

SULFONATED POLYETHERETHERKETONE/POLYVINYLIDENE FLUORIDE BLEND
POLYMERIC CATION EXCHANGE MEMBRANE AS SEPARATOR IN ZINC-IODINE FLOW
BATTERIES



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เมมเบรนแลกเปลี่ยนประจุบวกจากซิลโฟเนตพอลิอีเทอร์อีเทอร์คีโตน
และพอลิไวนิลิดีนฟลูออไรด์เพื่อเป็นแผ่นกั้นในแบตเตอรี่สังกะสี-ไอโอดีนแบบไหล



วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
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พิมพ์เพ็ญ ภูษณสุวรรณศรี : เมมเบรนแลกเปลี่ยนประจุบวกจากซัลโฟเนตพอลิไอโธเรอซีโตนและพอลิไวนิลิดีนฟลูออไรด์เพื่อเป็นแผ่นกั้นในแบตเตอรี่สังกะสี-ไอโอดีนแบบไหล. (SULFONATED POLYETHERETHERKETONE/POLYVINYLIDENE FLUORIDE BLEND POLYMERIC CATION EXCHANGE MEMBRANE AS SEPARATOR IN ZINC-IODINE FLOW BATTERIES) อ.ที่ปรึกษาหลัก : ศ. ดร.อนงค์นาฏ สมหวังธนโรจน์, อ.ที่ปรึกษาร่วม : รศ. ดร.สุรเทพ เขียวหอม

แบตเตอรี่สังกะสี-ไอโอดีนแบบไหล (ZIFBs) กำลังได้รับความสนใจเป็นอย่างมาก เนื่องจากวัสดุสำคัญที่ใช้ในการทำปฏิกิริยามืออยู่มาก, ราคาต่ำ, ความปลอดภัยสูง และเป็นมิตรต่อสิ่งแวดล้อม เมมเบรนแลกเปลี่ยนประจุบวก (CEM) ถือเป็นองค์ประกอบสำคัญที่มีผลต่อราคาและกำหนดประสิทธิภาพของแบตเตอรี่ ซัลโฟเนตพอลิไอโธเรอซีโตน (SPEEK) เป็นหนึ่งในตัวเลือกที่น่าสนใจสำหรับแผ่นกั้นแบบ CEM โดยค่าความสามารถการนำไอออนของ SPEEK CEM สามารถเปลี่ยนแปลงได้โดยการปรับค่าระดับของปฏิกิริยาซัลโฟเนชัน (DS) แต่อาจส่งผลให้คุณสมบัติเชิงกลของ CEM เสื่อมถอยลง ซึ่งการผสมพอลิไวนิลิดีนฟลูออไรด์ (PVDF) กับ SPEEK จะสามารถช่วยปรับปรุงคุณสมบัติเชิงกลของเมมเบรน SPEEK ได้ ดังนั้นในงานวิจัยนี้จึงมุ่งศึกษาผลกระทบของปริมาณ PVDF (5, 10, 15 และ 20 wt.%) ที่มีต่อคุณสมบัติทางเคมีฟิสิกส์ของเมมเบรน SPEEK/PVDF สำหรับใช้เป็น CEM ใน ZIFBs ZIFBs จะถูกขึ้นรูปเป็นเซลล์แบบนั่งรูปตัว H และเซลล์แบบไหลรูปแบบชั้น โดย SPEEK ที่มีค่า DS ปานกลาง (53%) จะถูกใช้ในงานวิจัยนี้ และคุณสมบัติทางเคมีฟิสิกส์ ซึ่งได้แก่ ลักษณะรูปร่างของพื้นผิว, ภาคตัดขวาง, การดูดซึมน้ำ, การดูดซึมน้ำ, อัตราการบวมตัว, ความสามารถในการนำไอออน และความสามารถการป้องกันไอโอดีนสปีชีส์ ของเมมเบรนสังเคราะห์ และประสิทธิภาพของแบตเตอรี่จะถูกศึกษาและเปรียบเทียบกับเมมเบรนทางการค้าแนฟิออน115 โดยผลงานวิจัยพบว่าเมมเบรน SPEEK, เมมเบรนผสมด้วย 5 wt.% PVDF (เรียกแทนด้วย SP 5) และเมมเบรนแนฟิออน115 มีพื้นผิวที่หนาแน่น, สม่าเสมอ และเป็นเนื้อเดียวกัน เมมเบรน SPEEK และ SP 5 ถูกนำไปศึกษาต่อเนื่องจากคุณสมบัติทางเคมีฟิสิกส์และประสิทธิภาพของแบตเตอรี่ที่ดี อีกทั้งพบว่า ZIFBs ที่ใช้เมมเบรน SPEEK/PVDF สามารถทำงานได้มากกว่า 700 รอบ ซึ่งแสดงถึงประสิทธิภาพด้านการใช้งานระยะยาวที่ดี ZIFB ที่ใช้เมมเบรน SP 5 แสดงประสิทธิภาพด้านพลังงานที่สูงกว่า ZIFB ที่ใช้เมมเบรนแนฟิออน115 (77.52% vs. 69.71%) ในทางเดียวกัน ZIFB ที่ใช้เมมเบรน SP 5 แสดงความเสถียรได้ดีกว่าเมมเบรนแนฟิออน115 อย่างเห็นได้ชัด ซึ่งสอดคล้องกับคุณสมบัติเชิงกลของเมมเบรน นอกจากนี้ราคาของเมมเบรน SP 5 ยังต่ำกว่าเมมเบรนแนฟิออน115ประมาณ 2.5 เท่า เนื่องจากราคาที่ต่ำและคุณลักษณะที่ดีอื่นๆ พิสูจน์ให้เห็นว่าเมมเบรนที่ใช้ SPEEK เป็นองค์ประกอบหลักมีคุณภาพและสามารถใช้งานเป็นแผ่นกั้นแบบ CEM ใน ZIFBs ได้

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KEYWORD: Zinc-iodine flow batteries, Cation Exchange Membrane, Sulfonated poly (ether ether ketone), Poly (vinylidene fluoride), Ionic conductivity, Iodine species crossover preventability

Pimpen Pusanasuwansri : SULFONATED POLYETHERETHERKETONE/POLYVINYLIDENE FLUORIDE BLEND POLYMERIC CATION EXCHANGE MEMBRANE AS SEPARATOR IN ZINC-IODINE FLOW BATTERIES. Advisor: Prof. ANONGNAT SOMWANGTHANAROJ, Ph.D. Co-advisor: Assoc. Prof. SOORATHEP KHEAWHOM, Ph.D.

Zinc-iodine flow batteries (ZIFBs) are very appealing owing to their abundance of active materials, low cost, high safety and environmental friendliness. The cation exchange membrane (CEM) separator contributes a significant part to the cost and determines battery performance. Sulfonated poly (ether ether ketone) (SPEEK) is a promising candidate as a CEM separator. The ionic conductivity of SPEEK CEM can be tuned by adjusting a degree of sulfonation (DS), but the mechanical property of CEM could be deteriorated. Blending poly (vinylidene fluoride) (PVDF) with SPEEK can improve the mechanical strength of SPEEK membrane. Therefore, this study examined the effect of PVDF contents (5, 10, 15 and 20 wt.%) on the physicochemical properties of SPEEK/PVDF membranes for using as CEMs in ZIFBs. ZIFBs were fabricated as static H cell and flowing stack cell configuration. Moderate DS of SPEEK (53%) was used in this study. The physicochemical properties, which are surface morphology, cross section, water uptake, electrolyte uptake, swelling ratio, ionic conductivity and iodine species crossover preventability, of the synthesized membranes and battery performances were investigated and compared with commercial Nafion115 membrane. It was found that the SPEEK, blend membrane with 5 wt.% PVDF (denoted as SP 5) and Nafion115 membrane were dense, uniform and homogeneous. The SPEEK and SP 5 membranes are further investigated for their good physicochemical properties and good battery performances. ZIFBs using SPEEK/PVDF membranes were able to be operated over 700 cycles indicating long cycle life performance. ZIFB with SP 5 membrane showed higher energy efficiency compared with Nafion115 membrane (77.52% vs. 69.71%). In addition, ZIFB with SP 5 membrane also showed significantly better stability than Nafion115 membrane corresponding to the mechanical property of membranes. Furthermore, the cost of SP 5 membrane is lower than Nafion115 membrane by around 2.5 times. Due to its low cost and other good features, the SPEEK based membranes prove to have the quality for use as CEM separator in ZIFBs.

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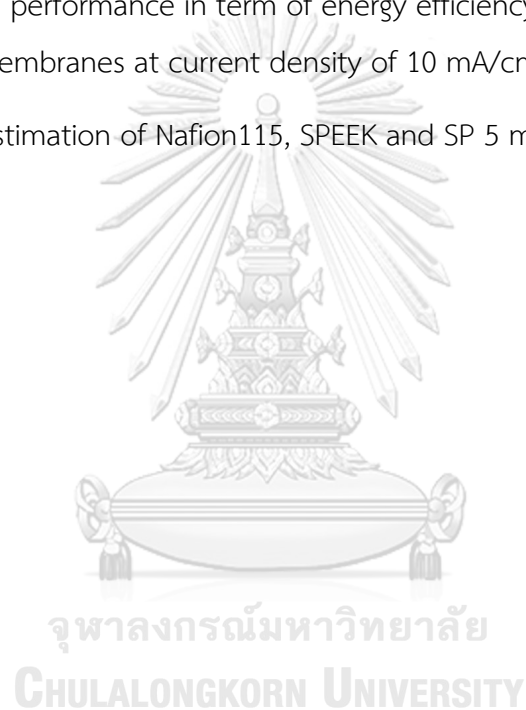


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Chapter I

Introduction

1.1 Background

Recently, there is an increasing energy demand all around the world as a result of the rapidly expanding economic and industrial, technological advancement and the growing of population. Significant attention has been paid in using renewable and sustainable energy to solve the global warming problem. There are many forms of energy such as mechanical, thermal, chemical and electrical energy. Electrical energy is one form of energy that has a steadily increasing demand rate. Therefore, the devices for storing electrical energy or energy storage system (ESS) have an increasing important role [1, 2]. One of the most common and well known electrical energy storage device is rechargeable batteries. The most popular and dominating market area is lithium-ion batteries (LIBs) because of their high energy density, long cycle life, small in size and light weight. However, LIBs also has disadvantages such as high cost, environmental toxicity, risk of lithium supply and safety issue. Therefore, the other types of batteries are constantly being invented [2, 3].

Conventional batteries have limitations on the power and energy components. They depended on each other or cannot be scaled independently which make them having low feasibility in applications. Their electro-active materials are stored inside the electrodes. On the other hand, for flow batteries (FBs), the energy and power components are decoupled and can be scaled independently. Their electro-active materials are stored in electrolyte and their redox reactions take place on the electrodes surface. Because of unique configuration, FBs are attracting at this time [4, 5]. The main components of flow batteries are contained of electrodes (cathode and anode), electrolyte (catholyte and anolyte), separator (ion exchange membrane) and current collector [5, 6].

There are different types of FBs based on anode materials such as all vanadium FBs and Iron-Chromium FBs [5, 7]. Among those reports, zinc-based FBs (ZFBs) get much attention from many researchers due to their high theoretical capacity (820 mAhg^{-1} or high volumetric energy density 5854 mAhcm^{-3}), low cost, balanced kinetics, stability and reversibility in aqueous solution of zinc metal. Besides that, zinc metal has abundance in natural resources, safety and environmental friendliness [8]. Later, ZFBs were developed continuously in several types such as zinc-air and zinc-ion FBs. They have been successfully commercialized and most of them are still in use today [9, 10]. Apart from these types, zinc-iodine flow batteries (ZIFBs) are very appealing owing to their high solubility and good electrochemical

kinetics of I^-/I_3^- [11, 12]. Moreover, iodine has high theoretical capacity (211 mAhg^{-1}), non-toxic, environmental friendly, low cost and abundance in ocean ($50\text{--}60 \text{ mg L}^{-1}$). From these reasons, iodine is one of the most promising materials to be used as the catholyte [13-15].

A separator in ZIFBs acts as cation exchange membrane (CEM), which is an essential component, prevents physical contact between the positive and negative electrodes, allows zinc ions to transport between both electrodes, and inhibits cross-over of iodine species from the positive electrode to the negative electrode. The CEM separator contributes a significant part to the cost and determines battery performance [16]. The conventional and efficient ion exchange membrane (IEM) is Nafion membrane due to its high ionic conductivity and excellent thermal, chemical and mechanical properties [17-19]. Anywise, Nafion membrane is very expensive, leading to infeasible for commercial scale application therefore considering the efficient materials to prepare membranes is very important [19-21]. Previous studies have shown that sulfonated aromatic polymers such as sulfonated poly (arylene ether ketone) [22, 23] and sulfonated poly (arylene ether sulfone) are promising to be an alternative to Nafion [24, 25]. Apart from them, sulfonated poly (ether ether ketone) (SPEEK) is the attractive material due to its good mechanical, thermal and chemical properties, low cost and easy preparation [26-28]. Winardi S. et al., synthesized SPEEK membranes for vanadium redox FBs and the results show that its

coulombic efficiency and energy efficiency is slightly higher than Nafion117 membrane [29]. Sulfonation of PEEK leads to high ionic conductivity but compromises mechanical strength of membrane [30]. Blending polymer is typically method to make good and desired properties of polymer. Poly (vinylidene fluoride) (PVDF) is considered as promising choice to blend with SPEEK owing to its excellent mechanical and electrochemical properties (stable fluoropolymer) and low cost [31]. Inspired by the good performances of SPEEK/PVDF blend membranes in fuel cell and all-vanadium redox FBs, in this work SPEEK/PVDF blend membranes with different PVDF contents were prepared and applied in ZIFBs system for the first time.

This dissertation is included synthesis of SPEEK and SPEEK/PVDF blending polymeric CEM and the application of the prepared membranes in ZIFBs. For the first part, the effect of PVDF contents in SPEEK/PVDF CEM on the physical (such as thermal and mechanical) properties of CEM were studied. In the second part, the prepared membranes were applied in ZIFBs. The electrochemical properties and battery performance are consequently investigated. All of the results will be compared with the results of the commercial Nafion115 membrane as benchmark.

1.2 Objectives

1.2.1 To synthesize SPEEK and SPEEK/PVDF blend polymeric CEM for using in ZIFBs system.

1.2.2 To study effect of PVDF contents in SPEEK/PVDF CEM on the physicochemical properties.

1.2.3 To investigate performance of ZIFBs that using synthetic SPEEK and SPEEK/PVDF membrane.

1.3 Scopes of research

In this research, zinc electro-deposited on porous carbon felt was used as negative electrode and 0.5 N of iodine (I_2) and potassium iodide (KI) solution absorbed on pure carbon felt was used as positive electrode. Stainless steel and titanium steel were used as current collector for both of positive and negative electrodes. Zinc sulfate ($ZnSO_4$) 2 M was used as electrolyte for negative side and 0.5 N of I_2 and KI solution was used as electrolyte for positive side.

1.3.1 Synthesized SPEEK and SPEEK/PVDF blend polymeric CEM and Nafion115 membrane were used as separator.

1.3.2 The PVDF contents in SPEEK/PVDF blend polymeric CEM were varied as 5, 10, 15 and 20 wt.%.

1.3.3 The physicochemical properties such as degree of sulfonation (DS), surface morphology, cross-section, functional group, water uptake, swelling ratio, electrolyte uptake, ionic conductivity, iodine species crossover, tensile strength and dispersing elements of synthesized membranes were investigated.

Activities	Period							
	2020						2021	
	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb - Jul
1.4.3 Selecting polymer that can be used to synthesize CEM for using in this thesis								
1.4.4 Synthesis CEM and applying it in ZIFBs and testing electrochemical properties and batteries performance								
1.4.5 Analysis the experimental results								
1.4.6 Writing thesis and preparing for publication								

Chapter II

Theory and Literature Reviews

2.1 Flow Batteries

2.1.1 General Information

Flow batteries (FBs) are one type of rechargeable energy storage system (ESS) that convert chemical energy from chemical reactions into electrical energy. FBs store electrolyte externally, generally in tanks, and electrolyte usually pumped into cell in application. Electrolyte of FBs is generally in liquid state and it contains of one or more dissolved electro-active species. The chemical reaction in FBs is redox (reduction-oxidation) reaction and it takes place at electrodes' surface. In conclusion, FBs are rechargeable batteries in which electrolyte is stored externally system and contains electro-active materials that are pumped into cell to start redox reaction at electrode's surfaces on both sides of ion exchange membrane (IEM) and results in electrical potential [5, 6].

2.1.2 Components of Flow Batteries

The main components of FBs consist of electrodes (cathode and anode), electrolyte (catholyte and anolyte), separator (IEM) and current collector [5, 6]. The schematic of the main components for FBs is illustrated in Figure 2.1.

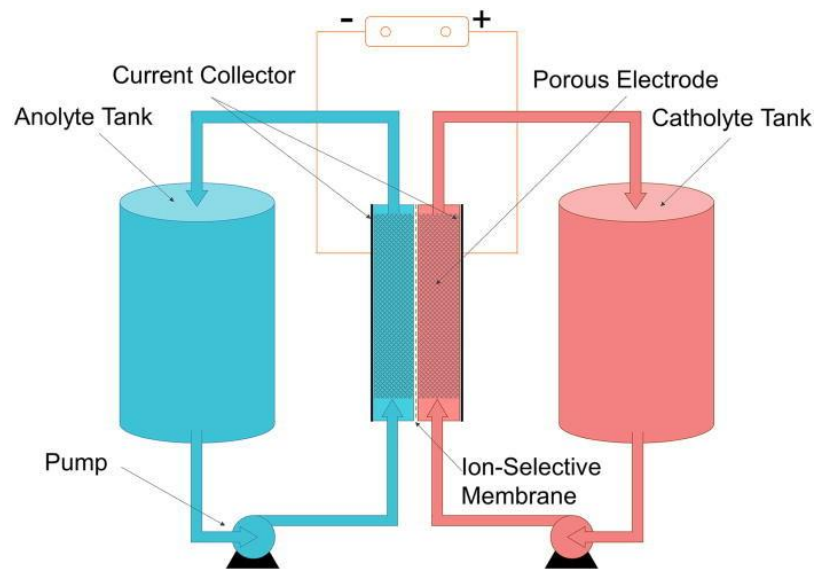


Figure 2.1 Schematic illustration of redox flow battery [32]

2.1.2.1 Electrode

Electrode is divided into positive and negative electrode. An electrode of FBs is a solid electric conductor that chemical reaction (redox, reduction-oxidation reaction) takes place on its surface. Electrode which reduction reaction takes place is called cathode and electrode which oxidation reaction takes place is called anode [33].

2.1.2.2 Electrolyte

An electrolyte is a chemical compound substance that acts as medium to support ion movement for balancing electric charge of system. Dissolved ions are both of cation and anion. Electrolyte, generally can be in solid and liquid form. An electrolyte in FBs is in liquid state. Traditionally, FBs have two divided electrolyte

reservoirs. An electrolyte which reduction reaction occurs is called catholyte and which oxidation reaction occurs is called anolyte. Catholyte and anolyte are separated by separator or membrane [6, 32].

2.1.2.3 Separator

A separator, generally is a barrier to separate positive electrode and negative electrode for preventing touching each other that results in electric current passing or short circuit. Not only that, but separator of FBs also acts as IEM, to select ion that can pass through membrane. Traditionally, there are two types of IEM, cation exchange membrane (CEM) and anion exchange membrane (AEM). Separator contributes a significant part to the cost and determines battery performance [34].

2.1.2.4 Current Collector

Current collector is one of an important components of batteries. It acts as an electrical conductor or medium that connects between external circuit and electrode. The function of current collector is to support electron movement along external circuit and electrode. Examples of materials that can be used as current collector are copper (Cu), nickel (Ni) and stainless steel [35].

2.1.3 Advantages and Disadvantages of Flow Batteries

For FBs, the energy and power components are decoupled and can be scaled independently so that FBs have much feasibility in commercial and industrial application than conventional batteries. The electro-active materials of FBs are stored in electrolyte. The electrolyte reservoirs, generally be tanks, are stored external system. The capacity that determines energy of batteries depends on amount of electrolyte and concentration of electrolyte or active ions. As for the power of batteries, it depends on the electrode area that stores within the cell. Among many advantages of FBs, there still have some disadvantages such as low power density, high complex structure and some types of them were found with low cycle life [5, 6, 32].

