UNIVERSITI SAINS MALAYSIA

Laporan Akhir Projek Penyelidikan Jangka Pendek

Investigation Of Chitosan-SiO$_2$-NH$_4$CH$_3$COO Membranes For Proton Batteries Application

by

Assoc. Prof. Dr. Ahmad Azmin Mohamad
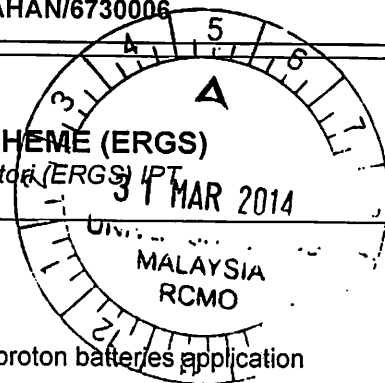**Assoc. Prof. Dr. Zulkifli Mohamad Ariff**
Siti Salwa Alias

2014

BORANG ERGS – P3(R)

Kod Projek : 203/PBAHAN/6730006

FINAL REPORT
EXPLORATORY RESEARCH GRANT SCHEME (ERGS)
Laporan Akhir Skim Geran Penyelidikan Eksploratori (ERGS) IPT
2014

3 1 MAR 2014
MALAYSIA
RCMO

A		
PHASE *Fasa*	: THIS PROJECT WAS COMPLETED	
RESEARCH TITLE *Tajuk Penyelidikan*	: Investigation of chitosan-SiO₂-NH₄CH₃COO membranes for proton batteries application	
PROJECT LEADER *Ketua Projek*	: Assoc. Prof. Dr. Ahmad Azmin Mohamad	
PROJECT MEMBERS **(including GRA)** *Ahli Projek*	: 1. Assoc. Prof. Dr. Zulkifli Mohamad Ariff 2. Siti Salwa Alias (GRA)	

PROJECT ACHIEVEMENT *(Prestasi Projek)*

B

ACHIEVEMENT PERCENTAGE		
Project progress according to milestones achieved up to this period	**0 - 50%**	**51 - 75%**	**76 - 100%**
Percentage			100%

RESEARCH OUTPUT

	Refereed Journal	**Non-Refereed Publication**
Number of articles/ manuscripts/ books *(Please attach the First Page of Publication)*	1. N Alias, AA Mohamad Morphology Study for Electrodeposited Zinc from Zinc Sulfate Solutions as Anode for Aqueous Batteries, Journal of King Saud University-Engineering Sciences, 2013, in press. 2. MN Masri, MFM Nazeri, CY Ng, AA Mohamad, Tapioca Binder for Porous Zinc Anodes Electrode in Zinc-Air Batteries, Journal of King Saud University-Engineering Sciences, 2013, in press. 3. Siti Salwa Alias; Siew Mian Chee; A.A. Mohamad, Chitosan-ammonium acetate-ethylene carbonate Membrane for Proton Batteries, Arabian Journal of Chemistry, 2014 minor correction.	[Book] Siti Salwa Alias Ahmad Azmin Mohamad, Synthesis of Zinc Oxide by Sol-Gel Method for Photoelectrochemical Cell, SpringerBriefs in Materials, 2014

KEMENTERIAN PENDIDIKAN MALAYSIA

	International	National
Conference Proceeding (Please attach the First Page of Publication)	1. S. S. Alias and A. A. Mohamad. Preparation and Characterization of Porous Chitosan Membrane for Proton Battery. Proceeding International Conference on Materials for Advanced Technologies (ICMAT 2013), page 34. 2. Siti Salwa Alias, Zulkifli Mohamad Ariff, and Ahmad Azmin Mohamad. Preparation and Characterization of Porous Silica-Chitosan Membrane for Proton Batteries. Proceeding Asia-Pacific Conference on Electrochemical Energy Storage and Conversion (APEnergy2014).	
Intellectual Property (Including Paten,Copyright, Industrial Design,layout Design of Integrated Circuit & Trademarks)	-	

