest primary zinc-air battery performance was obtained at 49% for discharge capacity efficiency and 41% for energy density efficiency from using 0% PVP combine with 2.5% MCM-41 of the composite membrane. On the other hand, in term of rechargeable battery it was found that MCM-41 has no influence on

the battery performance. It was also found that the presence of PVP in membrane could lead to the reduction of the cycle of the battery due to the porous structure of the composite membrane with PVP promoting high zincate crossover from zinc anode to air cathode. In the future, the development of a membrane separator to prevention high zincate crossover may lead to enhancing rechargeable zinc-air batteries performance.



Appendix

Appendix A

I) The calculation of the electrolyte uptake of a membrane

The electrolyte uptake of the blend membrane can be calculated from Eq. (4.1).

$$\text{Electrolyte uptake (\%)} = \left[\frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \right] \times 100 \quad (4.1)$$

W_{wet} = The weight of a membrane separator/electrolyte after immersed with electrolyte (6M KOH) at room temperature for 24 h

W_{dry} = The weight of a membrane separator/electrolyte before immersed with electrolyte (6M KOH) at room temperature

Example

The electrolyte uptake of PVA/KOH membrane

$$W_{\text{wet}} = 0.5633 \text{ g}$$

$$W_{\text{dry}} = 0.2096 \text{ g}$$

$$\text{Electrolyte uptake (\%)} = \left[\frac{(0.5633 - 0.2096)}{0.2096} \right] \times 100$$

So, the electrolyte uptake of 0%PVP/PVA/50% 6M KOH membrane is 169%

II) The calculation of ionic conductivity of a membrane

The calculation of ionic conductivity is expressed in Eq (4.2).

$$\sigma = \frac{L}{(R_b \times A)} \quad (4.2)$$

L = The membrane sample thickness (cm)

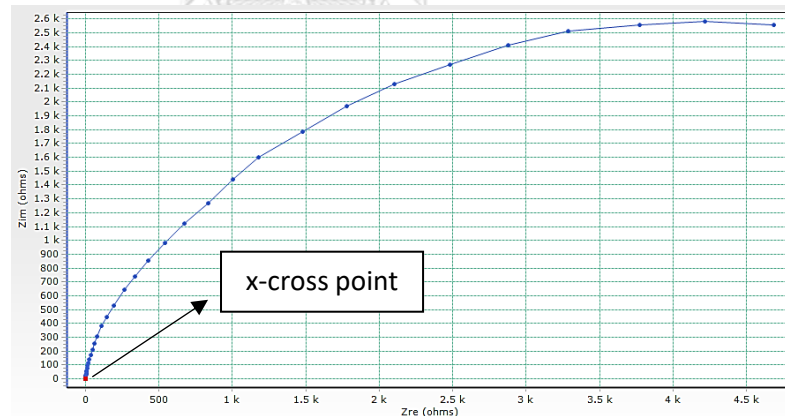
R_b = The bulk resistance (ohm). The bulk resistance can be analyzed from the x-cross point of the Nyquist curve (graph between Z_{im} and Z_{re}).

A = Area of the stainless electrode (cm²)

** The bulk resistance or R_b (ohm) can be measured by electrical impedance spectroscopy (EIS) at a frequency range of 0.15-150,000 Hz at room temperature.

Example

The ionic conductivity of PVA/KOH membrane



The bulk resistance at x-cross point = 0.3655 ohms

The thickness of blend PVA/KOH membrane = 0.21 cm

Area of the stainless electrode = 1.7678 cm²

$$\sigma = \frac{0.21 \text{ cm}}{(0.3655 \text{ ohms} \times 1.7678 \text{ cm}^2)}$$

So, the ionic conductivity of the blend membrane is 0.33 S/cm

Appendix B

I) The calculation of discharge capacity on primary zinc-air battery

Discharge capacity (mAh/g) can be estimated from the capacity (mAh) of the prepared battery per the weight of zinc-anode in the battery

$$\text{Discharge capacity (mAh/g)} = \frac{\text{capacity (mAh)}}{\text{the weight of zinc as the anode (gram)}} \quad (4.3)$$

Example

Primary zinc-air batteries from using PVA/KOH membrane

The prepared battery has 0.0383 gram of zinc as the zinc anode

The capacity of the zinc-air coin cell battery testing was shown 13.71 mAh

So, the discharge capacity of the prepared battery is 358 mAh/g

II) The calculation of the energy density of a primary zinc-air battery

The energy density of a primary zinc-air battery can be estimated from energy (Wh) per the weight of zinc.

$$\text{Energy density (Wh/kg)} = \frac{\text{energy (Wh)}}{\text{the weight of zinc as the anode (gram)}} \quad (4.4)$$

Example

Primary zinc-air batteries from using PVA/KOH membrane

The prepared battery has 0.0000383 kilograms zinc as the zinc anode.