2.1.4 Examples of Flow Batteries

2.1.4.1 All Vanadium Flow Batteries

All vanadium FBs is one type of FBs that use same elements in both of half cells. Figure 2.2 is illustrated configuration of all vanadium FB which includes stack of battery cell, electrolyte tanks and pumps. V^{2+}/V^{3+} and V^{4+}/V^{5+} are all dissolved in sulfuric acid and used as negative electrolyte and positive electrolyte respectively. The schematic of all vanadium FBs was shown in Figure 2.2. The electrochemical reactions those occur during discharge and charge process were indicated as followings [36]:

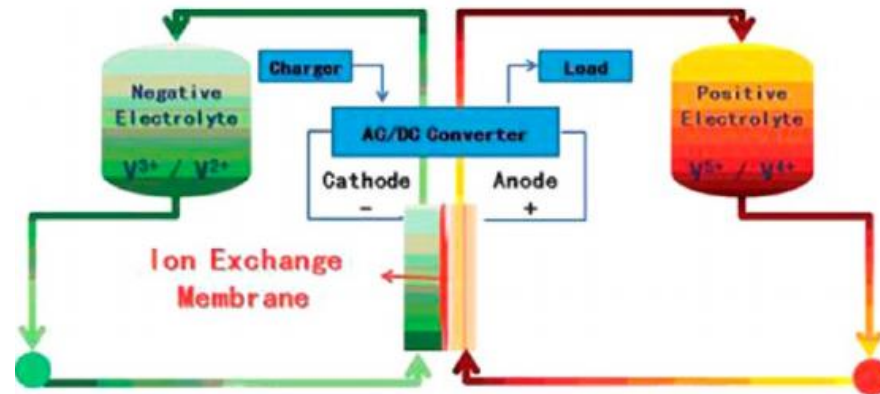
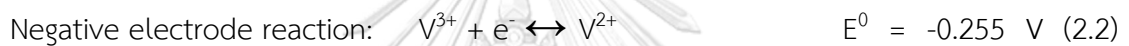
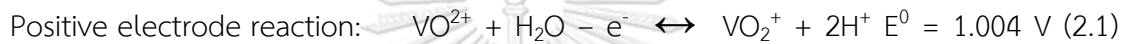


Figure 2.2 The schematic of all vanadium flow battery [36]



The IEM works by isolating vanadium ion and allow transferring of H^+ and SO_4^{2-} .

2.1.4.2 Iron-chromium Flow Batteries

Iron-chromium FBs are one type of FBs that use of $\text{Cr}^{2+}/\text{Cr}^{3+}$ and $\text{Fe}^{2+}/\text{Fe}^{3+}$ dissolved in acid as negative electrolyte and positive electrolyte respectively. The iron-chromium FBs use of plentiful iron and chromium as the electro-active materials for redox reaction in cell. Figure 2.3 illustrates the configuration of iron-chromium FB. The IEM in this cell acts as CEM that allows active species (iron and chromium ion) and proton pass through membrane. The schematic of iron-chromium FBs was

illustrated in Figure 2.3. The electrochemical reactions of iron-chromium FB were indicated as follows [37]:

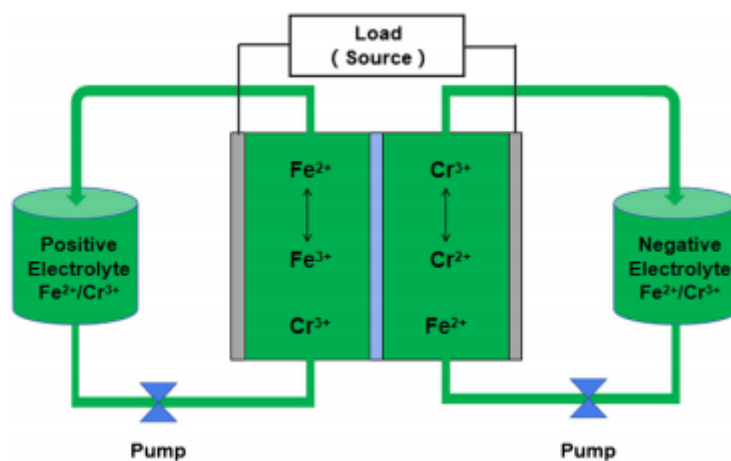
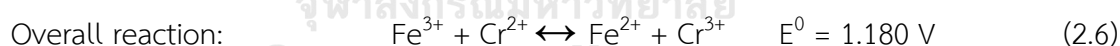
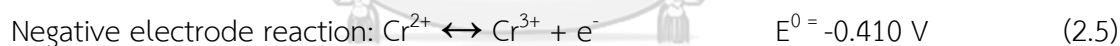


Figure 2.3 The schematic of iron-chromium flow battery [38]



2.1.4.3 Zinc-based Flow Batteries

Zinc-based flow batteries (ZFBs) are one promising type of FBs due to their high theoretical capacity (820 mAhg^{-1} or high volumetric energy density 5854 mAhcm^{-3}), low cost, balanced kinetics, stability and reversibility in aqueous solution of zinc metal. Besides that, zinc metal has abundance in natural resources, safety, low toxicity and environmental friendliness [8]. Later, ZFBs were developed continuously

in several types such as zinc-air and zinc-ion ones. They have been successfully commercialized and most of them are still in use today [9, 10]. Zinc redox couple (Zn/Zn^{2+}) can be dissolved in various pH of aqueous electrolyte. If zinc has dissolved in acid electrolyte, the reaction would be as illustrated in equation (2.7). But if zinc has dissolved in alkaline electrolyte, the reaction would be as illustrated in equation (2.8) [39].



2.2 Zinc-iodine Flow Batteries

2.2.1 General Information

Zinc-iodine flow batteries (ZIFBs) have zinc and iodine species as their electro-active materials. ZIFBs were first demonstrated by the PNNL National Laboratory at Northwestern University [40]. ZIFBs have reached a promising high energy density (167 WhL^{-1}) which is approaching the energy of low end conventional lithium-ion batteries (LIBs) [41]. Figure 2.4 illustrated the ZIFB components, which include negative electrode, positive electrode, electrolyte and separator. All of these components are the key factors to enhance discharge and charge process of ZIFBs.

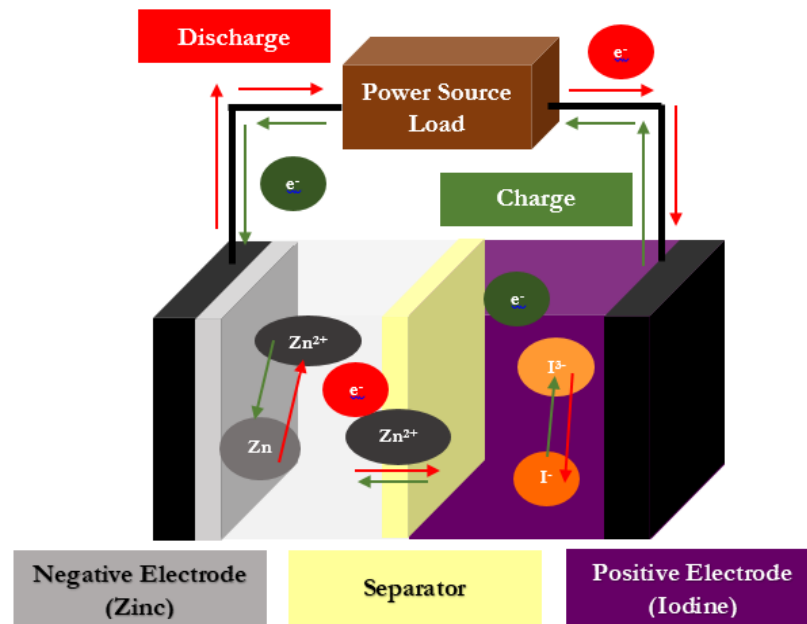
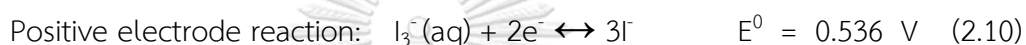
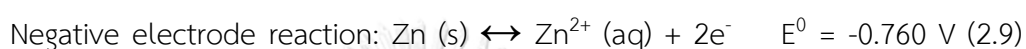


Figure 2.4 The schematic for main components and operation for zinc-iodine flow battery

The principle of ZIFB is to convert chemical energy to electrical energy by enhancing redox reactions. During discharge process, oxidation reaction occurs at negative electrode surface or zinc surface which is indicated in equation (2.9). Thus, zinc reduces electrons to external device circuit. While positive electrode surface or iodine species gain electrons from the external device circuit which is indicated in equation (2.10), that is called reduction reaction. Meanwhile, zinc ions transport from negative side to positive side for balancing electric charges of system. In contrast, during charge process, oxidation reaction occurs at positive electrode surface but reduction reaction occurs at negative electrode surface. Thus iodine species reduce electrons to external device circuit which is indicated in equation (2.10). Then, zinc

ion gains electron from external device circuit which is indicated in equation (2.9). Meanwhile, zinc ions transport from positive side to negative side for balancing electric charges of system. The other positive ions in system can also be used to balance electric charges of system. The overall or redox reaction is indicated in equation (2.11) [39].



2.2.2 Components of Zinc-iodine Flow Batteries

2.2.2.1 Zinc electrode (Negative electrode)

Zinc metal is usually selected to be a negative electrode (anode, called from discharge process) due to their many advantages. Their advantages have been already illustrated in section 2.1.4.3. Zinc can be used in various pH of electrolyte as mentioned in section 2.1.4.3. Although dissolving zinc in alkaline increases the battery voltage, but the dissolution of zinc in alkaline is slower than dissolving in acid. Besides that, it will cause more zinc dendrites to occur. Mainly, for ZIFBs, they have used zinc electro-depositing as negative electrode [3, 41, 42].

2.2.2.2 Iodine electrode (Positive electrode)

An iodine electro-active species are found in several forms in solution such as I^- , I_3^- and other polyiodide. In the presence of active materials, the redox reaction is occurred at the electrode surface. Lost of active materials (iodine species) is leading to serious capacity deterioration and severe self-discharge of iodine cathode. So that researchers try to develop solid matrix for confining or encapsulating the iodine and polyiodide. Among of the research, various carbonaceous materials with abundant porous structures (carbon cloth, carbon nanotube, activated carbon and hollow carbon) are the most widely used as positive electrode to suppress the dissolution of polyiodide and encapsulate iodine, as well as enhance conductivity [16].

2.2.2.3 Electrolyte

The general functions of electrolyte are mentioned in section 2.1.2.3. The electrolyte of ZIFBs acts as the reservoir for zinc ions in the system. Generally, for ZIFBs, zinc sulfate ($ZnSO_4$) that is mildly aqueous acidic has recently been used as electrolyte due to its low cost and safety [3, 42, 43].

2.2.2.4 Separator

As mentioned in section 2.1.2.3, separator for FBs acts both of preventing short circuit of cell and selecting ion that can pass through it. It was called IEM. IEM is divided into two types as mentioned in section 2.1.2.3. In ZIFBs system, separator is used as CEM. CEM is allowed transferring of cation (zinc ions in ZIFBs) but not

allowed transferring of anion (I^- and polyiodide in ZIFBs) for preventing self-discharge that leads to bad performance of cell. In conventional way, the membrane that is used in ZIFBs is Nafion membrane [16].

2.2.2.5 Current Collector

The functions of current collector are mentioned in section 2.1.2.4. This part acts an important role for battery performance in term of the distance between current collector and electrode.

2.2.3 Advantages and Disadvantages of Zinc-iodine Flow Batteries

ZIFBs have many advantages in view point of their active materials and the whole cell. In view point of active materials, advantages of zinc metal are mentioned in section 2.1.4.3. For iodine species, iodine has high solubility and good electrochemical kinetics of I/I_3^- . Moreover, iodine has high theoretical capacity (211 mAhg^{-1}), non-toxic, environmental friendly, low cost and abundance in ocean ($50\text{--}60 \text{ mg L}^{-1}$) so that iodine is one of the most promising materials to be used as catholyte [12, 14, 15]. In view point of the whole cell, ZIFBs exhibit higher volumetric energy density than other flow battery systems and their safety working conditions [42]. However, ZIFBs promoted short cycle life and low power density or low operation current densities [11, 16]. The CEM separator contributes a significant part to cost and determines battery performance [42].

2.3 Types of Ion Exchange Membranes

2.3.1 General Information

Ion exchange membrane (IEM) is developed continuously until this present. In the past, only in 1930s ion exchange materials were obtained on the polymer matrix that is called ion exchange resins. After that, ion exchange materials are not only used in form of granules, but they were developed to be used in form of thin plates, those are called membranes. The materials of IEM are divided into three types those are polymers (organic materials), inorganic materials and hybrid materials [44].

As a long time, IEM is gained much attention from many researchers due to their widely fields of applications. Traditionally, IEM is used in electro dialysis for concentrating or diluting solutions. Recently, IEM is contributed to use in the field of energy and environment that is electrochemical technologies such as in fuel cells and FBs. In conventional, the IEM which is commercialized and get acceptance in the field of FBs application is Nafion membrane [17-19].

IEM is the semi-permeable membrane which allows transferring of ions those have counter charge with the charge that attach to its structure. IEM structure is typically composed of the hydrophobic substrates, ion-functionalized groups and the movable ions. Ion-functionalized groups are the exchange sections which are capable to form an electrostatic bond with the counter ions. In general, the ion-functionalized groups attached on the IEM will dissociate when they are penetrated

with sufficient water molecules, releasing cations or anions for transfer corresponding ions. Generally, IEM can be divided into two types depending on the ion-functionalized groups attached on their structures [44, 45], which are cation exchange membrane (CEM) and anion exchange membrane (AEM).

2.3.2 Cation Exchange Membrane

CEM is the membrane which contains negative ion-functionalized groups such as $-\text{SO}_3^-$, $-\text{COO}^-$, $-\text{PO}_3^{2-}$, $-\text{PO}_3\text{H}^-$ and $-\text{C}_6\text{H}_4\text{O}^-$. It allows the transferring of positive charges or cations but not allows transferring of negative charges or anions [46]. It works with the electrostatic principle that represented its mechanism in the equation (2.12). The examples of polymers which are used as CEM materials such as styrene, poly (vinyl alcohol) and poly (vinyl chloride). CEM is classified into strong acid and weak acid types [47].



where R is ion functionalized group and A^+ is positive charge ion

2.3.2.1 Weak Acid Cation Exchange Membrane

Typically, weak acid cation exchanger behaves as same as weak acid, they are weakly dissociated. Mainly, weak acid cation exchanger usually contains carboxylic groups ($-\text{COOH}$). The weak acid cation exchanger has limitation that it is not active at pH values below 4-6. This value will differ depending on materials.

2.3.2.2 Strong Acid Cation Exchange Membrane

Typically, strong acid cation exchanger has chemical behaviour as same as strong acid. It is highly dissociated than weak acid. Mainly, strong acid exchanger usually contains sulfonic acid group (-SO₃H). This type of cation exchangers can be used over the entire pH range.

2.3.3 Anion Exchange Membrane

AEM is the membrane which contains positive ion-functionalized groups such as -NH₃⁺, -NRH₂⁺ and -NR₂H⁺. It allows the transferring of negative charges or anions but not allows transferring of positive charges or cations. It works with the electrostatic principle that is represented its mechanism in the equation (2.13). The examples of polymers which are used as anion exchange materials are styrene and vinylpyridine.



where R is ion functionalized group and B⁻ is negative charge ion

2.4 Requirements of Cation Exchange Membranes for Using as ZIFBs Separators

[48]

2.4.1 Chemical Stability

Chemical stability is one of the important properties for separator that refers to the changing of compositions by chemical reactions such as oxidation and polymerization. CEM that can be used as separator in FBs must have chemical

stability which mean that it must not react with electrolytes and electrode materials in system. It must have high chemical resistance so that it will not have the contamination of other substances in system.

2.4.2 Thermal Stability

Thermal stability is the ability that materials can resist heat action and maintain their original structure and properties such as strength and toughness. Thermal stability of polymer significantly depends on chemical structure, degree of crystallinity and molecular weight. Generally, the aromatic structures in polymer backbone improve thermal stability. Melting temperature of polymers is one of the characteristic properties that relates to thermal stability. Thermal stability is usually investigated by thermogravimetric analysis (TGA).

2.4.3 Mechanical Strength

Mechanical strength is an important property for separators to ensure safety operations along cycle life of FBs. CEM using in FBs applications must have high mechanical strength because they have to be placed in the stack of the cell and there is applied force on them. Mechanical failures causing to the contacting between cathode and anode results in failure of the cells.

2.4.4 Porosity and Pore size

CEM which is used in FBs application must have sufficient pore density to hold electrolyte solution so that ion-functionalized groups will dissociate and enable cations exchanging. Pore size of separators must be smaller than electrode materials for preventing contamination of each side. Ideally, separator must have uniform pore distribution to support ions movements.

2.4.5 Wettability

The separators should be easily wetted with electrolyte. An electrolyte should be able to permanently wetted separator for preserving cycling life of FBs. CEM which is wetted with electrolyte will enhance ions transferring.

2.4.6 Thickness

Ideally, a separator must be thin to enhance ions transferring that affect on battery performance. But a separator that is too thin will lose in mechanical strength and safety. Separator should have uniform thickness for supporting in using. Separator thickness can be controlled in membrane fabrication method.

2.4.7 Ionic Conductivity

Ionic conductivity is the main important property which is needed in CEM for using in FBs systems. Ionic conductivity is the degree of permeability of ions through membrane. Ionic conductivity is the ability of membrane that mainly affect on

battery performance. Ionic conductivity can be measured by electrochemical impedance spectroscopy (EIS). For ZIFBs system in our dissertation, the positive ions are Zn^{2+} , K^+ and H^+ .

2.5 Examples of Cation Exchange Membranes

2.5.1 Nafion

As regarding to above section, Nafion is an conventional CEM that has been used as separator in ZIFBs and it exhibits good performance. From this reason, in this dissertation, Nafion was chosen to be a benchmark for comparing results with our synthesized membranes. Nafion is a brand name of polymer that is polytetrafluoroethylene or Teflon (PTFE) backbone with perfluorinated-vinyl-polyether side chains containing sulfonic acid end groups. Nafion was discovered and developed by DuPont Company in early 1960s [49]. The melting temperature of PTFE is around $327\text{ }^{\circ}\text{C}$ [50]. Nafion is synthesized by copolymerization of a perfluorinated vinyl ether comonomer with sulfonic acid groups and tetrafluoroethylene (TFE) resulting in the chemical structure that is shown in Figure 2.5.

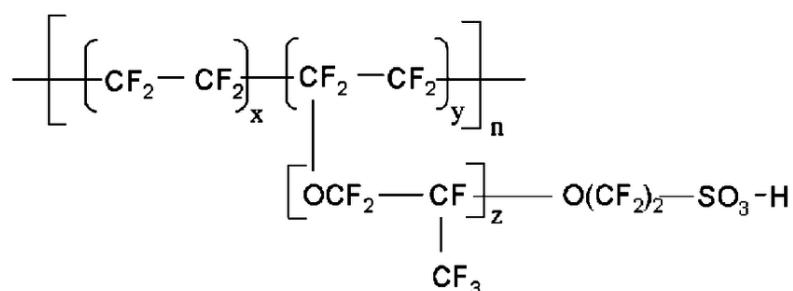


Figure 2.5 The chemical structure of Nafion [49]

Nafion was developed continuously in several of thickness and applications such as Nafion 115 and Nafion 117. Nafion was attracted and accepted to many researchers in many applications such as fuel cells and FBs, all-vanadium FBs, ZIFBs and others due to its chemical and thermal stability [17-19, 49]. Besides that, Nafion has high mechanical strength and high ionic conductivity so that it enhances battery performance. However, Nafion is an expensive membrane so that researchers try to develop the alternative materials for casting membranes [20, 21]. Previous studies have shown that sulfonated aromatic polymers such as sulfonated poly (arylene ether ketone) and sulfonated poly (arylene ether sulfone) are promising to be an alternative materials to Nafion [22-25]. Apart from them, SPEEK is very attractive to many researchers due to its good mechanical, thermal and chemical properties, low cost and easy preparation [27-30].

2.5.2 Sulfonated Poly (Ether Ether Ketone)

SPEEK is nonfluorinated membranes which are being less expensive than perfluorinated membranes such as Nafion. Nonfluorinated membranes typically have aliphatic or aromatic polymeric structures with the benzene ring or the pendant groups attached to the polymeric backbone. As mentioned above, SPEEK is one of an alternative material to be used as CEM for ZIFBs due to its chemical and thermal stability, high mechanical strength, low cost, easily to handle and moderate ionic conductivity [30, 31].

PEEK is a tough, hydrophobic, semicrystalline high performance thermoplastic polymer with good thermal and mechanical properties. PEEK was inertially introduced by Victrex PLC and then Imperial Chemical Industries (ICI) in the early 1980s [51]. The melting temperature of PEEK is around 373 °C [52]. The chemical structure of PEEK was shown in Figure 2.6.