HUMAN CAPITAL DEVELOPMENT

Human Capital	Number				Others (please specify)
	On-going		Graduated		
Citizen	Malaysian	Non Malaysian	Malaysian	Non Malaysian	
PhD Student	2		2		
Master Student	1		1		
Undergraduate Student					
Total	3		3		

EXPENDITURE (Perbelanjaan)

C

Budget Approved (Peruntukan diluluskan) : **RM 139,000**
Amount Spent (Jumlah Perbelanjaan) : **RM 138,952**

Balance (Baki) : **RM 48.00**

Percentage of Amount Spent : 100.00 %
(Peratusan Belanja)

ADDITIONAL RESEARCH ACTIVITIES THAT CONTRIBUTE TOWARDS DEVELOPING SOFT AND HARD SKILLS
(Aktiviti Penyelidikan Sampingan yang menyumbang kepada pembangunan kemahiran insaniah)

D

International

Activity	Date (Month, Year)	Organizer
(e.g : Course/ Seminar/ Symposium/ Conference/ Workshop/ Site Visit)	-	-

National

Activity	Date (Month, Year)	Organizer
(e.g : Course/ Seminar/ Symposium/ Conference/ Workshop/ Site Visit)	Workshop on writing references using End Note and Mandaley. (12 NOVEMBER 2013)	Universiti Kuala Lumpur Malaysian Spanish Institute, Kulim Hi-TechPark, 09000 Kulim, Kedah.

PROBLEMS / CONSTRAINTS IF ANY *(Masalah/ Kekangan sekiranya ada)*

E

Some problems that have been facing during preparation and characterization of the porous chitosan membranes:

1) The experimental method need to change to a few parameter in order to produce membranes with better structural properties.

2) Due to some difficulities and instruments maintaining problems, the fabrication of proton batteries and analyses process need to delayed several times.

3) The process of review paper after submitted to journals take a lots of time.

RECOMMENDATION *(Cadangan Penambahbaikan)*

F

    It suggested that future research work should focus on producing porous chitosan membrane using other simple technique such as ultrasonicator. This is because this technique will reduce the duration of sample preparation besides can produce uniform pore size and shape.

    Other kind of salt such as ammonium nitrate, ammonium bromide can be used to replace ammonium acetate. Different kind of salts can give various results in term of electrochemical properties. Besides that, all the electrochemical properties can be investigated at high temperature. The analysis of fabricated proton batteries can be focus on elevated temperatures to find the resistance of batteries besides focus on failure analysis of batteries.

RESEARCH ABSTRACT – Not More Than 200 Words (*Abstrak Penyelidikan – Tidak Melebihi 200 patah perkataan*)

G | The porous chitosan acetate-silica membranes were prepared using inverse porogen/polymer solubility technique. Different concentration of sodium hydroxide porogen removal solution was used to dissolve silica from chitosan acetate membrane. The optimum chitosan to silica ratio for producing largest macroporous membrane was 1:4. The morphology and structural properties showed optimum average pore size and degree of crystallinity of 5.9 μm and 90%, respectively. Fourier transform infrared analysis showed the interaction between chitosan, acetic acid and silica have been occurred based on the shifting of several functional group peaks intensity. The melting point of the membrane obtained from differential scanning calorimetry was 130°C. Thermogravimetry analysis shows the decomposition of the total of the membrane begins at a temperature of 200°C. The membrane had the higher conductivity of $(4.7 \pm 1.1) \times 10^{-2}$ S cm^{-1} after two-day immersion in 5.0 M ammonium acetate electrolyte solution compared with the membrane before immersed in ammonium acetate electrolyte $(6.0 \pm 0.1) \times 10^{-8}$ S cm^{-1}. Fabricated proton batteries displayed an open circuit potential of 1.5 V for 8 days and turned on LED for 40 hours. The internal current resistance of batteries was 0.02 Ω and maximum power density of 11.0 mW cm^{-2}. The specific discharge capacities of proton batteries were 6.4, 10.7, 35.6 and 53.3 mA h g^{-1} for 0.1, 0.2, 0.5 and 1.0 mA discharge current, respectively.