The energy of the zinc-air coin cell battery testing was 0.01465 Wh.

So, the energy density of the prepared battery is 382 Wh/kg

III) The calculate of discharge capacity efficiency of primary zinc-air battery

The discharge capacity efficiency of primary zinc-air coin cell battery can be calculated from the value discharge capacity from primary zinc-air battery test divided by the theoretical capacity of zinc (820 mAh/g).

Discharge capacity efficiency (%)

$$= \frac{\text{discharge capacity from experiment } \left(\frac{\text{mAh}}{\text{g}} \right)}{\text{the theoretical capacity of zinc } \left(820 \frac{\text{mAh}}{\text{g}} \right)} \times 100$$

Example

Primary zinc-air batteries from using PVA/KOH membrane provided discharge capacity at 358 mAh/g.

Therefore,

$$\text{Discharge capacity efficiency (\%)} = \frac{358 \text{ mAh/g}}{820 \text{ mAh/g}} \times 100$$

So, the discharge capacity efficiency of the prepared battery is 43.67%

IV) The calculate of energy density efficiency of primary zinc-air battery

The energy density efficiency of primary zinc-air coin cell battery can be calculated from the value of energy from primary zinc-air battery test divided by the theoretical energy of zinc (1084 Wh/kg).

$$\text{Energy density efficiency (\%)} = \frac{\text{energy density from experiment } \left(\frac{\text{Wh}}{\text{kg}}\right)}{\text{the theoretical energy of zinc } \left(1084 \frac{\text{Wh}}{\text{kg}}\right)} \times 100$$

Example

Primary zinc-air batteries from using PVA/KOH membrane showed energy density at 382 Wh/kg.

Therefore,

$$\text{Energy density efficiency (\%)} = \frac{382 \text{ Wh/kg}}{1084 \text{ Wh/kg}} \times 100$$

So, the energy density efficiency of the prepared battery is 35.28%

Appendix C

I) Phase separation between pure PVP polymer and 50% 6M KOH solution



The Figure was shown phase separation between PVP (polyvinylpyrrolidone) and 50% 6M KOH (potassium hydroxide) after pouring the polymer electrolyte solution into a petri dish. PVP polymer and KOH can't homogeneous, leading to the two-phase solution of PVP and KOH phase.

II) The alkaline electrolyte (KOH solution) absorption into the MCM-41/PVP/PVA/KOH membrane

a) Pure PVA polymer electrolyte

MCM-41 content	The volume of KOH solution in the membrane (wt.%)
0%	78
2.5%	95
5%	83
7.5%	64

b) 10% PVP content in the composite polymer electrolyte

MCM-41 content	The volume of KOH solution in the membrane (wt.%)
0%	70
2.5%	85
5%	77
7.5%	78

Appendix D

I) Characterization of MCM-41 by X-ray diffraction (XRD) and Transmission electron microscope (TEM)