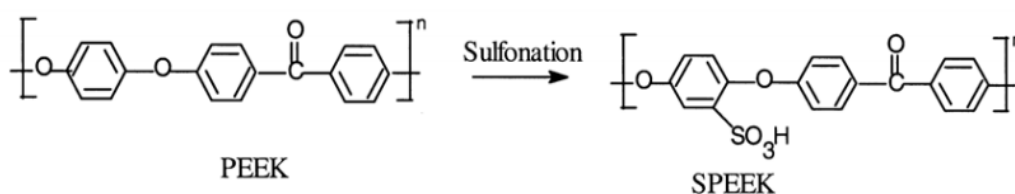


Figure 2.6 The sulfonation process of poly (ether ether ketone) [53]

In fact, pure PEEK cannot be used as CEMs so that it must be modified by the sulfonation process as shown in Figure 2.6. Sulfonation is an efficiently process to modify the polymer structure introducing sulfonic acid functional groups, which enable to transfer cations. It is the method to synthesize the CEM. It provides hydrophilic structure of polymers and increases the solubility of polymers. Many literatures have been described sulfonation in several methods. There were the sulfonation by concentrated sulfuric acid, by chlorosulfonic acid, by pure or complexed sulfur trioxide, and by acetylsulfate [53]. The PEEK can be modified or functionalized by sulfonation and the degree of sulfonation (DS), which indicates level of sulfonic acid groups that enhancing of ionic conductivity, can be controlled by reaction time and temperature. Sulfonated process promotes high ionic

conductivity of membranes but it will compromise the mechanical strength. The chemical structure of SPEEK is shown in Figure 2.6.

2.5.3 Poly (Vinylidene Fluoride)

As regarding to above section, sulfonation of PEEK compromises the mechanical strength of membranes. In addition, if SPEEK has too high DS, it can be dissolved very easily in water. Blending SPEEK with other polymers is regarded as effective method to solve this problem. PVDF is considered as promising choice owing to its excellent mechanical property, stable polymer structure, good processability and low cost [31]. The melting temperature of PVDF is around 177 °C. PVDF is a tough, hydrophobic, semi-crystalline and stable fluoropolymer with distinct engineering advantages. PVDF exhibits good electrical properties resulting from the polarity of alternating CH₂ and CF₂ groups on the polymer chain [54]. PVDF is used in many applications such as using in chemical processing equipments, using in electronic applications those are using as jacketing material for cable or using as binder for electrodes of lithium-ion batteries and in this dissertation, using in CEM as separator in ZIFBs. The chemical structure of PVDF is shown in Figure 2.7.

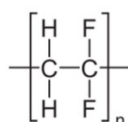


Figure 2.7 The chemical structure of poly (vinylidene fluoride) [54]

2.6 Membrane Characterizations

Membrane characterizations are necessary for investigating the properties of membranes those will significantly affect on battery performance. There are several properties of membranes in which is important to explore as follows:

2.6.1 Surface Morphology and Cross-Section

Surface morphology and cross-section of membrane can be observed by scanning electron microscopy (SEM). SEM will illustrate images of the morphology of material's surface that is invisible to the naked eyes. SEM is the effective method to investigate membranes' morphology.

Shaojian H. et al., studied the effect of DS and PVDF contents for SPEEK/PVDF membranes for fuel cell. The morphology of blend membranes was observed by SEM and the result is shown in Figure 2.8 [55].

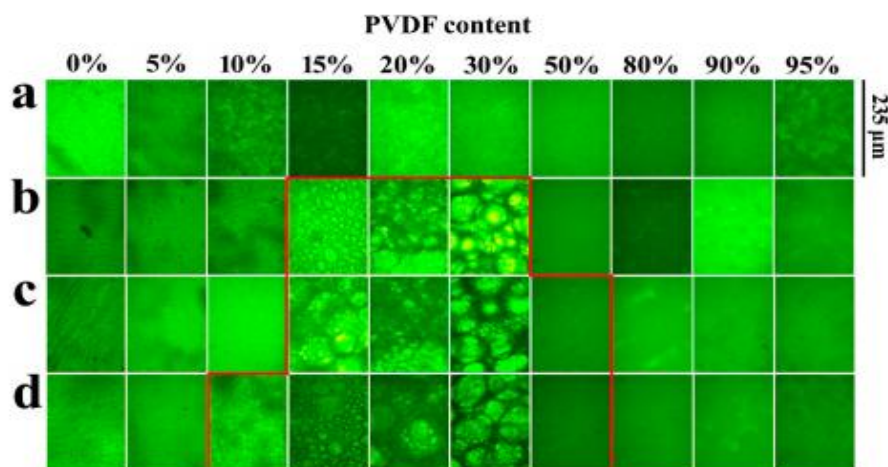


Figure 2.8 SEM images of SPEEK/PVDF blend membranes with various DS and different PVDF contents [55]

From Figure 2.8, for a-d it was ranged from low to high DS. It was found that low DS of blend membranes provided much miscible morphology than high DS of blend membranes due to their strong molecular interaction. At high DS of blend membranes, around 10-30 wt% of PVDF appeared the distinct phase separation.

2.6.2 Functional Groups

The functional groups in the structure of membrane can be observed by fourier transform infrared spectroscopy (FTIR). FTIR is a typically analytical technique to obtain infrared spectrum of absorption, emission, and photoconductivity of materials. FTIR can be used with all of state of materials those are solid, liquid and gas [56]. In this dissertation, this method is used to investigate the functional groups of membranes both before and after soaking in iodine solution. From previous studied, Sayed Daud S.N.S et al., studied the high DS of SPEEK/PVDF blend membranes for using in fuel cell system and they observed the success of sulfonation by FTIR. The result is shown in Figure 2.9 [30].

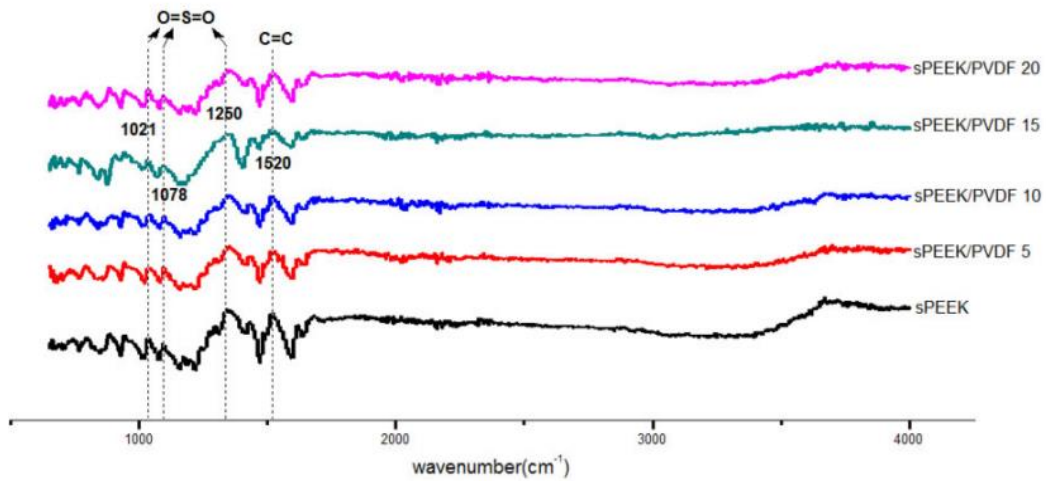


Figure 2.9 FTIR spectra of SPEEK and SPEEK/PVDF blend membranes with different PVDF contents [30]

From Figure 2.9, it was found that the blend membranes and the pristine SPEEK showed similar characteristics peaks. The absorption peaks at 1021, 1078 and 1250 cm^{-1} represent the sulfonic acid group in SPEEK. This ensure the success of sulfonation process. The absorption peak at 1520 cm^{-1} represents the carbonyl bond of SPEEK.

2.6.3 Degree of sulfonation

DS is the values which indicates the level of sulfonic acid groups that attached in polymer structures or the percentage of polymer repeating units of PEEK that have been sulfonated. The DS mainly depended on sulfonation process temperature and reaction time. This values can be determined by several methods. In this dissertation, DS was determined by proton nuclear magnetic resonance (H-

NMR) spectroscopy. The nomenclature of the aromatic protons for the SPEEK is given below [53, 57]:

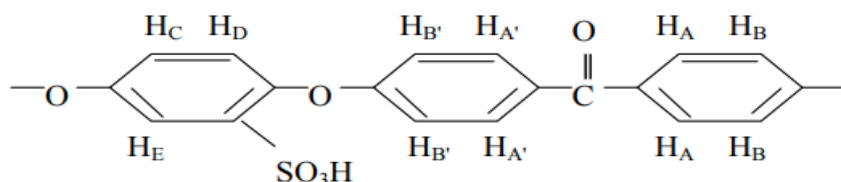


Figure 2.10 Nomenclature of the aromatic protons for the SPEEK repeat unit [53]

The presence of each SO_3H group results in a distinct signal for protons at the E position. In the H-NMR spectra, the presence of a sulfonic acid group causes a significant 0.25 ppm down-field shift of the hydrogen H_E compared with H_C , H_D in the hydroquinone ring. The intensity of this H_E signal, yields estimates of the H_E content which is equivalent to the SO_3H group content. The H-NMR signal for the SO_3H group is less easy to record directly because this proton is labile. DS can be determined by equation (2.14) and equation (2.15) from the H-NMR spectra at 6.9-7.9 ppm (the position of proton in the structure) as shown in Figure 2.11.

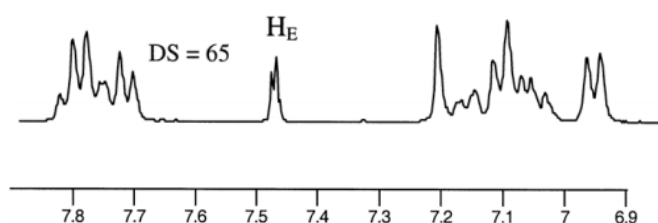


Figure 2.11 Example of H-NMR spectra of SPEEK sample [53]

The number of H_E per repeat unit (n) is expressed as:

$$n / (12-2n) = AH_E / \sum A_{H_{A,A',B,B',C,D}}, (0 \leq n \leq 1) \quad (2.14)$$

where AH_E is the peak area of the distinct H_E signal

$\sum A_{H_{A,A',B,B',C,D}}$ is the integrated peak area of the signals corresponding to all the other aromatic hydrogens

Finally, DS can be determined by equation (2.15)

$$DS (\%) = n \times 100 \quad (2.15)$$

From previous studies, Shaojian H. et al., studied the effect of DS for SPEEK/PVDF membranes for fuel cell and the result is shown in Table 2.1 The reaction was provided at room temperature. The result showed that increasing of sulfonation time, increasing of DS and ion exchange capacities (IECs) as same as ionic conductivity [55].

Table 2.1 IECs and DS of the prepared SPEEK [55]

Sulfonation Time (h)	IEC (mmol/g)	DS (%)
12	1.33	44
17	1.64	56
36	1.89	67
48	2.01	73

In addition, Yee R.S.L. et al., studied the sulfonated reaction of PEEK. It was found that the influence of reaction temperature was noted to be more significant on the DS than reaction time. The suitable reaction temperature is 50-60 °C [58].

2.6.4 Mechanical Property

As regarding in above section, mechanical properties is the important properties that related to cycling performance of battery. The mechanical properties of membrane in term of tensile strength was evaluated.

2.6.5 Water Uptake, Electrolyte Uptake and Swelling Ratio [31]

Water uptake is the value which indicates the quantity of water molecules that can be absorbed in the membrane. It was determined as percentage by the following equation:

$$\text{Water Uptake (\%)} = [(W_{\text{wet}} - W_{\text{dry}}) / W_{\text{dry}}] \times 100 \quad (2.16)$$

where W_{wet} is the weight of membrane after immersed in the deionized water for 24 hours at 35 °C and W_{dry} is the weight of membrane after drying at 80 °C in vacuum oven.

Electrolyte uptake is the value which indicates the quantity of electrolyte that can be absorbed in the membrane. It was determined as percentage by the following equation:

$$\text{Electrolyte Uptake (\%)} = [(W_{\text{wet}} - W_{\text{dry}}) / W_{\text{dry}}] \times 100 \quad (2.17)$$

where W_{wet} is the weight of membrane after immersed in the electrolyte for 24 hours at 35 °C and W_{dry} is the weight of membrane after drying at 80 °C in vacuum oven.

Swelling ratio is the ratio that indicates the increasing length of membrane due to water absorption. Swelling ratio can be determined by the following equation:

$$\text{Swelling Ratio} = [(l_{\text{wet}} - l_{\text{dry}}) / l_{\text{dry}}] \times 100 \quad (2.18)$$

where l_{wet} is the length of membrane after immersed in the deionized water for 24 hours at 35 °C and l_{dry} is the length of membrane after dried at 80 °C in vacuum oven.

2.6.6 Ionic Conductivity

As regarding to above section about the definition of ion conductivity, it can be determined by electrochemical impedance spectroscopy (EIS) via following equation:

$$\text{Ion Conductivity (mS/cm)} = L / (A \times R) \quad (2.19)$$

where L is the thickness of membrane (cm)

A is the area of membrane that transferring ions (cm²)

R is the zero intercept of real resistance (Z_{Re}) in ohms with imaginary resistance ($-Z_{\text{im}}$) axis in ohms

Sayed Daud S.N.S. et al. studied the performance of high DS for SPEEK/PVDF blend membranes for fuel cell with different contents of PVDF. The proton conductivity of different membranes was shown in Figure 2.12. The result showed that increasing the operating temperature, increasing proton conductivity as same as ionic conductivity. It was found that SPEEK's proton conductivity value was similar to that of Nafion117. It was only 34.87% difference from Nafion117. This indicated the attractive of SPEEK polymer [30].

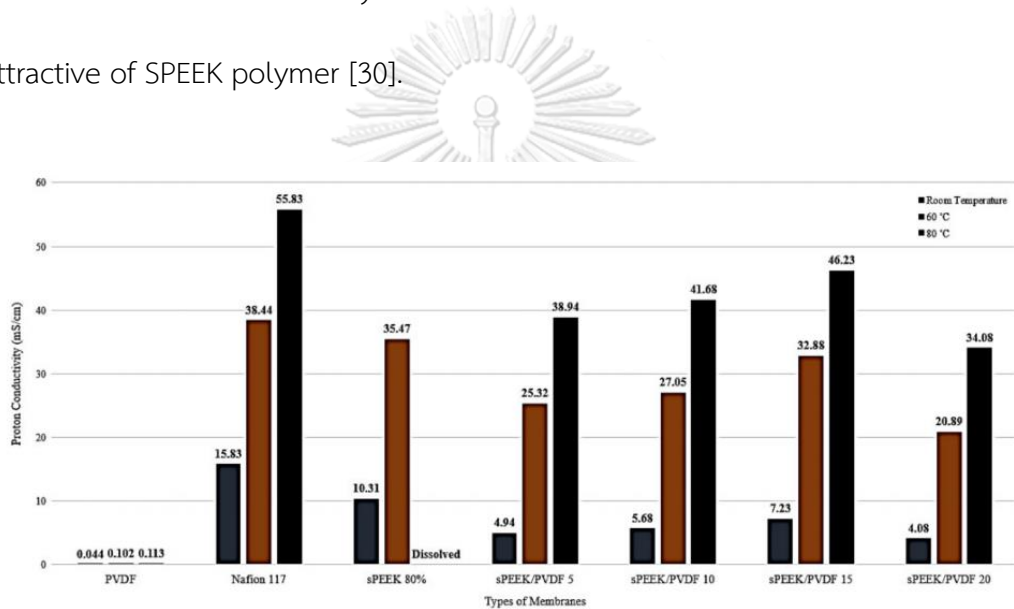


Figure 2.12 Proton conductivity of blend membranes with different PVDF contents [30]

2.6.7 Iodine Species Crossover

For ZIFBs, iodine species crossover is the important value that should be evaluated. Iodine species crossover leads to bad battery performance due to self discharging (losing in the maximum capacities) and losing active species of battery.

In this dissertation, iodine species crossover can be determined by ultraviolet visible (UV-VIS) spectroscopy [59].

2.6.8 Dispersing Elements

Dispersing elements in the structure of membranes can be observed by energy dispersive x-ray spectroscopy (EDX). EDX analysis is used to discover the surface elemental composition and observe their distribution. It provided the overall mapping of samples. The energy of the beam is typically in the range of 10–20 keV which causes X-rays to be emitted from the sample. In general, the energy of the X-rays emitted depends on the test sample. The electron beam moves across the sample and the images are obtained for each element. The presence of Au, Ag, and Pd on the sample's surface can be easily identified [60].

2.7 Battery Performance Measurement

In battery application, the important factors that we should consider are stability and power of the cell. From this reason, the galvanostatic charge – discharge and polarization were observed.

2.7.1 Galvanostatic Charge - Discharge Test

Galvanostatic charge – discharge test is the typical method to determine battery performance and cyclability (stability of the cell). The preliminary results indicate charge and discharge voltage of battery that can be reached at constant capacity and constant current density. A repeating of charge – discharge loop is

called cycle [61]. Otherwise, the obtained results can be used to determine energy efficiency (EE) by following equation[31]:

$$EE (\%) = (E_{\text{discharge}} / E_{\text{charge}}) \times 100 = [(\int V_d I_d dt) / (\int V_c I_c dt)] \times 100 \quad (2.20)$$

where V_d and V_c is the discharge and charge voltage respectively

I_d and I_c is the discharge and charge current respectively

Winardi S. et al. studied the performance of pure SPEEK membrane for vanadium redox flow battery (VRB). The cycle performance is shown in Figure 2.13. The result showed that the cell using SPEEK membrane exhibited slightly higher coulombic efficiency and energy efficiency than the cell using Nafion117. It indicated the better battery performance and indicated the attractive of SPEEK polymer [29]. Besides, Zhaohua L. et al. studied the performance of SPEEK/PVDF blend membrane with different PVDF contents for VRB. The cycle performance was shown in Figure 2.14 and the result showed that the cell using blend membrane exhibited higher discharge capacity than the cell using Nafion117 indicating higher battery performance. From all of the results, they indicated the attractive and performance of SPEEK and SPEEK/PVDF blend polymeric membrane [31].

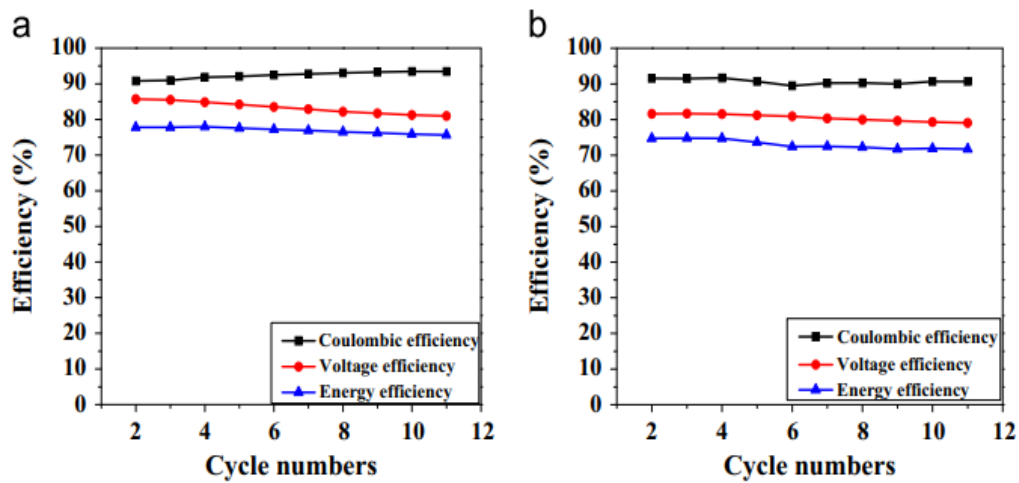


Figure 2.13 (a) Cycle performances of VRB cell using SPEEK48 and (b) Nafion117 at a current density of 40 mA/cm^2 [29]

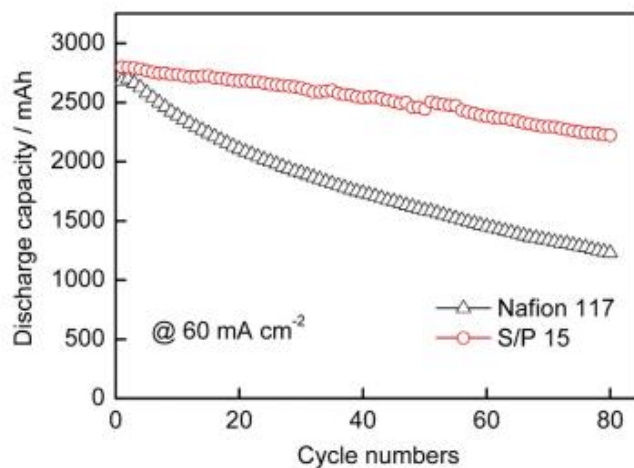


Figure 2.14 Cycling performance of discharge capacity declines for VRBs with S/P15 and Nafion117 membranes at 60 mA/cm^2 [31]

2.7.2 Polarization Test

Polarization is one important characteristic for flow battery and fuel cell. The polarization curve displays the output voltage at different input current. It determines battery performance in different input current. There are three significant

regions of polarization curve as shown in Figure 2.15.