Date : 26/3/14
Tarikh

Project Leader's Signature:
Tandatangan Ketua Projek

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COMMENTS, IF ANY/ ENDORSEMENT BY RESEARCH MANAGEMENT CENTER (RMC)
(*Komen, sekiranya ada/ Pengesahan oleh Pusat Pengurusan Penyelidikan*)

H | ....

Good output

....

....

PROF. MADYA LEE KEAT TEONG
Pengarah
Pejabat Pengurusan & Kreativiti Penyelidikan
Universiti Sains Malaysia
11800 USM, Pulau Pinang.

Name:
Nama:

Signature:
Tandatangan:

Date:
Tarikh:

UNIVERSITI SAINS MALAYSIA
UNIT KUMPULAN WANG PENYELIDIKAN/RU
JABATAN BENDAHARI KAMPUS KEJURUTERAAN
PENYATA KUMPULAN WANG
TEMPOH BERAKHIR 3/2014

Tajuk Projek : INVESTIGATION OF CHITOSAN-NH4NO3-EC-GA MEMBRANES FOR PROTON BATTERIES APPLICATION

PROFESOR MADYA AHMAD AZMIN MOHAMAD

Pusat Pengajian : Pusat Pengajian Kejuruteraan Bahan dan Sumber Mineral

Penyelidik : AHMAD AZMIN MOHAMAD

Status Projek : AKTIF

No Projek (Agensi) :

Tempoh Projek : 2011 / 8 - 2014 / 3

No Akaun : 203 / 6730006

Vot	Keterangan	Peruntukan Asal (a)	Perbelanjaan Tahun Lalu (b)	Peruntukan Semasa (c)	Tanggungan (d)	Belanja (e)	Jumlah Belanja (f) = (d) + (e)	Baki (a) - (f)	% ((b)+(f)) / (a)
11000	Gaji	40,000.00	$25,699.49	$0.00	$0.00	$0.00	$0.00	$14,300.51	0.00
		$40,000.00	$25,699.49	0.00	$0.00	$0.00	$0.00	$14,300.51	0.00
21000	PERJALANAN DAN SARA HIDUP	14,000.00	$8,546.35	$0.00	$720.00	$0.00	$720.00	$4,733.65	0.00
23000	PERHUBUNGAN DAN UTILITI	200.00	$1,200.00	$0.00	$0.00	$0.00	$0.00	($1,000.00)	0.00
27000	BEKALAN DAN ALAT PAKAI HABIS	58,800.00	$43,043.95	$0.00	$6,383.70	$0.00	$6,383.70	$9,372.35	0.00
28000	PENYELENGGARAAN DAN PEMBAIKAN KECIL	0.00	$100.00	$0.00	$0.00	$0.00	$0.00	($100.00)	0.00
29000	PERKHIDMATAN IKTISAS DAN HOSPITALITI	1,000.00	$23,615.88	$0.00	$2,278.82	$2,743.00	$5,021.82	($27,637.70)	0.00
		$74,000.00	$76,506.18	0.00	$9,382.52	$2,743.00	$12,125.52	($14,631.70)	0.00
35000	HARTA-HARTA MODAL LAIN	25,000.00	$22,600.00	$0.00	$0.00	$1,200.00	$1,200.00	$1,200.00	0.00
		$25,000.00	$22,600.00	0.00	$0.00	$1,200.00	$1,200.00	$1,200.00	0.00
		$139,000.00	$124,805.67	$0.00	$9,382.52	$3,943.00	$13,325.52	$868.81	0.00

FINAL REPORT OF EXPLORATORY RESEARCH GRANT SCHEME (ERGS)

Investigation of Porous Chitosan-SiO$_2$-NH$_4$CH$_3$COO Membranes for Proton Batteries Application

(203/PBAHAN/6730006)