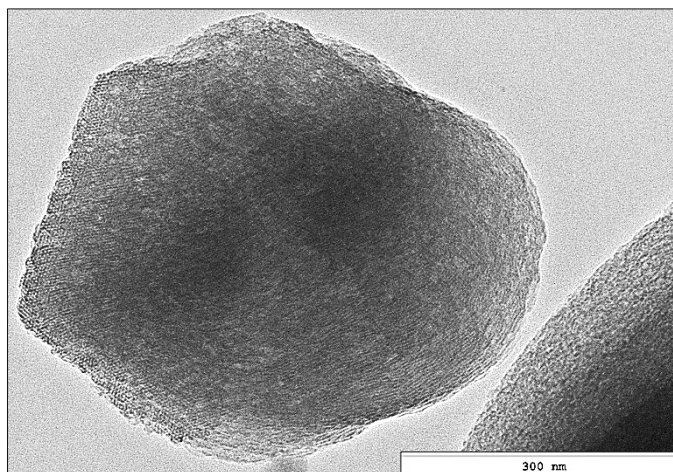


Figure D1 TEM Image of MCM-41

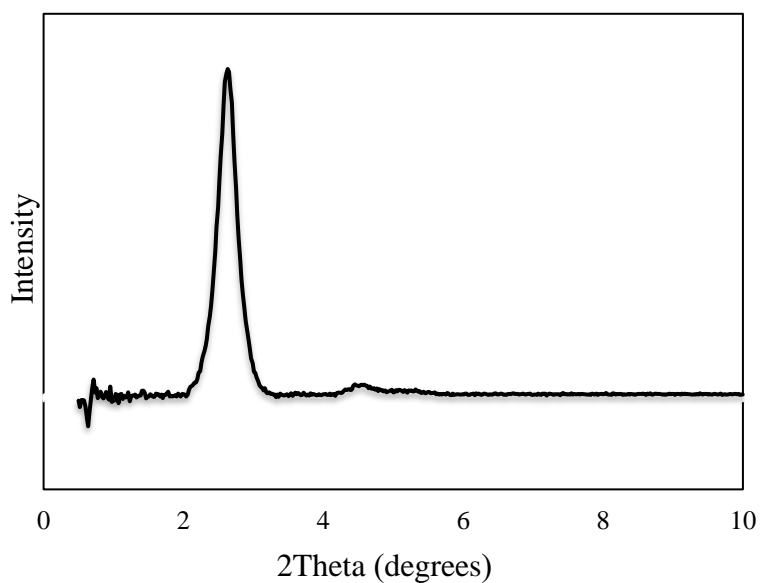


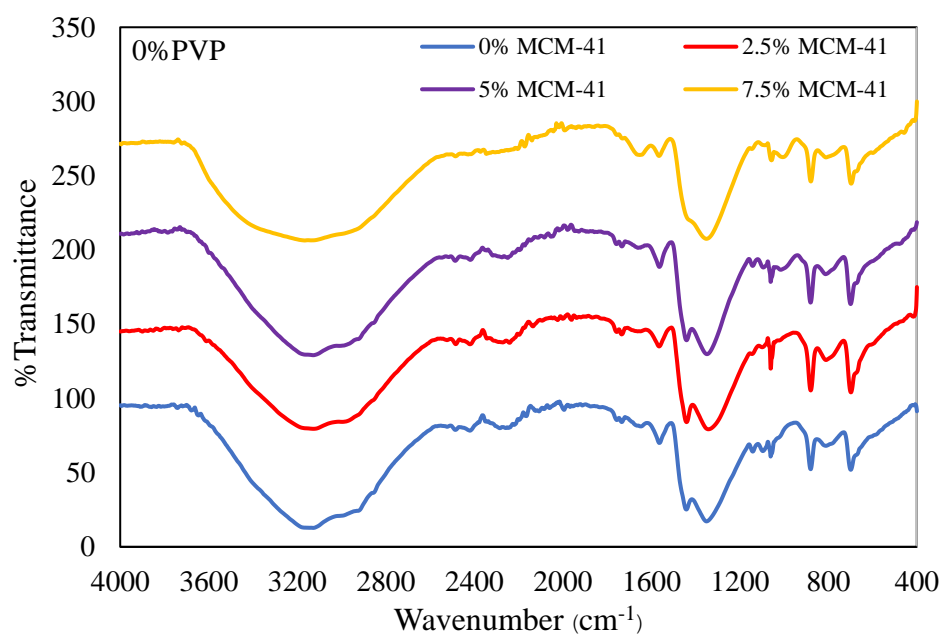
Figure D2 XRD patterns of MCM-41

The structure of the prepared filler from TEM image in Figure D1 showed that the sample has an ordered cylindrical pore. Figure D2 shows XRD pattern of the synthesized MCM-41. Narrow reflection peak at 2.3° and less pronounced peaks at 4.9° and 4.1° indicated the characteristics of mesopore MCM-41.