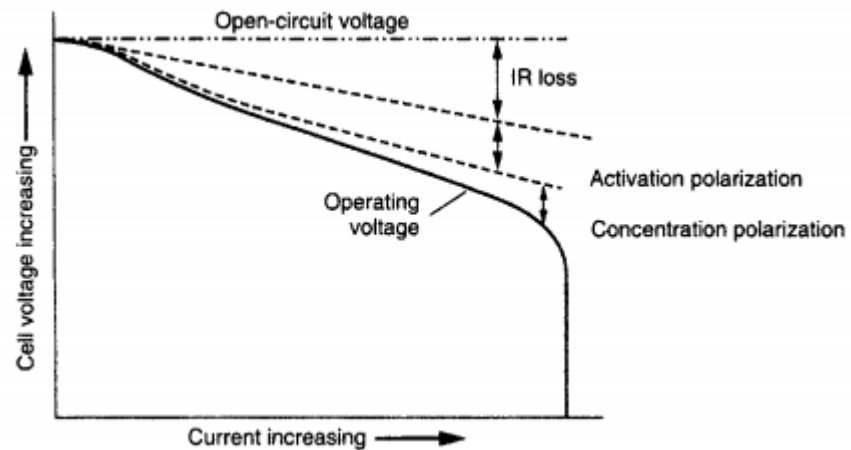


Figure 2.15 The polarization curve of fuel cell and flow battery [62]

The result in dropping of voltage from open-circuit voltage is from three major losses classifications as followings [63]:

2.7.2.1 Activation Polarization

Activation polarization is the voltage loss due to voltage overpotential that cause from the activation energy of the electrochemical reaction (redox reaction in flow battery). This type of polarization occurs at low current density.

2.7.2.2 Ohmic Polarization

Ohmic polarization is the voltage loss due to the electrical resistance in cell components. The cell components that provide electrical resistance are electrolyte and membrane. Ohmic polarization can be defined as the voltage loss due to charge transport. This type of polarization occurs at moderate current density. In this dissertation, we will focus on this type of polarization because it is the most related

to membrane.

2.7.2.3 Concentration Polarization

Concentration polarization is the voltage loss due to mass transport. This type of polarization occurs at high current density.



Chapter III

Experiments

3.1 Materials

Poly (ether ether ketone) (PEEK, 450PF) was purchased from Victrex USA Inc. Poly (vinylidene fluoride) (PVDF, $M_w = 275000$ g/mol) in pellet form, N,N Dimethylacetamide (DMAC, AR Grade), Dimethyl sulfoxide-D6 (DMSO-D6, deuteration degree, 99.8%) and the concentrated sulfuric acid (H_2SO_4 , 98%) were purchased from Sigma-Aldrich. Nafion115 membrane was purchased from Ion Power. Zinc sulfate 7-hydrate ($ZnSO_4 \cdot 7H_2O$, AR grade, $M_w = 287.58$ g/mol) and Iodine crystal (I_2 , 99.8%) were purchased from Kemaus. Carbon felt was purchased from China. Stainless steel mesh and titanium steel mesh were purchased from Alikaeii Trading Co.,Ltd. (China). Zinc metal sheet (99.9%) was purchased from Shandong AME Energy Co., Ltd., Shenzhen, China. Potassium Iodide (KI, 99%) was purchased from Univar.

3.2 Synthesis of Sulfonated PEEK (SPEEK) and SPEEK/PVDF membranes

3.2.1 Sulfonation of PEEK

15 g of PEEK was dried in vacuum oven for 6 h to remove moisture. 300 ml of concentrated H_2SO_4 was used for sulfonation process. 15 g of dried PEEK was slowly added into 300 ml concentrated H_2SO_4 to form a 5 wt./vol.% reaction solution. The solution was continuously stirred by mechanical agitation (using nylon propeller

stirrer) at room temperature for 1 h to form a rather homogeneous solution. After that, the solution was continuously stirred for another 3 h at 55 °C to form the SPEEK. The solution in this step must be homogeneous. Then, the solution was slowly poured into the cone and slowly dropped into the large excess of cold deionized water for terminating the sulfonation reaction. Next, SPEEK particles were washed several times with deionized water until pH reached about 5-6. The SPEEK particles were dried in the oven at 60 °C for 48 h. Finally, SPEEK particles were received.

3.2.2 Preparation of SPEEK membrane

1 g of SPEEK was dried in vacuum oven at 60 °C for 3 h before using to ensure removing of moisture. 10 ml of DMAC was used as solvent for solution casting method to form a membrane. 1g of SPEEK was added into 10 ml of DMAC to form a 10 wt./vol.% solution. The solution was continuously stirred by magnetic stirrer at room temperature for 24 h. The solution's color in this step is rather yellow. The solution was casted on a petri dish and dried at 80 °C for 48 h to remove solvent. The thickness of membrane was controlled by controlling the weight of solution that casted on petri dish. The SPEEK membrane was peeled off from a petri dish by immersing in deionized water. The wet SPEEK membrane was dried at room temperature and then immersed in 1 M of H₂SO₄ solution to activate the sulfonic acid group in its structure. The membrane was washed with deionized water and

then immersed in deionized water before using. The membrane must be kept in deionized water.

3.2.3 Preparation of SPEEK/PVDF membranes

The amount of SPEEK and PVDF that was used in the experiment was dried in a vacuum oven at 60 °C for 3 h before using for removing moisture. The SPEEK/PVDF blend membranes with 5, 10, 15 and 20 wt.% of PVDF contents (SP 5, SP 10, SP 15 and SP 20 respectively) were prepared as following procedures. Firstly, maintain the total amount of SPEEK and PVDF was fixed at 1 g and the desired weight of PVDF was continuously stirred by magnetic stirrer in 10 ml of DMAC at 70 °C for 2 h. Then, the SPEEK was slowly added into PVDF solution and continuously stirred at room temperature for 24 h to form a homogeneous solution. The solution was casted on a petri dish and dried at 80 °C for 48 h to remove solvent. The thickness of membrane was controlled by controlling the weight of solution that was casted on petri dish. The SPEEK/PVDF blend membranes were peeled off from a petri dish by immersing in deionized water. The wet SPEEK/PVDF blend membranes were dried at room temperature and then immersed in 1 M of H₂SO₄ solution to activate the sulfonic acid group in its structure. The membrane were washed with deionized water and then immersed in deionized water before using. All of membranes must be kept in deionized water.

3.3 Zinc-iodine Flow Batteries (ZIFBs) Fabrication

In this dissertation, two types of ZIFBs configuration were fabricated. For the first part, ZIFBs in H cell configuration was fabricated. ZIFBs in H cell configuration is used to preliminary screen the performance of synthesized membranes. This type of configuration is a static cell or it has not been flowed with electrolyte. For the second part, ZIFBs in stack cell configuration was fabricated. This type of configuration has been flowed with electrolyte by using a peristaltic pump.

3.3.1 ZIFBs in H Cell Configuration

3.3.1.1 Preparation of Electrodes

For negative electrode, zinc metal sheet was used to electro-deposit on a $1 \times 1 \text{ cm}^2$ cut piece of carbon felt by using 2 M of ZnSO_4 for electrolyte under the condition of 1.5 V for 1 h. For positive electrode, an absorbed 0.5 N of I_2 and KI solution on a $1 \times 1 \text{ cm}^2$ cut piece of carbon felt was used. For both electrodes, a $10 \times 1 \text{ cm}^2$ cut piece of stainless steel mesh was used as current collector.

3.3.1.2 Preparation of Electrolytes

For negative electrode, 2 M of ZnSO_4 was used as electrolyte. A certain amount of ZnSO_4 was dissolved in deionized water and continuously stirred by magnetic stirrer until the solution was changed into clear color. For positive electrode, 0.5 N of I_2 mixed with KI solution was used as electrolyte. A certain

amount of I_2 and KI was dissolved in deionized water and continuously stirred by magnetic stirrer for 2 h to ensure that the solution will be homogeneous.

3.3.1.3 Preparation of Separator or Ion Exchange Membrane (IEM)

The synthetic membrane was cut into a circular piece with the diameter of 3 cm for using as separator.

3.3.1.4 Battery Assembly

The batteries were fabricated as H cell configurations. Firstly, the prepared stainless steel mesh was put into both sides of H cell. Then, the prepared carbon felt with zinc electro-deposited and the pure carbon felt were attached on stainless steel mesh at both sides of H cells. The prepared membrane was put between two gaskets and then put into the middle of both sides of H cell. The H cell were articulated by clipping. The prepared electrolytes were poured into both sides of H cell. 13 ml of electrolyte was used for one side of H cell. The H cell configuration of ZIFBs is illustrated in Figure 3.1.

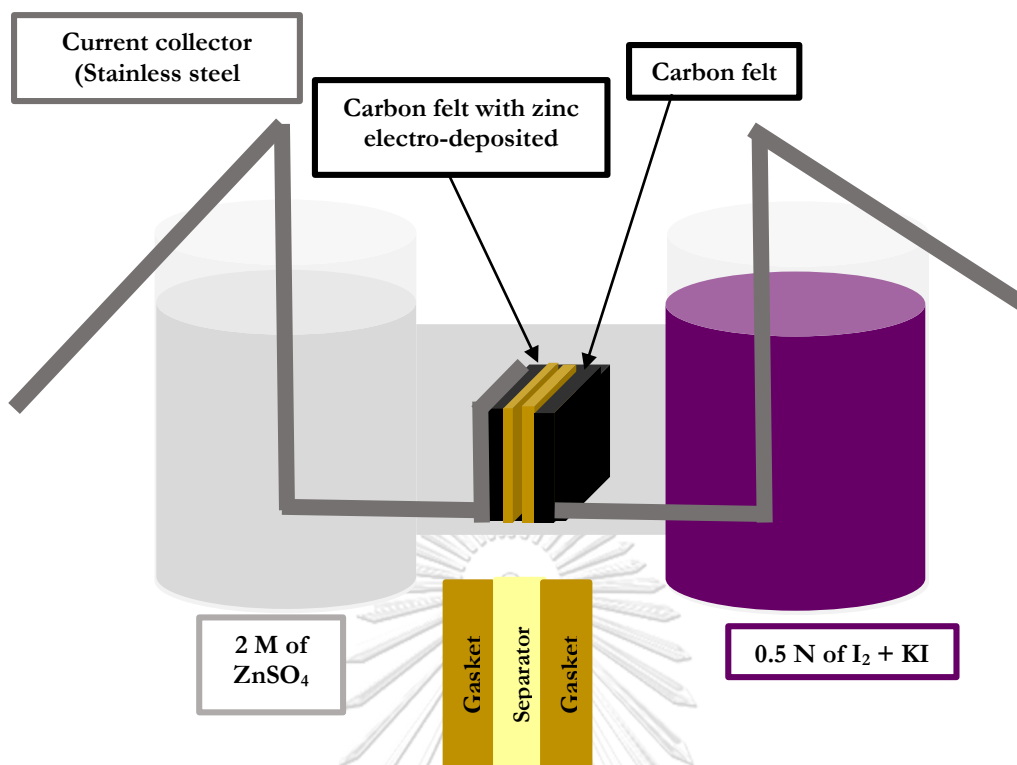


Figure 3.1 The schematic of ZIFBs in H cell configuration

3.3.2 ZIFBs in Stack Cell Configuration

3.3.2.1 Preparation of Electrodes

For negative electrode, zinc metal sheet was used to electro-deposit on a $1.5 \times 2 \text{ cm}^2$ cut piece of carbon felt by using 2 M of ZnSO_4 for electrolyte under the condition of 750 mAh for 1 h. For positive electrode, an absorbed 0.5 N of I_2 and KI solution on a $1.5 \times 2 \text{ cm}^2$ cut piece of carbon felt was used. For both electrodes, a $15 \times 2 \text{ cm}^2$ cut piece of titanium steel mesh was used as current collector.

3.3.2.2 Preparation of Electrolytes

The preparation of electrodes are as same as mentioned in section 3.3.1.2.

3.3.2.3 Preparation of Separator or IEM

The selected synthesized membrane was cut into a circular piece with the diameter of 4.5 cm.

3.3.2.4 Battery Assembly

A battery was fabricated in stack cell configuration. Firstly, the prepared electrodes were attached on titanium steel mesh. Then, the both of prepared titanium steel were put into both sides of stack cell. The prepared membrane was put between two electrodes. There are gaskets in all stacks of the cell. After that, the stack cell was assembled by tightening the nuts. The prepared electrolytes were poured into both sides of stack cell. 40 ml of electrolyte was used for each side of stack cell included with the electrolyte in silicone tube. The peristaltic pump was used to flow the electrolyte for each side of stack cell. The stack cell configuration is illustrated in Figure 3.2.

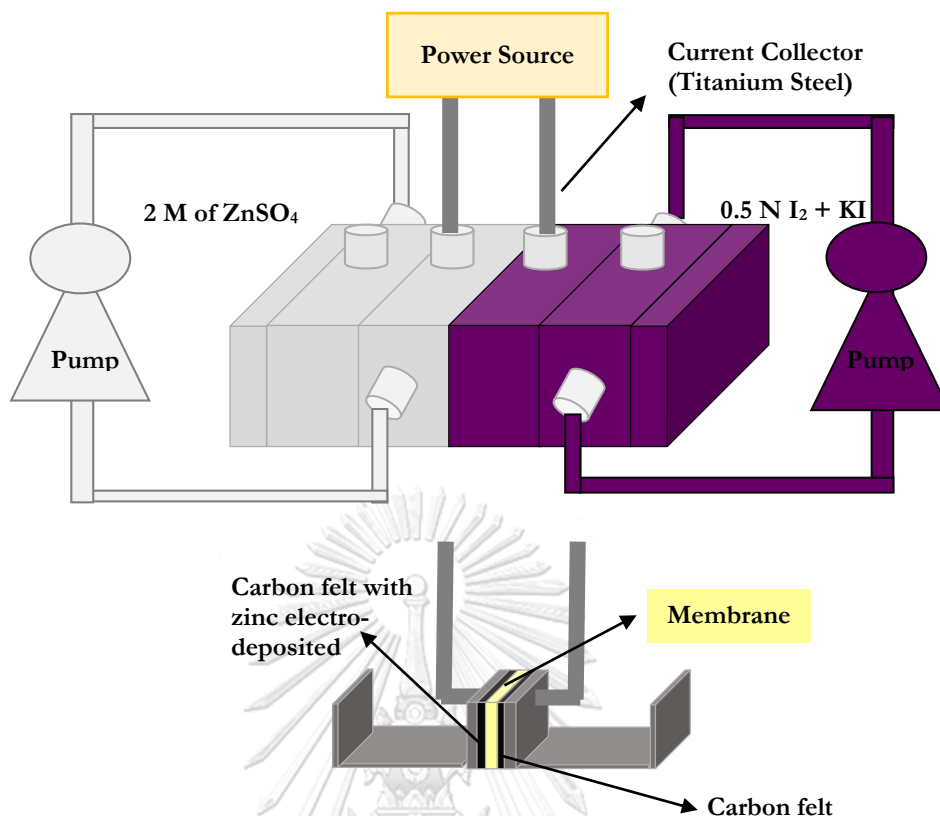


Figure 3.2 The schematic of ZIFBs in stack cell configuration

3.4 Membrane Characterizations

3.4.1 Surface Morphology and Cross-Sectional

The morphology and cross-sectional of membranes such as miscible, immiscible and porous structure of polymer blending of the prepared membranes was observed by SEM. The morphology and cross-sectional of all prepared membranes was examined. All of the prepared membranes were coated with a thin layer of gold via vacuum sputtering before analysis.

3.4.2 Functional Groups

The prepared membranes were observed by fourier transform infrared spectroscopy (FTIR) to ensure the sulfonic acid groups in their structure. Besides that, the selected prepared membranes were soaked in iodine solution (0.5 N of I₂ + KI) at different time (1, 6, 18, 24, 30 and 36 h). After that, the iodine species bond in membranes structure were evaluated by FTIR. The FTIR spectra were recorded in the range of around 400-4000 cm⁻¹.

3.4.3 Degree of Sulfonation (DS)

A certain amount (0.1 g) of the prepared SPEEK was dried in vacuum oven for 24 h to remove moisture. The prepared SPEEK particles were dissolved in 2 ml of DMSO-D₆ for 24 h to produce 5 wt.% solution. The prepared solution was characterized by proton nuclear magnetic resonance (H-NMR). The H-NMR spectra of SPEEK were recorded on an NMR spectrometer (Bruker Avance III HD/Oxford) at 30 °C with 500 MHz of resonance frequency. Tetramethylsiloxane (TMS) was used as an internal standard [53]. Finally, the result was analyzed and the DS was evaluated as mentioned in section 2.6.3.

3.4.4 Mechanical Property

The mechanical properties of the selected prepared membranes were measured in terms of tensile strength by using universal testing machine (Instron). The sample membrane with 130 mm x 10 mm dimensions was cut and used for

mechanical property test. The tensile speed was set at 12.5 mm/min. The testing conditions were referenced from American Society for Testing and Materials (ASTM D-882). Tensile strength at break of the selected membranes were identified.

3.4.5 Water Uptake, Electrolyte Uptake and Swelling Ratio

For water uptake and electrolyte uptake, the method is as same as each other by the following steps. The prepared membranes were immersed in deionized water for water uptake testing and immersed in 2 M of $ZnSO_4$ solution for electrolyte uptake testing for 24 h at 35 °C. After that, the wet weight of membranes were measured after removing excess water on surface. The membranes were dried at 80 °C for 24 h and the dry weight of membranes were measured. Then, the data was collected and calculated by equation (2.16) and equation (2.17) to obtain water uptake and electrolyte uptake respectively.

For swelling ratio, the prepared membranes were immersed in deionized water for 24 h at 35 °C. The wet length of membranes were measured after removing excess water in surface. The membranes were dried at 80 °C for 24 h and the dry length of membranes were measured. The data was calculated by equation (2.18) to obtain swelling ratio.

3.4.6 Ionic Conductivity

The ionic conductivity of the completely assembled H cells with different prepared membranes and Nafion115 were investigated by electrochemical

impedance spectroscopy (EIS) using Squidstat (Admiral Instruments) via Squidstat User Interface. The prepared membranes were kept in deionized water before test. The measurement was conducted between frequencies range between 200000 Hz and 0.1 Hz with amplitude of 10 mV. The ionic conductivity measurement was conducted at three different temperatures which are 35, 55 and 75 °C and three different ZnSO_4 concentrations which are 0.5, 1 and 2 M. The data was collected and analyzed, then calculated by equation (2.19) to obtain ionic conductivity.

3.4.7 Iodine Species Crossover

The iodine species crossover of sample membrane was measured by ultraviolet visible (UV-VIS) spectroscopy. The completely assembled H cells with different prepared membranes were left for a period of time. 3 ml of electrolyte sample was collected at a certain time. The electrolyte sample was analyzed by UV-VIS at that certain time. The UV-VIS spectroscopy spectrum of the sample were measured by scanning in the range of 190-500 nm wavelength.

3.4.8 Dispersing Elements

The dispersing elements of sample membrane was observed by energy dispersive x-ray spectroscopy (EDX). All of sample membranes were applied in ZIFBs H cell configuration under galvanostatic charge-discharge test before the EDX analysis. In addition, all of the membranes were coated with a thin layer of gold via

vacuum sputtering before the EDX analysis. The dispersing elements of all prepared membranes was examined.

3.5 Battery Performance Measurement

3.5.1 Galvanostatic Charge Discharge Cycle Test

Both complete assembled ZIFB in H cell and in stack cell were observed cyclability via charge discharge cycle test by using multi-channel battery tester. For ZIFB in stack cell configuration, the electrolytes were cyclically pump into corresponding half cell by two peristaltic pumps of 16 rpm (a flow rate of 20 ml/min). The ZIFB cell was charged and discharged at constant current density of 10 mA/cm² and at constant capacity at 0.174 mAh to investigate the cycling performance of ZIFB cell of different membranes.

3.5.2 Polarization Test

Both complete assembled ZIFB in H cell and in stack cell were conducted polarization test by using multi-channel battery tester. For ZIFB in stack cell configuration, the electrolytes were cyclically pump into corresponding half cell by two peristaltic pumps of 16 rpm (a flow rate of 20 ml/min). The ZIFB cell was charged and discharged at different current densities of 5-50 mA/cm² to get charge-discharge performance of different membranes. The maximum power density of different membranes was examined.

All of the measurements were used the results of Nafion115 membrane as a benchmark to compare with the results of our synthesized membranes.



Chapter IV

Results and Discussion

In this dissertation, the experiments were divided into four main sections. There are sulfonation of poly (ether ether ketone) (PEEK), synthesizing of membrane, fabrication zinc-iodine flow battery (ZIFB) in H cell configuration and fabrication ZIFB in stack cell configuration. According to this, the results and discussion parts were divided into four main sections for experiments and one main section for cost estimation as followings:

4.1 Sulfonation of PEEK and Synthesizing of Membrane

4.1.1 Functional Groups

All of the synthesized membranes and Nafion 115 membrane were observed by fourier transform infrared spectroscopy (FTIR) to ensure the success of sulfonation process. The pure PEEK was observed by FTIR to compare with the sulfonated PEEK (SPEEK). Figure 4.1 shows the FTIR spectra of the pure PEEK, the pristine SPEEK membrane, SPEEK/poly (vinylidene fluoride) (PVDF) blend membranes and Nafion115 membrane in the range of 4000-400 cm^{-1} .