PROJECT LEADER: Assoc. Prof. Dr. Ahmad Azmin Bin Mohamad

PROJECT MEMBERS: 1. Assoc. Prof. Dr. Zulkifli Mohamad Ariff

(including GRA) 2. Siti Salwa Binti Alias

ABSTRACT

This project is divided into three sections: the preparation of porous chitosan acetate-silica membranes in a range of ~ 6.0 μm pores size with good morphological, structural and thermal properties; improvement the conductivity of porous chitosan acetate-silica-ammonium acetate membranes up to 10^{-2} S cm^{-1}; and fabrication of Zn+ZnSO$_4$·7H$_2$O/porous chitosan acetate-silica-acetate membranes/MnO$_2$ coin cell to improve the battery specific capacity up to 55.0 mA h g^{-1}. The porous chitosan acetate-silica membranes were prepared using inverse porogen/polymer solubility technique. Different concentration of sodium hydroxide porogen removal solution was used to dissolve silica from chitosan acetate membrane. The optimum chitosan to silica ratio for producing largest macroporous membrane was 1:4. The morphology and structural properties showed optimum average pore size and degree of crystallinity of 5.9 μm and 90%, respectively. Fourier transform infrared analysis showed the interaction between chitosan, acetic acid and silica have been occurred based on the shifting of several functional group peaks intensity. The melting point of the membrane obtained from differential scanning calorimetry was 130°C. Thermogravimetry analysis shows the decomposition of the total of the membrane begins at a temperature of 200°C. The membrane had the higher conductivity of (4.7 ± 1.1) × 10^{-2} S cm^{-1} after two-day immersion in 5.0 M ammonium acetate electrolyte solution compared with the membrane before immersed in ammonium acetate electrolyte (6.0 ± 0.1) × 10^{-8} S cm^{-1}. Fabricated proton batteries displayed an open circuit potential of 1.5 V for 8 days and turned on LED for 40 hours. The internal current resistance of batteries was 0.02 Ω and maximum power density of 11.0 mW cm^{-2}. The specific discharge capacities of proton batteries were 6.4, 10.7, 35.6 and 53.3 mA h g^{-1} for 0.1, 0.2, 0.5 and 1.0 mA discharge current, respectively.

ABSTRAK

Projek ini terbahagi kepada tiga bahagian: penyediaan membran kitosan asetat-silika berliang dalam julat saiz liang ~ 6.0 μm; peningkatan kekonduksian berliang kitosan membran asetat-silika-ammonium asetat sehingga 10^{-2} S cm^{-1} dengan ciri morfologi, struktur dan terma yang baik; dan fabrikasi Zn+ZnSO$_4$·7H$_2$O/membran kitosan asetat-silika berliang/MnO$_2$ sel syiling dengan peningkatan kapasiti tertentu bateri sehingga 55.0 mA h g^{-1}. Membran kitosan asetat-silika berliang disediakan dengan menggunakan teknik songsang porogen/kelarutan polimer. Sodium hidroksida dengan kepekatan yang berbeza digunakan untuk mengeluarkan silika dari membran kitosan asetat-silika berliang. Nisbah kuantiti terbaik serbuk kitosan kepada nisbah silica ialah 1:4. Analisis morfologi dan struktur menunjukkan purata saiz liang terbesar dan darjah penghabluran bagi membran adalah 5.9 μm dan 90 %, masing-masing diperolehi. Analisis inframerah transformasi Fourier menunjukkan interaksi antara chitosan, asid asetik dan silika telah berlaku berdasarkan peralihan keamatan beberapa puncak kumpulan berfungsi. Takat lebur bagi membran yang diperoleh dari kalorimetri pengimbasan pembezaan adalah 130°C. Ujian termogravimetri menunjukkan penguraian total bagi membran bermula pada suhu 200°C. Membran yang direndam selama dua hari di dalam larutan elektrolit ammonium asetat berkepekatan 5.0 M mempunyai kekonduksian yang lebih tinggi iaitu (4.7 ± 1.1) × 10^{-2} S cm^{-1} berbanding membran sebelum direndam dalam 5.0 M larutan elektrolit ammonium asetat (6.0 ± 0.1) × 10^{-8} S cm^{-1}. Bateri proton yang difabrikasi menunjukkan potensi litar terbuka 1.5 V selama 8 hari dan boleh menghidupkan diod pemancar cahaya selama 40 jam. Rintangan dalam bateri adalah 0.02 Ω dan ketumpatan kuasa maksimum 11.0 mW cm^{-2}. Kapasiti tertentu proton bateri proton adalah 6.4, 10.7, 35.6 dan 53.3 mA h g^{-1} untuk arus nyahcas 0.1, 0.2, 0.5 dan 1.0 mA.