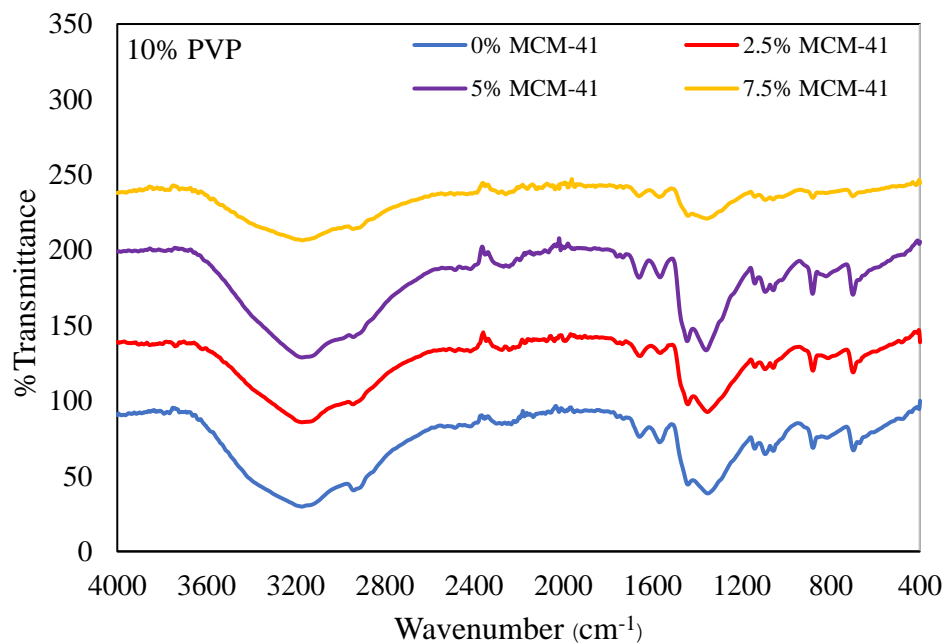
Appendix E

I) FT-IR characterization of the composite MCM-41/PVP/PVA/KOH membrane

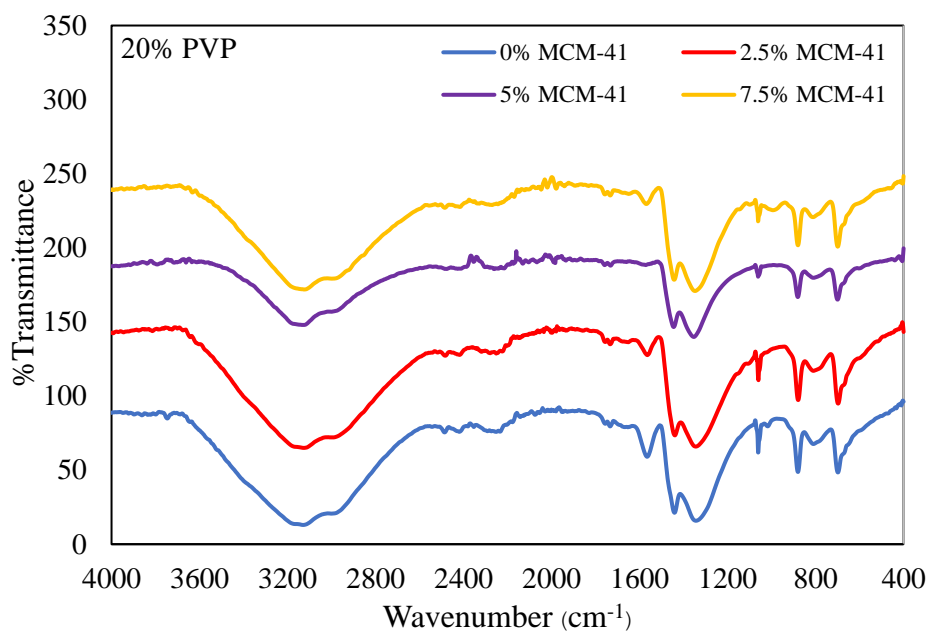
a) The addition of MCM-41 in pure PVA of the composite polymer electrolyte



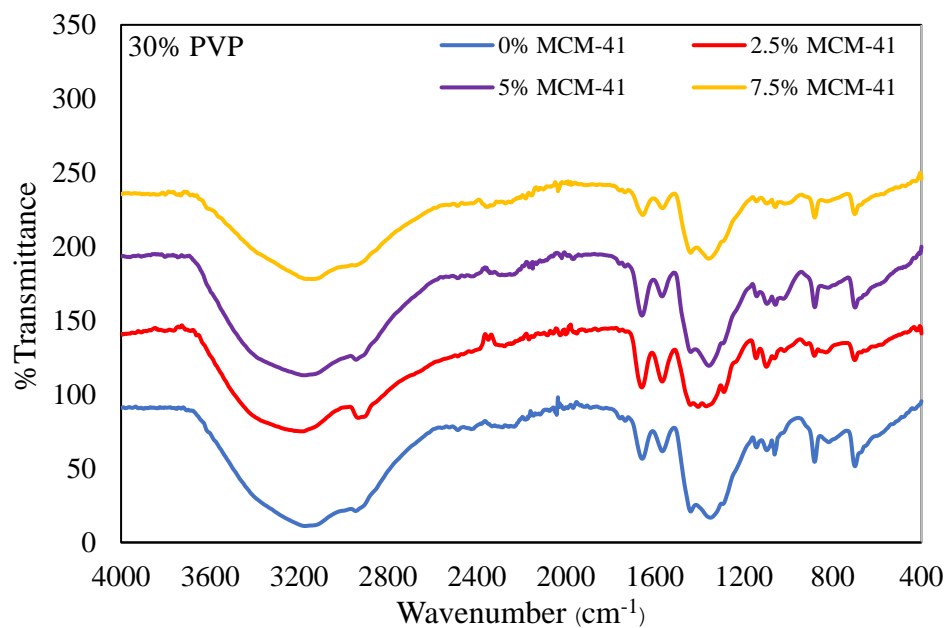
b) The addition of MCM-41 in 10% PVP of the composite polymer electrolyte



c) The addition of MCM-41 in 20% PVP of the composite polymer electrolyte



d) The addition of MCM-41 in 30% PVP of the composite polymer electrolyte





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