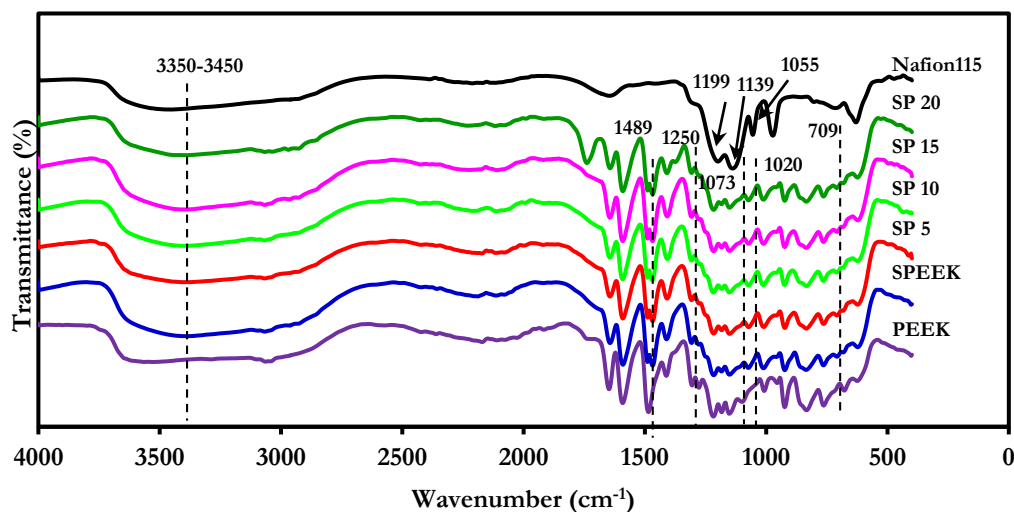


Figure 4.1 The FTIR spectra of PEEK powder, SPEEK, SPEEK/PVDF blend membranes and Nafion115 membrane

From Figure 4.1, significant difference in the IR spectrum of sulfonated PEEK was observed as compared to pure PEEK. The pristine SPEEK and the blend membranes showed similar characteristic peaks. The presence of sulfonic acid groups were observed with the absorption bands at 709, 1020, 1073 and 1250 cm^{-1} . The bands are tentatively assigned as various sulfur-oxygen vibrations; asymmetric O=S=O stretch (1250), symmetric O=S=O stretch (1073), S=O stretch (1020), and S-O stretch (709). The aromatic C-C band was observed at 1489 cm^{-1} . The broad band at 3350-3450 cm^{-1} can be assigned as the O-H vibration [53]. For Nafion115 membrane, the peak at 1055 cm^{-1} was observed due to symmetric S-O stretching, the band at 1139 cm^{-1} due to symmetric C-F stretching and a band at 1199 cm^{-1} due to asymmetric C-F stretching [64]. In summary, the changes observed in the FTIR spectra indicate the presence of $-\text{SO}_3\text{H}$ groups.

4.1.2 Degree of Sulfonation (DS)

In this dissertation, the concentrated H_2SO_4 was used to carry out the sulfonation process. The DS affects on several properties of SPEEK such as water uptake, swelling ratio and ionic conductivity. DS of three samples of SPEEK were evaluated by the proton nuclear magnetic resonance (H-NMR) analysis. In this study, the reported DS was the average DS values from the DS of three samples for ensuring the consistency as shown in Table 4.1. Based on the H-NMR analysis, the synthesized SPEEK was 53 % of DS and one of the spectrums was shown in Figure 4.2. The other two H-NMR spectrum were shown in Figure A.1 and Figure A.2.

Table 4.1 The DS of SPEEK at 3 h and 55 °C of sulfonation process

Samples	DS (%)
1	53
2	54
3	52
Average	53

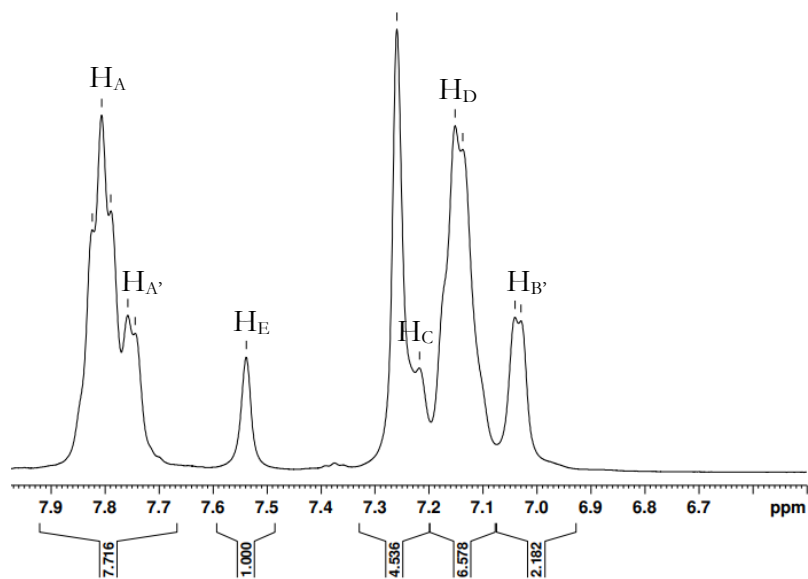


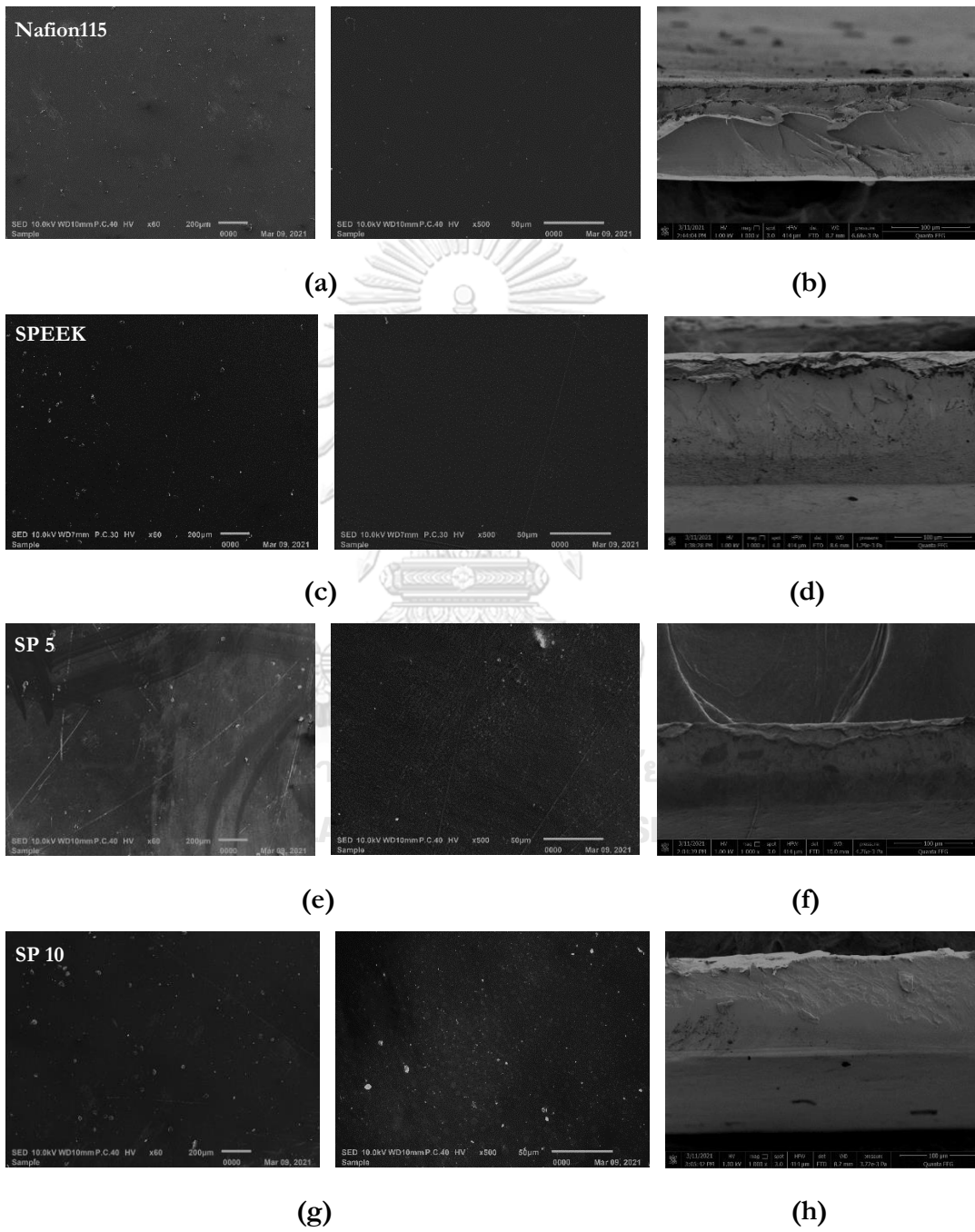
Figure 4.2 The ¹H-NMR spectra of SPEEK sample

From the ¹H-NMR spectrum in Figure 4.2, there was a peak at 7.5-7.55 ppm which indicates that the sulfonic acid group was successfully attached to PEEK backbone. Unlike the pure PEEK, the SPEEK can be dissolved in organic solvents such as dimethyl sulfoxide (DMSO), dimethylacetamide (DMAC) and N-methyl-pyrrolidone (NMP) depending on the DS value. Since the DS of SPEEK is 53 % in this study, it is soluble in all types of inorganic solvents.

4.1.3 Surface Morphology and Cross-Section of Membrane

The Nafion115 membrane and all of the synthesized membranes were examined by scanning electron microscopy (SEM) to determine the distribution of PVDF in SPEEK matrix, the surface morphologies and the cross-sections of all membranes. The surface morphologies and cross-sections of the synthesized

membranes and Nafion115 membrane were illustrated in Figure 4.3 (a-l). The blend membranes are denoted as SP X, where X is the PVDF mass ratio.



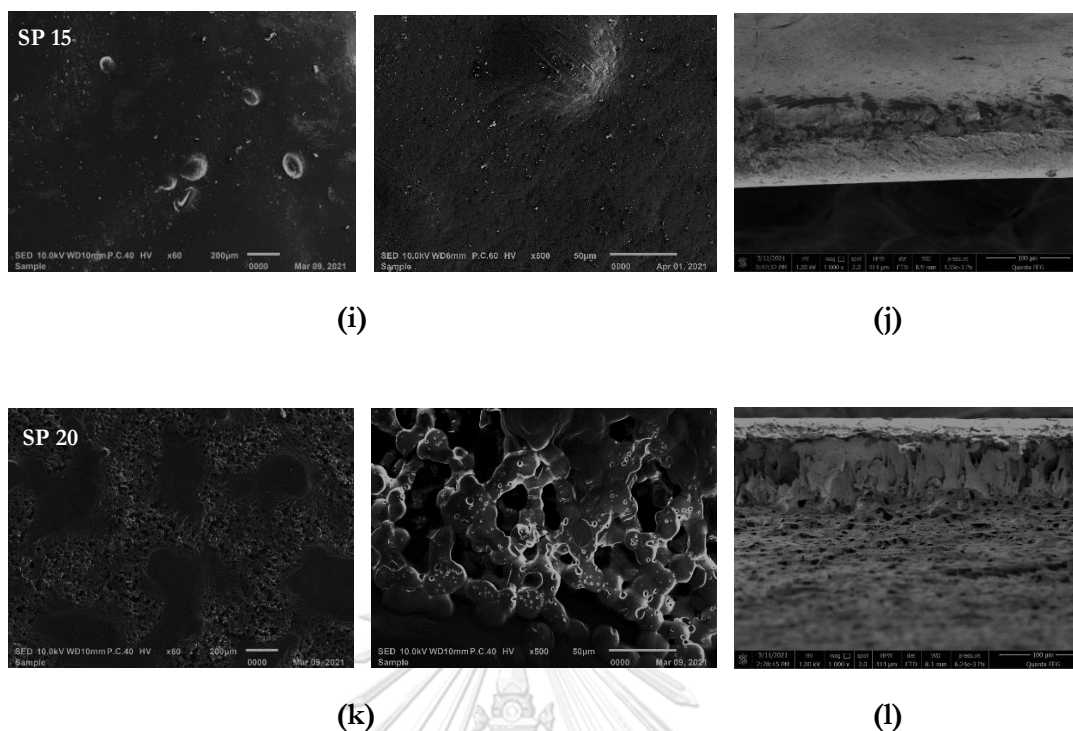


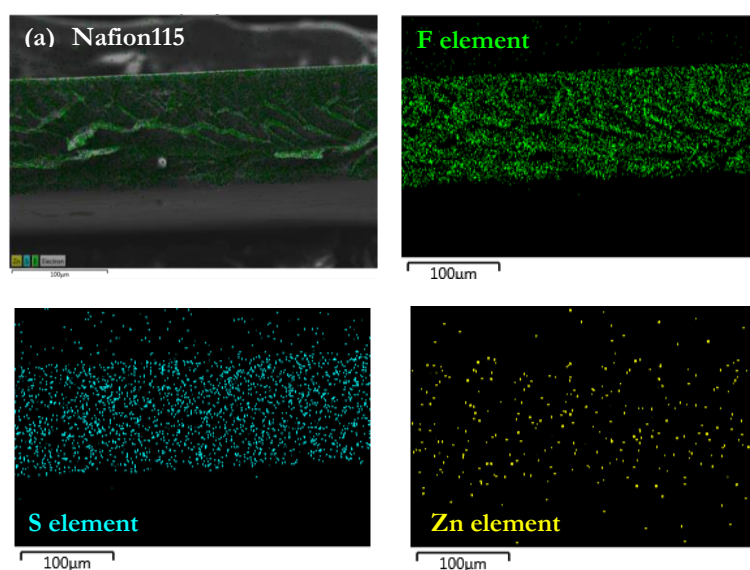
Figure 4.3 SEM images of surface (60 times) and surface (500 times) and cross section of membrane (a), (b) Nafion115; (c), (d) SPEEK; (e), (f) SP 5; (g), (h) SP 10; (i), (j) SP 15 and (k), (l) SP 20

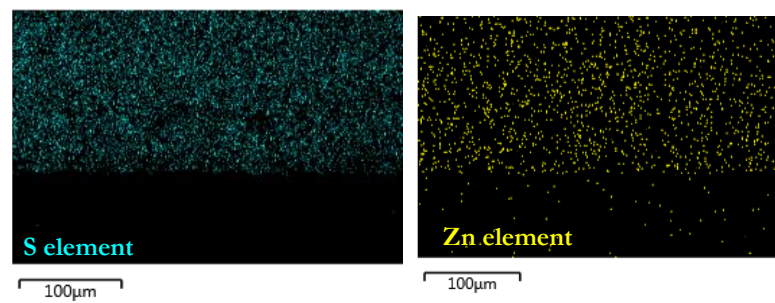
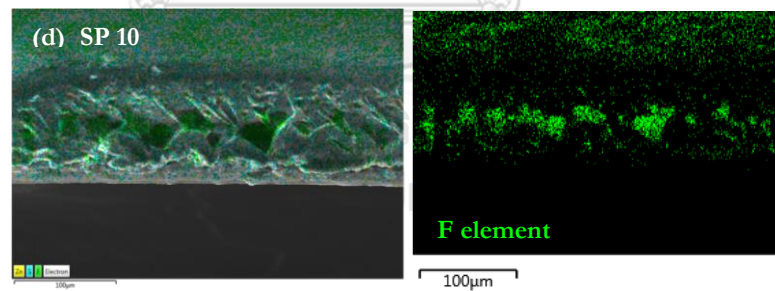
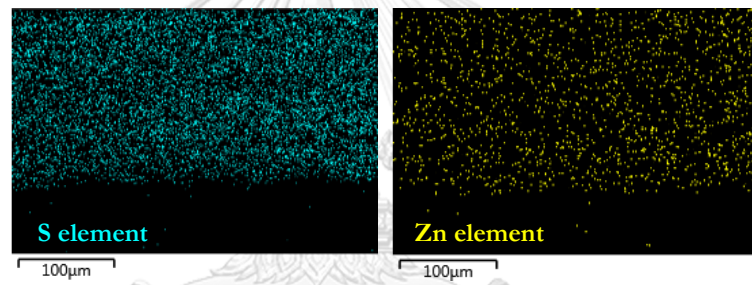
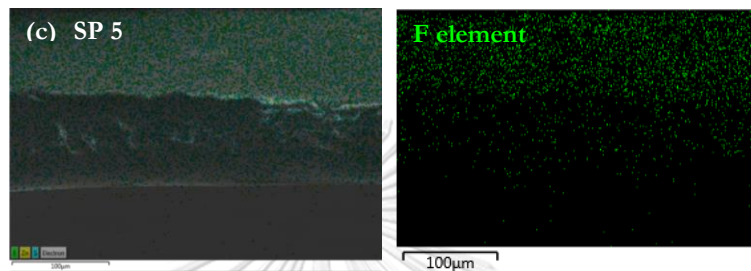
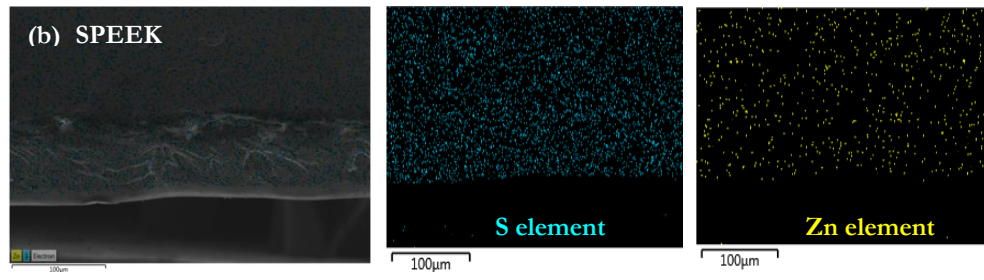
In Figure 4.3 (a), it was shown that Nafion115 membrane was dense and uniform. But in Figure 4.3 (b), it was shown that the cross-section of Nafion115 membrane was not smooth. As shown in Figure 4.3 (c), the SPEEK membrane was dense, uniform and defect-free. In addition, the cross-section of SPEEK membrane was dense and smooth. In considering at blend membranes, Figure 4.3 (e) and Figure 4.3 (g) indicated that the SP 5 and SP 10 membrane were almost dense, uniform and finer. In Figure 4.3 (f) and Figure 4.3 (h), the formation of defects were observed by adding PVDF. Meanwhile, a phase-separated morphology was significantly observed when 15 wt.% and 20 wt.% of PVDF were added in the SPEEK matrix, which may

occur due to low homogeneity between two polymers. The porous structure and lots of defect were observed due to phase-separated as shown in Figure 4.3 (i-l). From all of the results, the SP 5 membrane was dense, uniform and almost finer with the least defects. It indicated that the SP 5 membrane was more homogeneous compared to the other blend membranes. According to Inan et al., [65], the morphology structure affected the formation of ionic domains and influenced the conduction of ions and the hydration. The more uniform and finer membrane morphology formed better ionic domains as well as increased the ionic conductivity and hydration level.

4.1.4 Dispersing Elements

The electron dispersive spectroscopy (EDX) elemental maps of Nafion115 membrane and all of the synthesized membranes cross-sections after using was further investigated and shown in Figure 4.4 (a-f).