CHAPTER 1

INTRODUCTION

1.1 Battery and Its Components

A battery is a device which converts the energy liberated in a chemical reaction into electricity. The main functions of a battery are to act as portable sources of electric power as well as to store electrical energy supplied by an external source. A typical battery consists of a cathode, an anode and the electrolyte. The cathode is connected to the negative terminal while the anode is connected to the positive terminal. The electrolyte contains ions which react with the electrodes to generate chemical energy.

In general, there are two types of batteries-primary and secondary batteries. A primary battery has a life which only lasts until all the reactants have been consumed by the discharge process. On the other hand, secondary batteries can be charged or recharged and may be considered as an electrochemical storage unit. The cell may be restored to its original charged condition by applying current in the opposite direction to that of discharge. Due to this nature, secondary batteries are also known as rechargeable batteries (Vincent and Scrosati, 1997).

The first practical rechargeable battery invented was a lead-acid battery in 1859. This battery system is still being used extensively today as engine starting (starting, lighting and ignition, SLI) and stationary emergency power. Another well established rechargeable battery system is the nickel-cadmium (Ni-Cd) system which is used in portable tools, instruments, military and aerospace equipments. Other battery systems in commercial use today include nickel-metal hydride (Ni-MH), zinc-

manganese dioxide (Zn-MnO_2) and lithium (Li^+) ion batteries (Beck and Rüetschi, 2000).

Rüetschi proposed the "three E" criteria (energy, economics and environment) for determining the success of a battery system. In terms of energy, the battery should have high energy content with respect to unit weight and volume. Economics simply refer to low manufacturing costs, low maintenance during use and long service life. Lastly, environment means that the battery is free from toxic materials, safe, has low energy consumption during manufacture and use, has high reliability and is easy to recycle (Beck and Rüetschi, 2000).

The three criteria lead to rapid development of non-toxic, biodegradable and cheap materials for battery components especially in terms of solid state electrolytes. For example, chitosan is a naturally available and abundant biopolymer which has potential as a polymer host for ammonium salts in a polymer electrolyte (Ng and Mohamad, 2006). Ammonium acetate (CH_3COONH_4) also provides a cheap and safe choice of ammonium salt to be complexed with chitosan (Du et al., 2009).

While the term "battery" is often used, the basic electrochemical unit being referred to is the "cell". A cell provides a source of electric energy by direct conversion of chemical energy. The cell consists of an assembly of electrodes, separator, electrolyte, container and terminals. A battery consists of one or more of these cells, connected in series or parallel, or both, depending on the desired output voltage and capacity. Figure 1.1 shows an example of the cell components. The cell consists of three major components (Linden, 2002):

i.   The anode or negative electrode – the reducing or fuel electrode, which gives up electrons to the external circuit and is oxidized during the electrochemical reaction.

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ii. The cathode or positive electrode – the oxidizing electrode, which accepts electrons from the external circuit and is reduced during the electrochemical reaction.

iii. The electrolyte or the ionic conductor – which provide the medium for transfer of charge, as ions, inside the cell between the anode and cathode. The electrolyte is typically a liquid (water or alcohols solvents), with dissolved salts, acids or alkalis to impart ionic conductivity. Nowadays, some batteries use solid electrolytes.
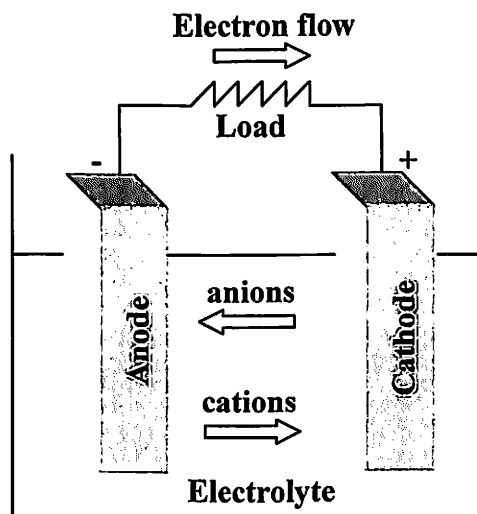
Figure 1.1: The cell components (discharge operation) (Linden, 2002).

A significant characteristic of a protonic battery is that charging/discharging can be done by shifting protons (H^+) (NEC TOKIN, 2004). The source of H^+ is from electrolyte. The electrolyte can be prepared either in liquid, gel or solid-state form. For a successful protonic battery, an anode capable of supplying or injecting H^+ ions into the battery electrolyte, a proton conducting electrolyte and a reversible cathode with layered oxides are needed (Pratap et al., 2006). In protonic battery, zinc (Zn)

and manganese (IV) oxide (MnO_2) have been used as anode and cathode material, respectively. The optimum concentration of electrolyte will provide highest mobility of H^+ ions. Consequently the conductivity of electrolyte can be enhanced.

1.2 Solid State Electrolyte

Solid materials which are capable of ionic conduction have many advantages over their liquid equivalents. This is especially true in preventing leakage of harmful liquids and the potential of producing miniaturized cells. Some of the solid state electrolyte systems are crystalline solid electrolyte, glass electrolyte and polymer electrolyte (Gray, 1997).

Crystalline solid electrolytes can conduct cations and anions. High concentration of mobile ions and a low activation energy for ionic motion from site to site result in high ionic conductivity. The number of sites available for mobile ions is much greater than the number of mobile ions present. This leads to high diffusion coefficients and fast ion conductors. According to Gray (1997), many researches on crystalline solid electrolytes revolve around sodium ion (Na^+) conduction owing to the well-studied sodium β-aluminas and Na superionic conductors (NASICON) systems.

Glasses can also transport ions. Glass electrolyte systems have a more complex composition. But in general, the composition consists of three basic constituents which are the network formers, network modifiers and ionic salts. Network formers such as silica (SiO_2) and phosphorus pentasulfide (P_2S_5) form the crosslinked macromolecular chains. Network modifiers interact with the network former structure by breaking the oxygen and sulfide bridges to introduce ionic bonds. Oxides and sulfides such as silver oxide (Ag_2O) and lithium sulfide (Li_2S) are

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network modifiers. The ionic salts do not react chemically with the macromolecular structure but increases the ionic conductivity (Gray, 1997).

Polymer electrolyte is generally known as a solvent-free system where the ionically conducting phase is formed by complexing salts with a high molecular weight polymer matrix. Some of the polymers researched as proton conducting material include polyethylene oxide (PEO), poly(vinyl alcohol) (PVA) and chitosan (Ng and Mohamad, 2008). Interestingly, when Gray (1997) compared crystalline solid and glass electrolytes to polymer electrolyte, the crystalline solid and glass electrolytes are at a disadvantage due to their hard and brittle nature. In contrast, polymer electrolytes have form flexibility which allows good interfacial contact with the electrodes.

1.3 Problem Statement

Ceramic fillers such as silica (SiO_2), alumina (Al_2O_3), copper oxide (CuO) or titanium oxide (TiO_2) particles have been used to enhance morphology, structural and electrical properties of polymer electrolyte (Kim et al., 2002; Liu et al., 2003; Li et al., 2005; Kim et al., 2006). Among of these fillers, SiO_2 has excellent properties to produce porous membrane (Zeng and Ruckenstein, 1996; Kim et al., 2001; Kim et al., 2006; Santos et al., 2008). It has been widely utilized in various application such as dehumidification processes (Chang et al., 2004), medical purpose (Vallet-Regi et al., 2006) and electrochemical sensors (Wang et al., 2009). However, the application limited only for rechargeable lithium battery (Kim et al., 2001; Kim et al., 2006).