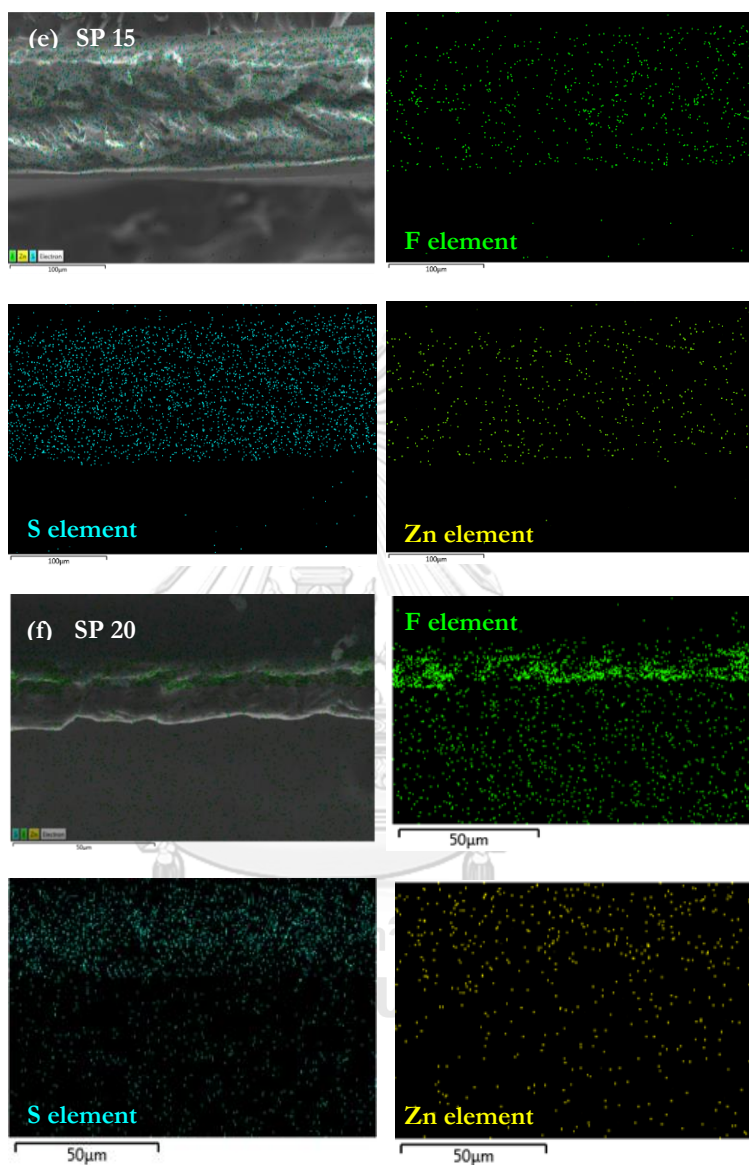


Figure 4.4 (a-f) The EDX elemental maps of (a) Nafion115; (b) SPEEK; (c) SP 5; (d) SP 10; (e) SP 15 and (f) SP 20

As considering to Nafion115 membrane, the mapping element F, the mapping element S and the mapping element Zn are uniformly distributed as shown in Figure 4.4 (a). In Figure 4.4 (b), it was shown that the mapping element S and the mapping

element Zn are uniformly distributed in the SPEEK membrane. For the synthesized blend membranes, the mapping element F for the presence of PVDF, the mapping element S for the presence of $-SO_3H$ group from SPEEK and the mapping element Zn are uniformly distributed in the SP 5 membrane as shown in Figure 4.4 (c), which reveals that the SP 5 membrane has a homogeneous microstructure. However, the F element, S element and Zn element are non-uniformly distributed in the SP 10, SP 15 and SP 20 membranes as shown in Figure 4.4 (d-f), which reveals that the SP 10, SP 15 and SP 20 membranes are heterogeneous with a phase-separated microstructure.

4.1.5 Water Uptake, Swelling Ratio and Electrolyte Uptake

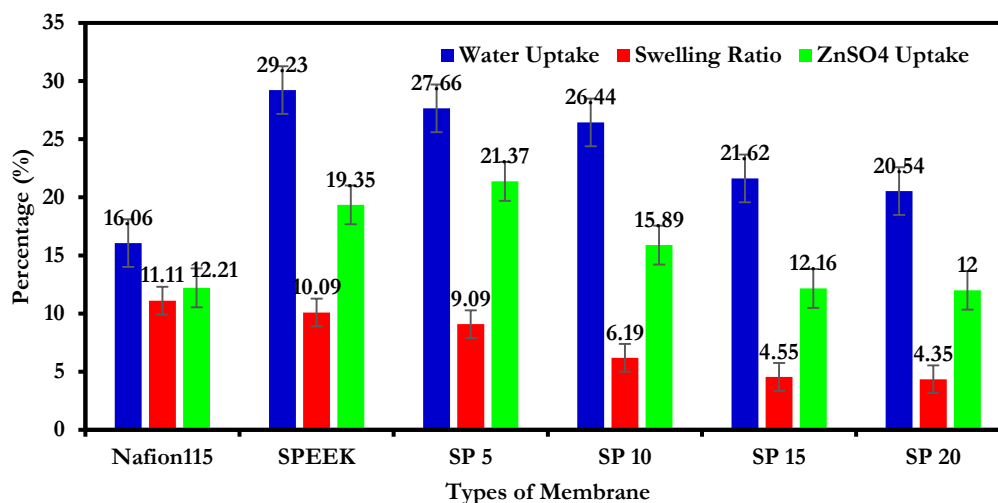


Figure 4.5 The water uptake, swelling ratio and electrolyte uptake of Nafion115 membrane, SPEEK and SPEEK/PVDF blend membranes

Figure 4.5 represents the water uptake, swelling ratio and electrolyte uptake of Nafion115, SPEEK and SP blend membranes with various PVDF mass ratios. The

water uptake result was illustrated in the blue bar chart in Figure 4.5. From the results, it was shown that the SPEEK membrane exhibited the highest percentage of water uptake. It can be observed that the water uptake of blend membranes decreases with the increasing of PVDF mass ratio. Addition of PVDF leads to low water uptake values due to its hydrophobic structure. The water uptake values of all synthesized membranes are higher than that of Nafion115 membrane. SPEEK membrane structure permits the polar sites as pendant groups in order to increase the water uptake. High water uptake is good for proton conductivity, because the increasing water uptake would facilitate the dissociation of $-SO_3H$ groups and the migration of protons in the membrane [66].

The swelling ratio data was illustrated in the red bar chart in Figure 4.5. In considering at the swelling ratio of all membranes, it can be seen that Nafion115 membrane exhibited the highest value of swelling ratio. High swelling ratio leads to the changing in membrane shape indicating the non-stability of membrane in application. For blend membranes, it was found that the swelling ratio decreases with the increasing of PVDF mass ratio, which indicates that the swelling behaviors of blend membranes are indeed suppressed by PVDF due to the extending of crystalline region (hydrophobic structure) in blend membranes.

The electrolyte uptake in term of $ZnSO_4$ uptake was illustrated in the green bar chart in Figure 4.5. It was found that the SP 5 blend membrane exhibited the highest value of $ZnSO_4$ uptake indicating the good performance of membrane. In

addition, the ZnSO_4 uptake values of most synthesized membranes are higher than Nafion115 membrane. High ZnSO_4 uptake is good for ionic conductivity that relates to the good battery performance. High ZnSO_4 uptake leads to the good ability in balancing the electric charges in ZIFBs application.

4.1.6 Ionic Conductivity

Ionic conductivity of Nafion115 membrane and each synthesized membrane was measured by electrochemical impedance spectroscopy (EIS). The experiment was conducted at three different temperatures which are 35, 55 and 75 °C and three different ZnSO_4 concentrations which are 0.5, 1 and 2 M. Ionic conductivity is an essential property to determine the efficiency of cation exchange membrane (CEM). The ionic conductivity result is shown in Figure 4.6.

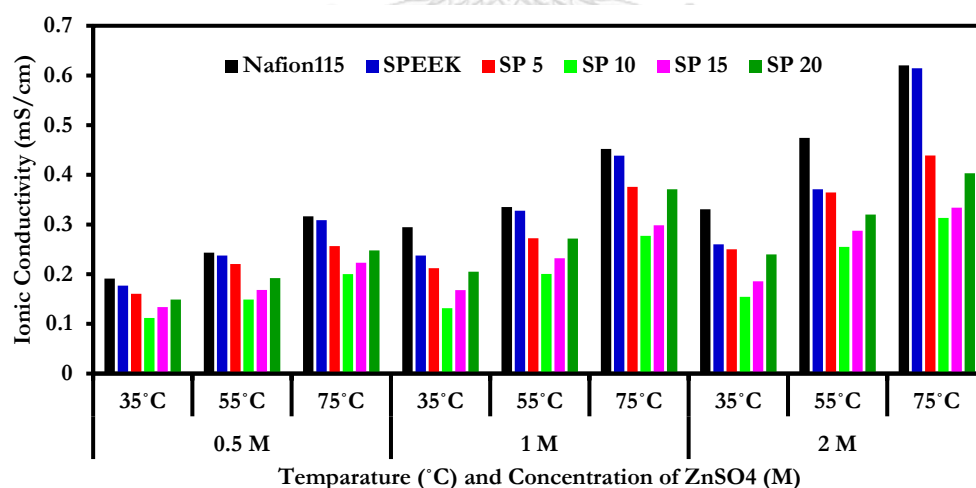


Figure 4.6 The ionic conductivity of Nafion115 membrane, SPEEK and SPEEK/PVDF blend membranes

According to Figure 4.6, the values of ionic conductivity for all synthesized membranes and commercial Nafion115 are increased with the increasing temperature because of the increasing of kinetic energy. High kinetic energy results in easy ions movement. In addition, the values of ionic conductivity for all synthesized membranes and commercial Nafion115 are also increased with the increasing electrolyte (ZnSO_4) concentration. High concentration of ZnSO_4 increased the amount of zinc ions in the solution. In considering at one temperature and one concentration, it can be seen that the ionic conductivity of blend membranes are less than the ionic conductivity of the SPEEK membrane due to the hydrophobic structure of PVDF structure. From Figure 4.6, the Nafion115 membrane exhibited the highest ionic conductivity. As considering to blend membranes, the SP 5 membrane exhibited the highest ionic conductivity due to hydrophilic structure of SPEEK and the uniform surface morphology, which indicates the good performance of membrane. For the other blend membranes, it was found that the ionic conductivity are increased with the increasing of PVDF mass ratio due to the porous structure in membrane. High PVDF mass ratio leads to high porous structure of membrane because of the phase separation of two polymers. The ionic conductivity is related to morphology, chemical structure, water uptake, electrolyte uptake, electrolyte concentration and temperature, especially the water uptake and electrolyte uptake [66]. Although the ionic conductivity of all synthesized membranes are lower than

Nafion115 membrane, the synthesized membranes still possess effective ZIFB cell performances, which could be verified by the following results.

4.1.7 Iodine Species Crossover

In this dissertation, the iodine species crossover was examined by ultraviolet visible (UV-VIS) spectroscopy. All of synthesized membranes and Nafion115 membrane were examined. The example of UV-VIS spectrum of ZnSO_4 solution at certain time was measured by scanning in the range of 190-600 nm wavelength, as shown in Figure A.3. The maximum adsorption wavelength was 288 and 350 nm for triiodide ion (I_3^-). To obtain the I_3^- concentration, the calibration curve was required as shown in Figure A.4 and Figure A.5. The change of iodine species (I_3^-) concentrations in ZnSO_4 solutions with time for all synthesized membranes and Nafion115 membrane is illustrated in Figure 4.7.

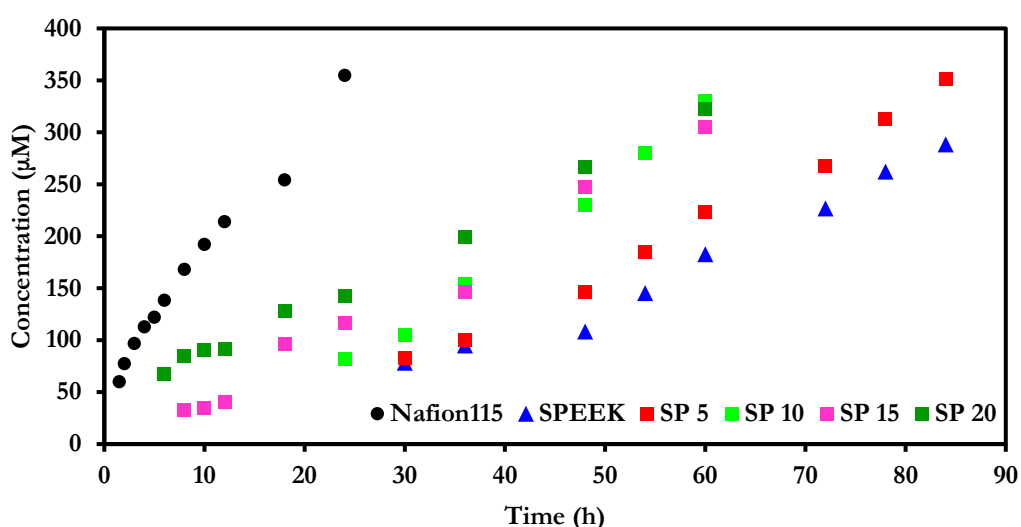


Figure 4.7 The iodine species crossover of Nafion115 membrane, SPEEK and SPEEK/PVDF blend membranes

From the results, all of the I_3^- concentrations of all membranes change linearly with time. According to Figure 4.7, it was shown that all of the synthesized membranes can better prevent the crossover of iodine species than Nafion115 membrane. The I_3^- concentrations in $ZnSO_4$ solution of Nafion115 membrane are significantly higher than the other synthesized membranes at the same time, which indicates the bad performance of membrane. The SPEEK membrane exhibited the best performance in preventing the crossover of I_3^- due to its hydrophilic structure of SPEEK. In focusing of blend membranes, the SP 5 membrane exhibited the best performance in preventing the crossover of I_3^- . In addition, it was found that the I_3^- concentrations in $ZnSO_4$ solution of blend membranes are increased with the increasing of PVDF mass ratio because of their hydrophobic structure of PVDF.

4.2 ZIFBs Fabrication in H Cell Configuration

In this section, all of synthesized membranes and the commercial Nafion115 membrane were applied in ZIFB as CEM separator. The ZIFB cell was fabricated in H cell configuration. This configuration is not flowed with the electrolyte. For battery application, there are three important factors those are operating range, power and stability of the battery. The polarization and galvanostatic charge discharge of ZIFB with different membranes were identified to obtain the results of operating range, power and stability of battery respectively.

4.2.1 Polarization Test

Polarization curve is the common method that is used to investigate the performance of CEM in ZIFBs. The polarization curve was conducted at current densities of 5-50 mA/cm². The polarization curve of ZIFBs with different types of membrane is illustrated in Figure 4.8.

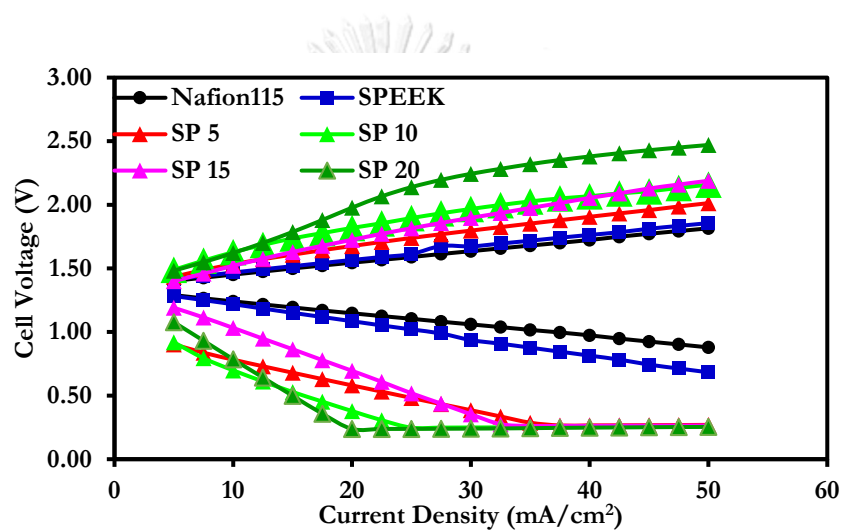


Figure 4.8 The polarization curve of ZIFBs with Nafion115, SPEEK and SPEEK/PVDF blend membranes at the current densities of 5-50 mA/cm²

From the result, it can be seen that the slope of polarization curve of the Nafion115, SPEEK and SP 5 membranes is lower than the slope of the other membranes polarization curve. Gentle slope of polarization curve indicates the wider operating range in battery application. Wide operating range leads to the feasibility in commercial scale application.

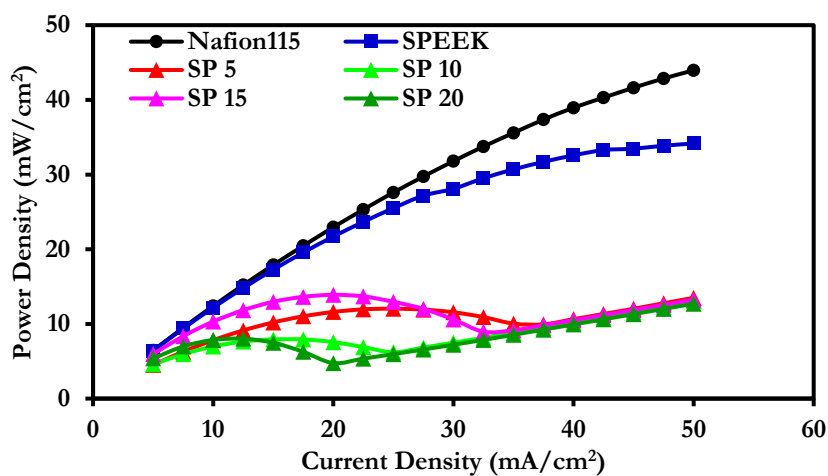


Figure 4.9 The power density curve of ZIFBs with Nafion115, SPEEK and SPEEK/PVDF blend membranes at the current densities of 5-50 mA/cm²

The power density curve of ZIFBs with different types of membrane was illustrated in Figure 4.9. According to Figure 4.9, it was shown that the ZIFB cell with Nafion115 and SPEEK membranes exhibited the highest maximum power density which are 43.96 mW/cm² and 34.16 mW/cm² respectively. For blend membranes, SP 5 exhibited the highest maximum power density.

4.2.2 Galvanostatic Charge Discharge Cycle Test

The cycling performance of battery can be determined by galvanostatic charge discharge test as shown in Figure 4.10 (a) and Figure 4.10 (b)

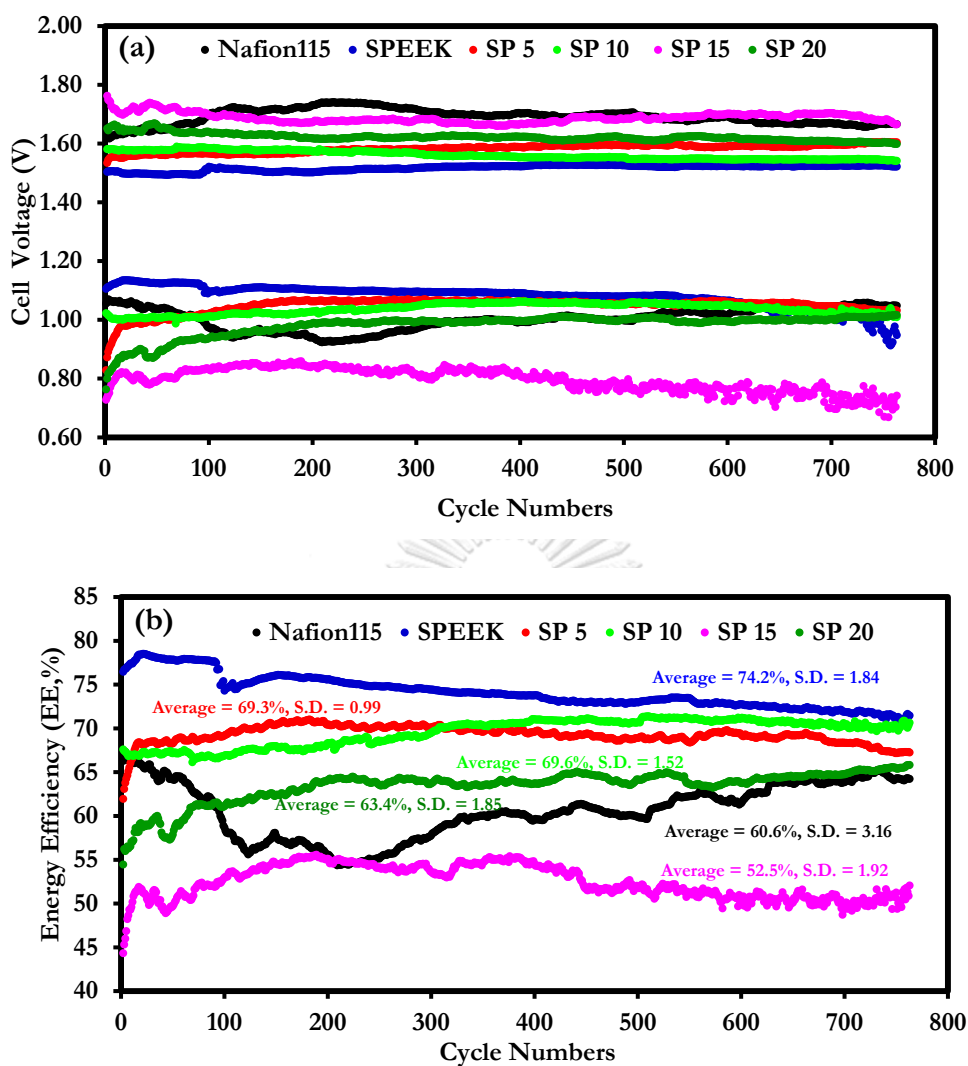


Figure 4.10 Cycling performance in terms of (a) charge and discharge voltage and (b) energy efficiency for ZIFBs with Nafion115, SPEEK and SPEEK/PVDF blend membranes at current density of 10 mA/cm²

The result was shown that all of ZIFBs with different membranes can be reached over 700 cycles indicating good cycling performance of the battery. As considering at Figure 4.10 (a) in discharge voltage from 100th cycle onwards, it was shown that most of ZIFBs that used the synthesized membranes exhibit more cell

discharge voltage than the ZIFB that used Nafion115. In addition, it can be seen that the cell discharge voltage values of ZIFB using Nafion115 membrane are more fluctuated compared to the other ZIFBs using the synthesized membranes. By considering at Figure 4.10 (a) in charge voltage from 100th cycle onwards, it was shown that ZIFB with Nafion115 membrane exhibited the highest cell charge voltage indicating the highest energy using for charging cell. All of ZIFBs with synthesized membranes exhibited less cell charge voltage than ZIFB with Nafion115 membrane. It can be mentioned that ZIFBs using synthesized membranes had much cycling stability than ZIFB using Nafion115 membrane.

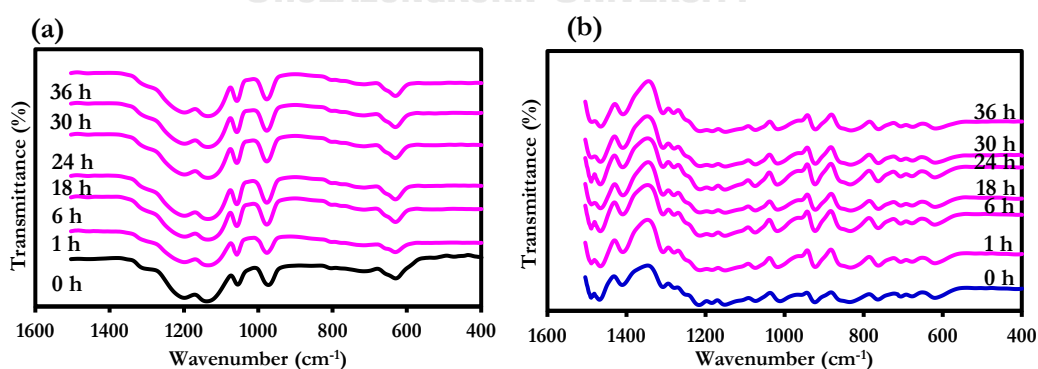
Energy efficiency (EE) is the important value to determine the battery performance. The EE for ZIFBs with different types of membrane was illustrated in Figure 4.10 (b). The result shows that almost all of ZIFBs that used synthesized membranes as separator can exhibit much EE than that with Nafion115 in almost every cycle numbers. According to Figure 4.10 (b), it was shown that the EE line of Nafion115 is more fluctuated than the other lines indicating less stability of the cell. In addition, it can be seen from the standard deviation (S.D.) values of the EE lines that the Nafion115 line exhibits the highest S.D. value indicating less stability of the cell. From the results, it was found that ZIFBs using the SPEEK and SP 5 membranes can exhibit the best performance in EE value and stability. Although ZIFB that used SPEEK membrane exhibited the highest EE, but ZIFB that used the SP 5 membrane exhibited the lowest S.D. indicating the highest stability cycling performance. The

difference of cells performance result from the difference properties of membranes such as morphology, swelling ratio, water uptake, electrolyte uptake, iodine species crossover and ionic conductivity. The highest swelling ratio and the lowest iodine species preventing ability of Nafion115 membrane lead to the bad cycling performance of the ZIFB cell.

According to all of the results, the SPEEK and SP 5 membranes have a homogeneous microstructure, suitable physiochemical properties (water uptake, electrolyte uptake, swelling ratio and ionic conductivity), an excellent preventing iodine species crossover and good battery performance. Therefore, the SPEEK and the SP 5 membranes were chosen to use for further investigation. In addition, the commercial Nafion115 membrane was selected to compare with our synthesized membranes.

4.3 Other Properties of the Selected Membranes

4.3.1 Iodine Species Bonding in the Structure of Membranes



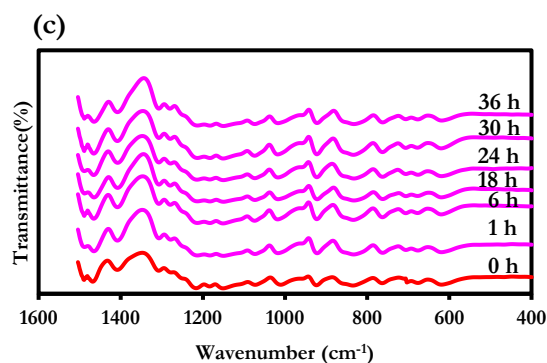


Figure 4.11 The FTIR spectra of (a) Nafion115, (b) SPEEK and (c) SP 5 membranes after soaking in iodine solution at different periods of time

The stability of the structure of the selected membranes were further studied via FTIR spectroscopy. Figure 4.11 (a-c) shows the FTIR spectra for the different membrane samples immersed in 0.5 N iodine solution at different periods of time (0-36 h). According to the previous studied [67], the alkyl halide absorption bands were appeared in the region of 550-850 cm^{-1} . Alkyl halides are the compounds in which one or more hydrogen atoms have been substituted by halogen atoms. Deepashree et al., [68] reported that absorption band at 490-620 cm^{-1} was attributed to halogen compounds (C-I stretching). According to Figure 4.11 (a-c), it can be seen that there were not any absorption bands occurred after soaking membranes in iodine solution. These results indicate the non-functionalized of iodine species in membranes structure. In this study, it can be mentioned that iodine species crossover was occurred by only the difference in concentration of iodine species in the electrolyte. From this result, it indicates the good stability in our membranes structure.

4.3.2 Mechanical Property

In this study, the mechanical property of all selected membranes (SPEEK, SP 5 and Nafion115) was investigated in term of tensile strength at break as shown in Figure 4.12.

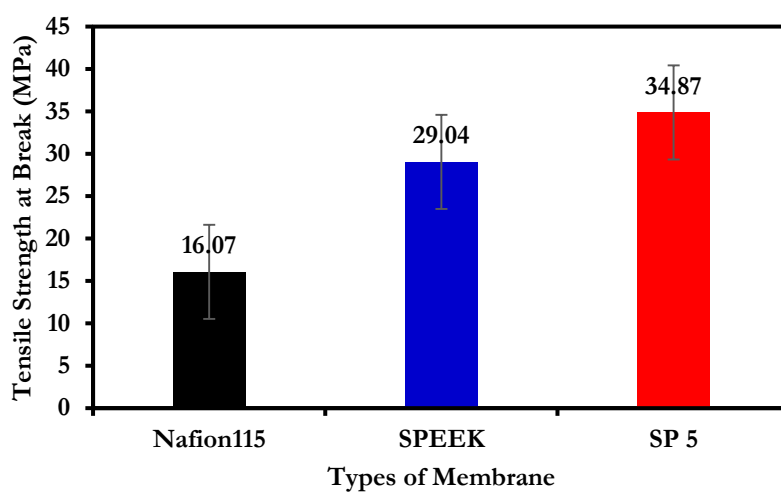


Figure 4.12 The mechanical property (tensile strength at break) of Nafion115, SPEEK and SP 5 membranes

In Figure 4.12, it was shown that the tensile strength at break of the SPEEK and SP 5 membranes are larger than Nafion115 membrane, which indicates that the mechanical property of our synthesized membranes (SPEEK and SP 5) are better than Nafion115 membrane. The SP 5 membrane exhibits the highest tensile strength at break. According to this, it can be mentioned that the addition of PVDF leads to the higher mechanical property (tensile strength at break). Furthermore, this mechanical property data is corresponding to the swelling ratio values of these three

membranes, indicating that the addition of PVDF can improve the swelling behaviors and mechanical property of blend membranes, which is due to its hydrophobic and high crystallinity structure.

4.4 ZIFBs Fabrication in Stack Cell Configuration

In this section, the selected synthesized membranes and the commercial Nafion115 membrane were applied in ZIFB as CEM separator. The ZIFB cell was fabricated in stack cell configuration. The peristaltic pump was used to flow the electrolyte for each side of stack cell. As mentioned above, the operating range, power and stability are important for battery application. Therefore, the polarization and galvanostatic charge discharge of ZIFB with different membranes were identified to obtain the results of operating range, power and stability of battery respectively.

4.3.1 Polarization Test

In this dissertation, the polarization curve was conducted at current densities of 5-50 mA/cm² as shown in Figure 4.13.

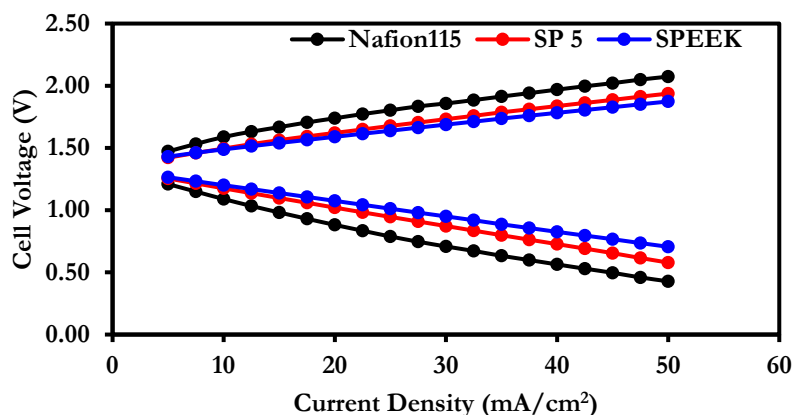


Figure 4.13 The polarization curve of ZIFBs with Nafion115, SPEEK and SP 5 membranes at the current densities of 5-50 mA/cm²

From Figure 4.13, it can be seen that all of the ZIFBs with different membranes can be used in widely operating range. The results show the good performance of battery. In considering at the discharge voltage, it was found that the ZIFBs with the SPEEK and SP 5 exhibits higher discharge voltage than the ZIFB with Nafion115 membrane. The reason is the good balance of ionic conductivity and iodine species crossover. These indicates the good performance of ZIFBs with the SPEEK and SP 5 membrane.

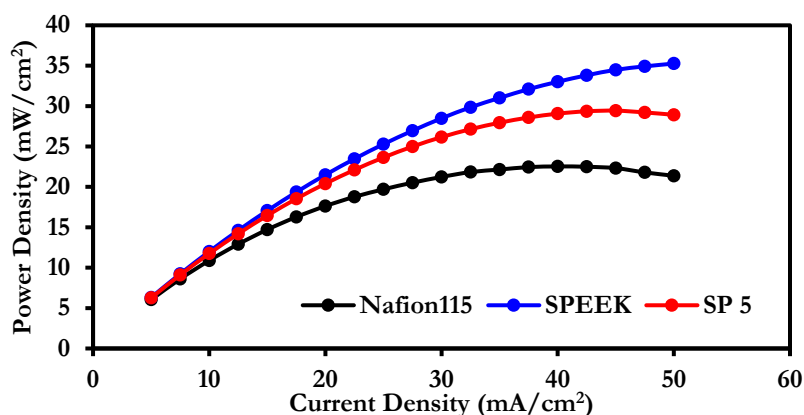


Figure 4.14 The power density curve of ZIFBs with Nafion115, SPEEK and SP 5 membranes at the current densities of 5-50 mA/cm²

The power density curve of the ZIFBs with different membranes was illustrated in Figure 4.14. According to Figure 4.14, it was shown that ZIFBs with the SPEEK and SP 5 membranes exhibit much higher maximum power density than ZIFB with Nafion115 membrane. This result indicates the good performance of battery with the SPEEK and SP 5 membrane. The ZIFBs with Nafion115, SPEEK and SP 5 exhibited the maximum power density which are 22.53, 35.26 and 29.43 mW/cm² respectively.

4.3.2 Galvanostatic Charge Discharge Cycle Test

The cycling performance of ZIFBs with the SPEEK, SP 5 and commercial Nafion115 membranes is illustrated in Figure 4.15.

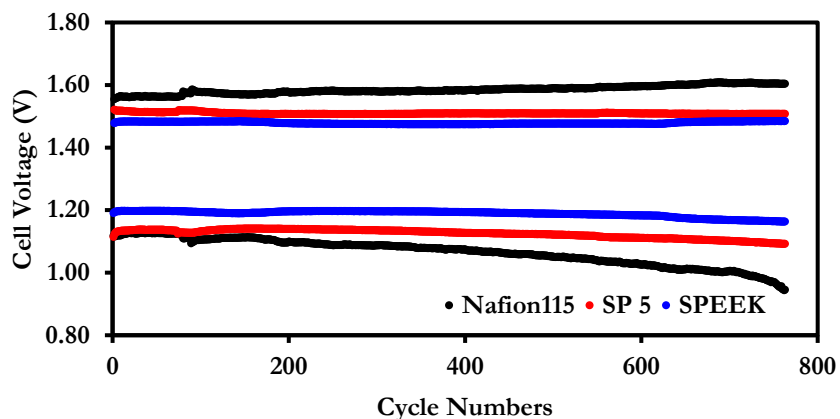


Figure 4.15 Cycling performance in term of charge and discharge voltage for ZIFBs with Nafion115, SPEEK and SP 5 membranes at current density of 10 mA/cm^2

In Figure 4.15, it can be seen that all of the ZIFBs with different membranes can be reached over 700 cycles, which indicated the good cycling performance in term of long cycle life. According to Figure 4.15, both of ZIFBs with the SPEEK and SP 5 membranes exhibited higher cell discharge voltage and lower cell charge voltage than ZIFB with Nafion115 membrane. Therefore, it can be mentioned that ZIFBs with the SPEEK and SP 5 membranes had better battery performance than ZIFB with Nafion115 membrane. Beside that, ZIFBs with the SPEEK and SP 5 membrane had much stable cell voltage than ZIFB with Nafion115 membrane, leading to the good cycling battery performance in term of long term stability.

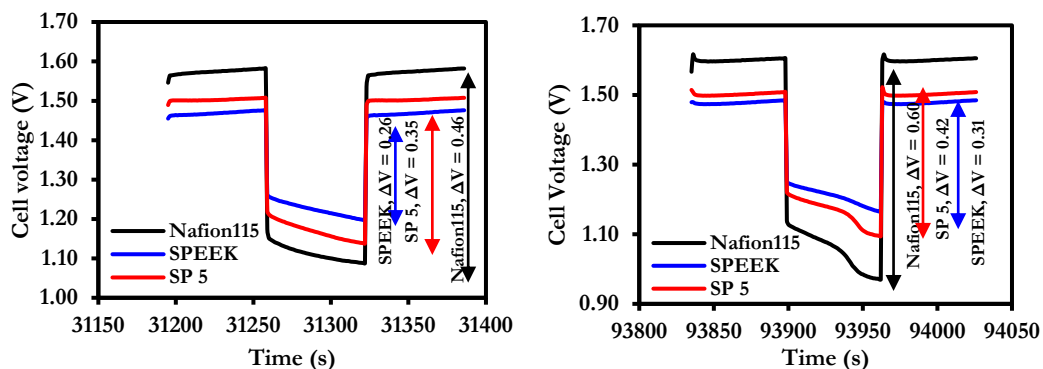


Figure 4.16 Cycling performance in term of charge and discharge voltage for ZIFBs with Nafion115, SPEEK and SP 5 membranes at current density of 10 mA/cm^2 (a) 250th cycle and (b) 750th cycle

The galvanostatic cycling performance of charge and discharge voltage at 250th cycle and 750th cycle were shown in Figure 4.16 (a) and Figure 4.16 (b) respectively. These results will help in explaining the stability performance of battery in more details. From Figure 4.16 (a) and Figure 4.16 (b), it can be seen that both of ZIFBs with the SPEEK and SP 5 membranes had less voltage gap than ZIFB with Nafion115 membrane. In addition, the percentage changing in voltage from 250th cycle to 750th cycle of ZIFB with Nafion115 is the highest value as 30.18% indicating bad long term stability performance. On the other hand, the percentage changing in voltage from 250th cycle to 750th cycle of ZIFB with the SP 5 is the lowest value as 19.58% indicating good long term stability performance. This result indicates the good performance of the SP 5 membrane.

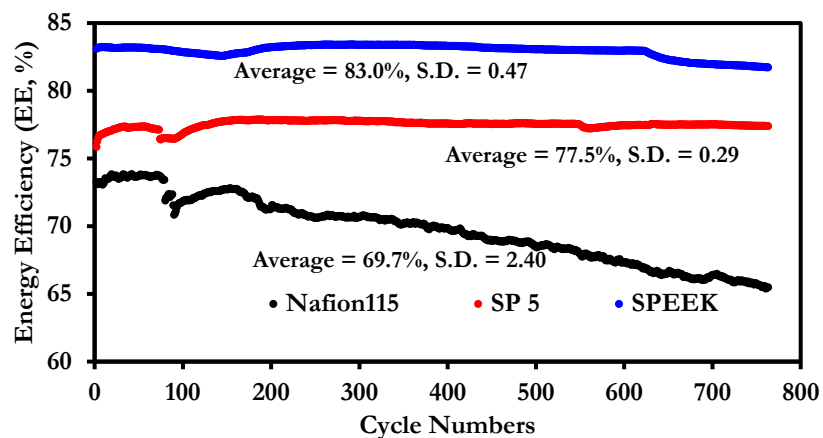


Figure 4.17 Cycling performance in term of energy efficiency for ZIFBs with Nafion115, SPEEK and SP 5 membranes at current density of 10 mA/cm^2

The cycling performance of battery in term of EE is illustrated in Figure 4.17. From the result, it was shown that both of ZIFBs with the SPEEK and SP 5 membranes can exhibit much EE than ZIFB with Nafion115. The EE of ZIFBs with the SPEEK, SP 5 and Nafion115 membranes were 83.0%, 77.5% and 69.7% respectively. As shown in Figure 4.17, the ZIFB with Nafion115 membrane had the lowest stability according to the decreasing of EE through time. In Figure 4.17, it can be seen that the S.D. of SP 5 in red line was the lowest value as only 0.29. Therefore, it can be mentioned that ZIFB with the SP 5 membrane had the best performance in term of long term stability.

4.5 Cost Estimation of the Selected Membranes

The cost of ZIFBs is mainly from the CEM separator, which is critical related to the application in commercial scale. The raw material of SPEEK and SP 5 are lower

than Nafion115. Figure 4.18 shows the cost estimation of Nafion115, SPEEK and SP 5 membrane.

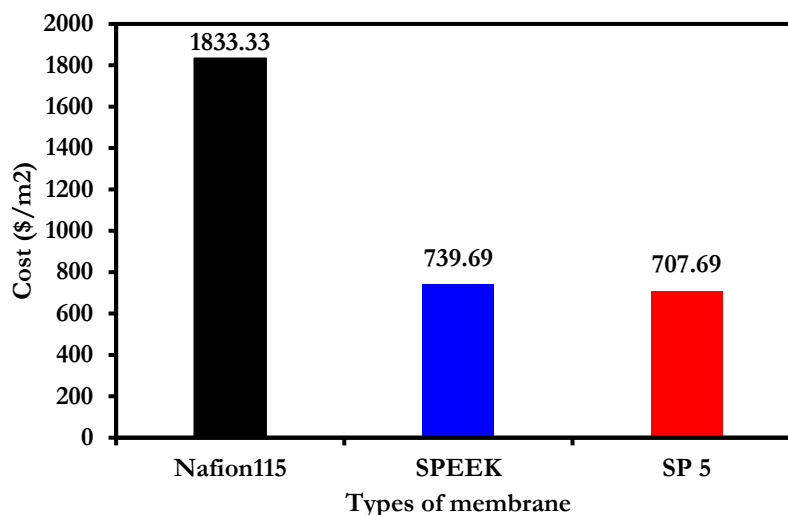


Figure 4.18 Cost estimation of Nafion115, SPEEK and SP 5 membranes

According to Figure 4.18, we can see that the cost of SPEEK and SP 5 membrane are much lower than Nafion115 membrane by around 2.5 times. The cost of SP 5 membrane is the lowest, indicating the high feasibility in commercial scale application. In this study, the cost of SPEEK and SP 5 membranes are based on the market price of raw materials in lab and preparation cost while the cost of Nafion115 is collected according to the market price of ion power company. From the results, it is very competitive to use a SPEEK based membrane (SP 5 in this study) for large ESS. Based on the scale cost, the cost of SPEEK based membrane may far less than current value that we obtained.

The best performance of ZIFB resulted from the best performance of membrane. The performance of membrane depended on the properties of

membrane. The SP 5 membrane had lower swelling ratio than the SPEEK and Nafion115 membrane, resulted in the stability of membrane. Because of its better mechanical property, the SP 5 membrane showed better cycling performance than Nafion 115 membrane as mentioned above. The SP 5 membrane has a homogeneous structure and the highest electrolyte uptake value leading to acceptable ionic conductivity. Beside that, the SP 5 membrane is the cheapest membrane leading to high feasibility in commercial scale application. In conclusion, the SP 5 membrane is the most suitable membrane for our ZIFB in this study.