Normally, SiO_2 particles are insoluble in acidic media but soluble in alkaline sodium hydroxide (NaOH) solutions (Zeng and Ruckenstein, 1996; Santos et al., 2008). The extraction of SiO_2 particles after immersed in NaOH can generate porous

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chitosan membrane. The large pore size of chitosan membrane is somewhat important in solid polymer electrolyte requirement. The combination of porous chitosan membrane with good salts will allow more chelation of proton (H^+) compared to the dense membrane. This can produce batteries with good properties. However, the previous studies only focused on one concentration of NaOH solution such as 8.0 wt. % (Clasen et al., 2006), 1.0 M (Mei et al., 2012), 0.067 M (Zeng and Ruckenstein, 1996) and 0.25 M (Shirosaki et al., 2005) instead of vary NaOH in different concentration to remove SiO_2 particles.

1.4 Objectives

The main objectives of this project are:

a) To prepare of porous chitosan acetate-silica membranes in a range of $\sim$ 6.0 μm pores size with good morphological, structural and thermal properties.

b) To improve the conductivity of porous chitosan acetate-silica-ammonium acetate membranes up to 10^{-2} S cm^{-1}.

c) To fabricate Zn+ZnSO$_4 \cdot$7H$_2$O/porous chitosan acetate-silica-acetate membranes/MnO$_2$ coin cell and improve the battery specific capacity up to 55.0 mA h g^{-1}.

1.5 Approach of Study

The porous chitosan acetate membrane (CA) was prepared using the stirring mixed solution-cast method by applying SiO_2 as porogen agent. After that, SiO_2 particles were dissolved in NaOH at different concentration. Then, the porous SiO_2-CA membrane with optimal morphological, structural and thermal properties was immersed in the NH$_4$CH$_3$COO electrolyte solution. Finally, the porous SiO_2-CA-

NH$_4$CH$_3$COO membrane was used to fabricate proton batteries. The proton batteries open circuit potential (OCP), discharge profile, current-voltage (I-V), and current density-power density (J-P) characteristics were investigated in this studies.

CHAPTER 2

EXPERIMENTAL PROCEDURE

2.1   Introduction

This chapter explains the experimental materials, methodologies, and testing instruments. Various kinds of testings have been performed in order to obtain the best results from the proposed methodologies. This chapter is made up of three parts including:

a) Preparation and characterization of porous chitosan acetate-silica membranes using inverse porogen/polymer solubility technique.

b) Immersion of porous chitosan acetate-silica membrane in ammonium acetate ($NH4CH_3COO$) solution electrolyte and electrochemical analysis of membrane.

c) Fabrication and characterization of $Zn+ZnSO_4 \cdot 7H_2O$/porous chitosan acetate-silica-ammonium acetate membranes/MnO_2 proton battery coin cell.

2.2 Materials

2.2.1 Porous membrane and electrolyte materials

a) Chitosan powder (Chito-Chem)

b) High-purity grade silica gel, (60 Å pore size and 5 μm to 25 μm particle size; Sigma–Aldrich)

c) Acetic acid (CH_3COOH, 99-100%, Merck))

d) Sodium hydroxide (NaOH, Merck)

e) Ammonium acetate (CH_3COONH_4, Merck)

f) Glycerol ($C_3H_5(OH)_3$, 85%, Merck)

2.2.2 Proton Battery materials

a) Zinc powder (Zn, Merck)

b) Acetylene black (AB, Gunbai)

c) Polytetrafluoroethylene (PTFE, Fluka)

d) Manganese dioxide (MnO_2, Battery grade, Aldrich)

e) Nickel mesh

f) Coin cell

2.3 Porous CA-SiO₂: preparation and characterization

Chitosan acetate (CA) membranes were prepared using stirring and solution-cast technique. Chitosan powder (1.0 g; Aldrich) was dissolved in 1% acetic acid solution (CH_3COOH, Merck). The CA mixture was stirred continuously at 25 °C for 1 d using magnetic stirrer.