Chapter V

Conclusion

In this work, the sulfonated poly (ether ether ketone) (SPEEK) and SPEEK/poly (vinylidene fluoride) (PVDF) blend membranes are successfully synthesized by solution casting method with various contents of PVDF (5-20 wt.%) in membranes. The blend membranes are denoted as SP X, where X is the PVDF mass ratio. The 53% of degree sulfonation (DS) for SPEEK was used in this work. The scanning electron microscopy (SEM) and electron dispersive spectroscopy (EDX) results show that the surface morphologies and cross-sections of Nafion115, SPEEK and SP 5 membranes are dense, uniform and homogeneous structure. On the other hand, the surface morphologies and cross-sections of SPEEK/PVDF blend membranes (PVDF mass ratio ranges from 10 wt%. to 20 wt%.) are almost non-uniform and heterogeneous microstructure. The physiochemical properties of the synthesized membranes and the commercial Nafion115 membrane including water uptake, swelling ratio, electrolyte uptake, ionic conductivity and preventing iodine species crossover ability are characterized, indicating that the addition of PVDF indeed limits the swelling behaviors, ionic conductivity and preventing iodine species crossover ability of blend membranes. All of synthesized membranes and Nafion115 membrane were applied in static zinc-iodine flow batteries (ZIFBs) in H cell configuration. The ZIFBs with SPEEK and SP 5 membranes exhibits higher cell

efficiencies (EE), and more stable cycling performance than the other blend membranes and Nafion115. It can be implied that our synthesized membrane can be replaced the Nafion115 membrane for using in ZIFBs application. The SPEEK and SP 5 membrane are chosen for characterized other properties and for ZIFB in stack cell configuration (with flowing electrolyte) test. The commercial Nafion115 is also chosen to compare the results. From the results, the ZIFBs with SPEEK and SP 5 membranes exhibits higher cell efficiencies (EE), and more stable cycling performance than Nafion115 membrane. The high performance of SPEEK and SP 5 membranes is due to their good balance in ionic conductivity and preventing iodine species crossover ability. The stable performance of SPEEK and SP 5 membranes is due to its good mechanical property and swelling ratio. By comparing the EE between ZIFB with the SPEEK and SP 5 membranes, the results show that the EE of ZIFB with the SPEEK membrane is similar to the ZIFB with SP 5 membrane as 83.0% and 77.5% respectively. In addition, the ZIFB with SP 5 membrane shows significantly more stable cycling performance than that with SPEEK membrane, noticing from the standard deviation (S.D.) values. In conclusion, the SP 5 is the most suitable membrane for using in ZIFBs due to its excellent properties, good battery efficiencies and good stable cycling performance. Furthermore, the cost of SP 5 membrane is the lowest, leading to high feasibility in commercial scale application. The long term stability and long cycle life can be achieved by our synthesized membranes.

Recommendations

In future work, ZIFBs can be enhanced battery performance by reducing the ohmic loss from other components. Ohmic loss is the loss of energy from resistances in battery (those are electrodes, electrolyte and membrane). We can investigate other components in ZIFBs or changing materials for ion exchange membrane. Besides that, we can maintain the same materials in this work (SPEEK and PVDF) but use other advanced technologies to fabricate the better performance of ion exchange membrane.



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Appendix A Membrane Characterizations

In this dissertation, the sulfonated poly (ether ether ketone) (SPEEK) and SPEEK/poly (vinylidene fluoride) (PVDF) blend membranes were synthesized by solution casting method. The physicochemical properties of all of the synthesized membranes were characterized and compared with the commercial Nafion115 membrane. All of the synthesized membranes and Nafion115 membrane were used as cation exchange membrane (CEM) separator for zinc-iodine flow batteries (ZIFBs) and the battery performances were investigated. Almost all of the results were described in Chapter IV but the rest of them will be described in this section to explain more details of this dissertation.

A.1 Proton nuclear magnetic resonance (H-NMR) Analysis

In fact, PEEK cannot be used as CEM separator because its hydrophobic structure. Therefore, sulfonation process must be provided to PEEK for attaching the functional group or increasing the hydrophilic structure. PEEK that passed through sulfonation process was the SPEEK. Degree sulfonation (DS) is the value that related to ionic conductivity. Three samples of SPEEK, which passed through sulfonation process for 3 h at 55 °C, were observed by H-NMR to obtain the DS. The H-NMR spectrum of SPEEK were illustrated in Figure A.1 and Figure A.2. One of them was illustrated in chapter IV in Figure 4.2.

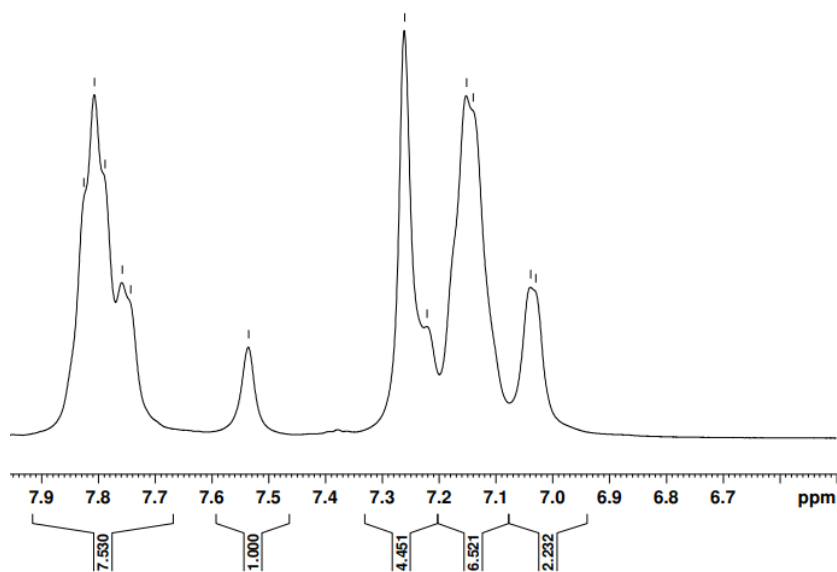


Figure A.1 The H-NMR spectra of SPEEK sample

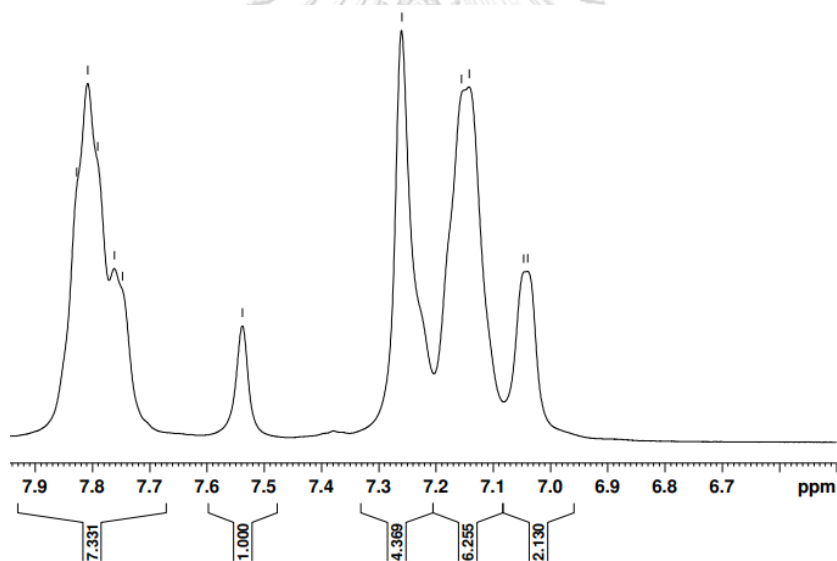


Figure A.2 The H-NMR spectra of SPEEK sample

A.2 The Water Uptake, Swelling Ratio and Electrolyte Uptake Analysis

For the CEM separator, the ionic conductivity is the important property. The water uptake, swelling ratio and electrolyte uptake are related to the ionic conductivity. Therefore, the water uptake, swelling ratio and electrolyte uptake of all

synthesized membranes and Nafion115 membrane were investigated. The blend membranes are denoted as SP X, where X is the PVDF mass ratio. All of the results were discussed and shown in chapter IV section 4.1.5. The raw datas of these results were illustrated in Table A.1, Table A.2 and Table A.3.

Table A.1 The water uptake values of Nafion115, SPEEK and SPEEK/PVDF blend membranes

Types of Membrane	W_{wet} (g)	W_{dry} (g)	Water Uptake (%)
Nafion115	0.159	0.137	16.06
SPEEK	0.084	0.065	29.23
SP 5	0.060	0.047	27.66
SP 10	0.110	0.087	26.44
SP 15	0.180	0.148	21.62
SP 20	0.088	0.073	20.54

Table A.2 The swelling ratio values of Nafion115, SPEEK and SPEEK/PVDF

blend membranes

Types of Membrane	l_{wet} (g)	l_{dry} (g)	Swelling Ratio (%)
Nafion115	1.20	1.08	11.11
SPEEK	1.20	1.09	10.09
SP 5	1.20	1.10	9.09
SP 10	1.20	1.13	6.19
SP 15	1.15	1.10	4.55
SP 20	1.20	1.15	4.35

Table A.3 The electrolyte uptake (ZnSO_4 uptake) values of Nafion115, SPEEK

and SPEEK/PVDF blend membranes

Types of Membrane	W_{wet} (g)	W_{dry} (g)	ZnSO_4 Uptake (%)
Nafion115	0.193	0.172	12.21
SPEEK	0.111	0.093	19.35
SP 5	0.142	0.117	21.37
SP 10	0.124	0.107	15.89
SP 15	0.083	0.074	12.16
SP 20	0.084	0.075	12.00

A.3 The Iodine Species Crossover Analysis

For ZIFBs, the iodine species crossover leads to the bad battery performances, which are the losing of maximum capacity and self-discharging. Therefore, the iodine species crossover of all synthesized membranes and Nafion115 membrane was investigated. The iodine species crossover can be examined by ultraviolet visible (UV-VIS) spectroscopy. The concentration is shown in Figure 4.7 in section 4.1.7. As mentioned in section 4.1.7, the example of UV-VIS spectrum was illustrated in Figure A.3. The raw datas, which are the absorbance (Abs.) of the electrolyte samples at different certain period time for all membranes, were shown in Table A.4 and the calibration curves were illustrated in Figure A.4 and Figure A.5.

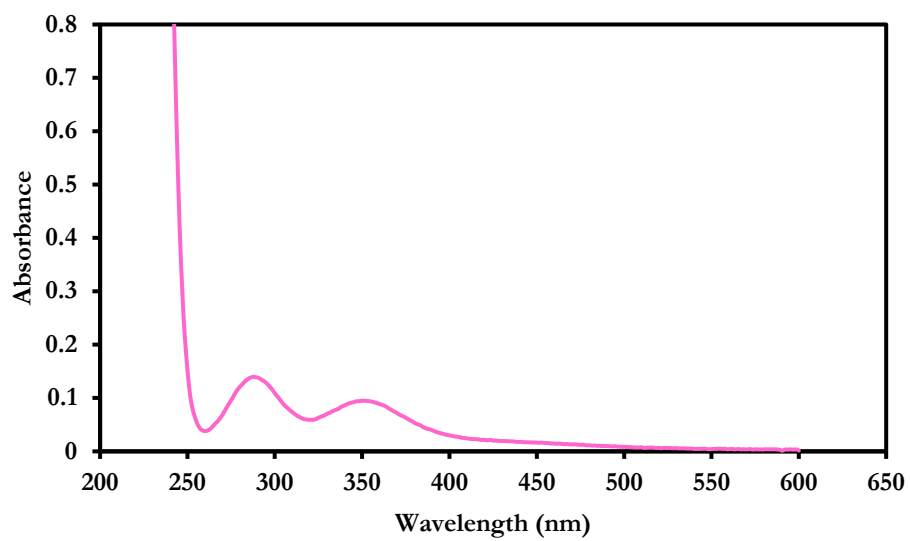


Figure A.3 The UV-VIS spectrum of the ZnSO_4 solution sample Nafion115 membrane at 3 h



Table A.4 The absorbance (at wavelength 288 and 350 nm) of ZnSO₄ samples solution at different certain period time for Nafion115, SPEEK and SPEEK/PVDF membranes

Types of Membrane	Nafion115		SPEEK		SP 5		SP 10		SP 15		SP 20	
	Abs. at 288 nm	Abs. at 350 nm	Abs. at 288 nm	Abs. at 350 nm	Abs. at 288 nm	Abs. at 350 nm	Abs. at 288 nm	Abs. at 350 nm	Abs. at 288 nm	Abs. at 350 nm	Abs. at 288 nm	Abs. at 350 nm
0.5	-	-										
1	-	-										
1.5	0.0486	0.0357										
2	0.0812	0.0552										
3	0.1394	0.0948										
4	0.2065	0.1386										
5	0.2521	0.1668										
6	0.3412	0.2269									0.0511	0.0506
8	0.5313	0.3554								0.0395	0.0834	0.0806
10	0.7025	0.4774								0.0444	0.1062	0.0883
12	0.8705	0.5956								0.0611	0.1072	0.0914
18	1.2044	0.8187							0.1167	0.1100	0.2605	0.2014
24	1.9789	1.3419							0.2021	0.1648	0.3461	0.2524
30			0.0753	0.0623	0.0894	0.0687	0.0817	0.0714				
36			0.1114	0.1066	0.1494	0.1067	0.1673	0.1159	0.3719	0.2729	0.7500	0.5209
48			0.1820	0.1278	0.3834	0.2617	0.4281	0.2975	1.1349	0.7842	1.3021	0.8944
54			0.3804	0.2564	0.6486	0.4395	1.1054	0.6740				
60			0.6287	0.4315	0.9723	0.6586	1.4258	0.9561	1.6150	1.1053	1.7574	1.1829
72			0.9763	0.6638	1.3215	0.8845	1.8273	1.2214				
78			1.2730	0.8630	1.6933	1.1299						
84			1.4992	1.0017	1.9595	1.3273						

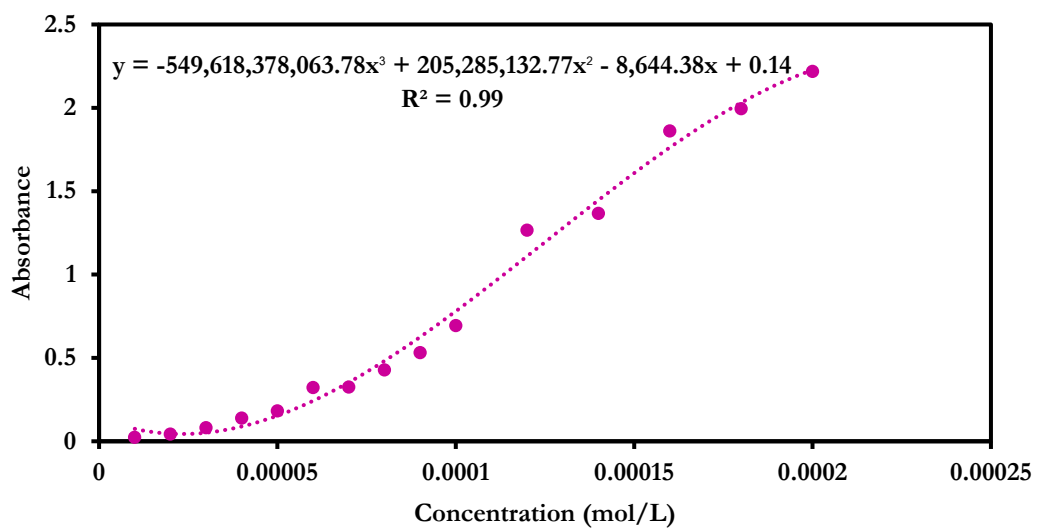


Figure A.4 The calibration curve of iodine concentration at wavelength 288 nm

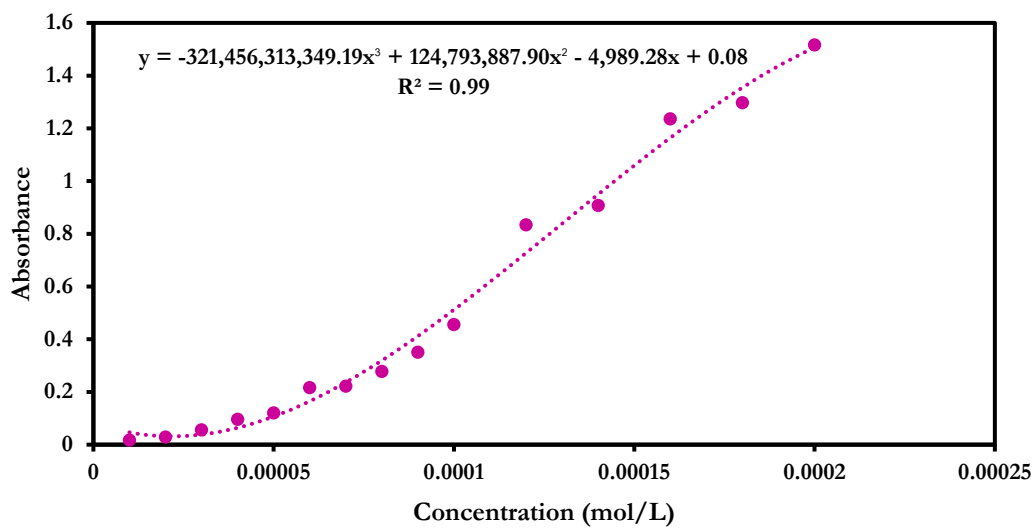


Figure A.5 The calibration curve of iodine concentration at wavelength 350 nm

A.4 Mechanical Property Analysis

For CEM separator, the mechanical property is the important property. The mechanical property is related to the battery performances in term of cycling performance. Therefore, the tensile strength of Nafion115, SPEEK and SP 5 membranes were observed. The average result was illustrated and discussed in section 4.3.2. The raw data of the tensile strength of 5 specimens for each type of membranes was illustrated in Table A.5.

Table A.5 The tensile strength at break (MPa) of the Nafion115, SPEEK and SP 5 membranes

Specimens	Nafion115	SPEEK	SP 5
1	17.7844	20.8190	35.7617
2	14.7914	23.3616	32.1020
3	17.0608	25.8561	32.0492
4	12.7120	38.8077	38.1190
5	17.9973	36.3475	36.2955
Average	16.0692	29.0384	34.8655
S.D.	2.0271	7.1941	2.4084

A.5 Cost Estimation Analysis

The CEM separator is the important component in ZIFBs that determines the cost of ZIFBs. The high cost of CEM separator leads to the low feasibility in ZIFBs commercial scale application. Therefore, the cost of Nafion115, SPEEK and SP 5 was estimated. In this dissertation, the cost was estimated from the raw material price and the lab preparation method. The result was shown and discussed in section 4.5 in chapter IV. The raw data of cost analysis of Nafion115, SPEEK and SP 5 membranes was shown in Table A.6, Table A.7 and Table A.8 respectively.

Table A.6 The raw data of cost analysis for Nafion115 membrane

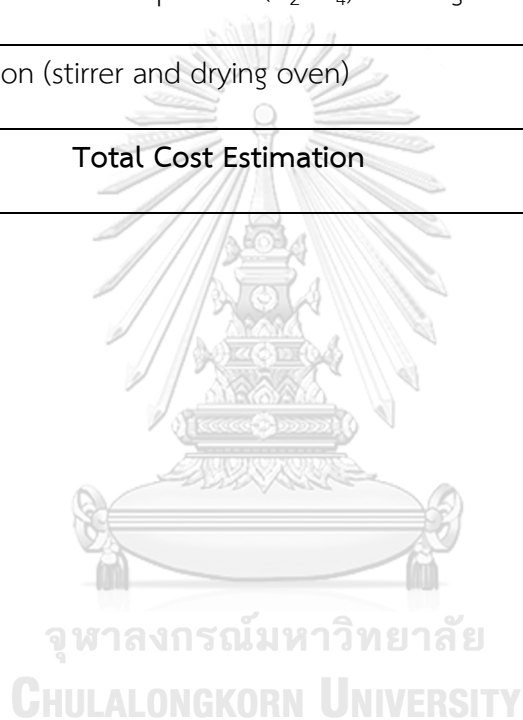
Lists	Price (\$/m ²)
Nafion115 membrane (from ion power company)	1833.33

Table A.7 The raw data of cost analysis for SPEEK membrane

Lists	Price (\$/m ²)
Raw material (SPEEK powder, from goodfellow company)	642.04
Solvent (DMAC, from sigma-aldrich company)	83.79
Chemical for sulfonation process (H ₂ SO ₄ , from sigma-aldrich)	9.54
Lab preparation (stirrer and drying oven)	4.32
Total Cost Estimation	739.69

Table A.8 The raw data of cost analysis for SP 5 membrane

Lists	Price (\$/m ²)
Raw material (SPEEK powder, from goodfellow company)	609.94
Raw material (PVDF pellets, from sigma-aldrich company)	0.58
Solvent (DMAC, from sigma-aldrich company)	83.79
Chemical for sulfonation process (H ₂ SO ₄ , from sigma-aldrich)	9.06
Lab preparation (stirrer and drying oven)	4.32
Total Cost Estimation	707.69



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