High-purity grade silica (SiO_2, 60 Å pore size and 5 μm to 25 μm particle size; Sigma-Aldrich) were dispersed with chitosan/SiO_2 weight ratio 1:4 into the CA

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solution. The CA-SiO$_2$ solutions were then stirred for 1 day. The solutions were further dispersed using sonicator for 30 min. After complete dispersion of SiO$_2$, the solutions were placed into Petri dishes and left to dry at 25 °C to obtain CA-SiO$_2$ membranes.

Next, the CA-SiO$_2$ membranes were immersed in different concentration of NaOH (Merck) from 1.3, 3.0, 5.0 and 8.0 M at 60 °C for 1 d to dissolve SiO$_2$ particles from the membrane. The porous CA-SiO$_2$ membranes were washed with deionized water at first. The porous membranes were then plasticized by immersion in 2.2 M glycerol (Merck) for 30 min. Subsequently, the porous CA-SiO$_2$ membranes were washed with deionized water and allowed to dry at 25 °C. Membranes compositions were coded as tabulated in Table 2.1. Figure 2.1 illustrates the process preparation of porous CA-SiO$_2$ using inverse porogen/polymer solubility technique.

Table 2.1: Membranes codes based on CA-SiO$_2$-NaOH composition.

Sample name	Chitosan (g)	SiO$_2$ (g)	NaOH (M)
Chitosan powder	-	-	-
Chitosan acetate (CA)	1	-	-
CA4S	1	4	-
CA4S 1.3N	1	4	1.3
CA4S 3.0N	1	4	3.0
CA4S 5.0N	1	4	5.0
CA4S 8.0N	1	4	8.0

(a) SiO₂ powder mixed with CA solution

(b) CA-SiO₂ membrane — Solution cast of CA-SiO₂ solution until dry

(c) SiO₂ particles / SiO₂ particles — CA-SiO₂ membrane after drying process

(d) Dissolution of SiO₂ particles — Immersion of CA-SiO₂ membrane in NaOH at 60 °C

(e) Pores / Pores — Porous CA-SiO₂ membrane

(f) Porous CA-SiO₂ membrane — Immersion of porous CA-SiO₂ membrane in glycerol

(g) Final of porous CA-SiO₂ membrane

Figure 2.1: Preparation of porous CA-SiO$_2$ using inverse porogen/polymer solubility technique.

The morphology and composition of the porous CA-SiO$_2$ membranes was investigated using field emission scanning electron microscopy (FESEM) and energy dispersive X-ray spectroscopy (EDX, Zeiss Supra 35VP). Average pore sizes were calculated using Image J software. Structural properties were examined using X-ray diffraction (XRD; Bruker Advanced X-ray Solutions D8). Deconvolution of XRD

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and degree of crystallinity of porous $CA-SiO_2$ membranes were further analyzed using Origin 8 software.

The thermal analysis of membrane were carried out using differential scanning calometric (DSC, Perkin Elmer DSC-6) and thermogravimetri analysis (TGA, Perkin Elmer Pyris 6 TGA analyzer). The DSC was used to determined the melting characterization of membranes. The heating and cooling rate was set at 10°C/min from 30-200°C. The samples were held at that temperature for 1 minute to eliminate thermal history, then the non isothermal crystallization process was recorded from 200-30°C. Meanwhile, TGA analysis was scanned from 30-600°C in a nitrogen flow of 30ml/min with heating rate 20°C/min.

2.4 Porous $CA-SiO_2-NH_4CH_3COO$: preparation and characterization

The electrolyte solution was prepared by dissolving different concentration of ammonium acetate (NH_4CH_3COO, Merck) from 1.0-7.0 M in deionized water. The amount NH_4CH_3COO of is tabulated in Table 2.2.

Next, electrochemical impedance spectroscopy (EIS) was used to measure the conductivity of NH_4CH_3COO electrolyte at room temperature using the Autolab PGSTAT 30 Frequency Response Analyzer (Eco Chemie B.V.) and frequency response analyzer (FRA) was set with frequency range of 0.1 Hz to 1.0 MHz and amplitude of 10 mV. The conductivity of an electrolyte can be calculated from the bulk resistance value (R_b) using the Equation 2.1:

$$\sigma = \frac{t}{R_b A} \qquad (2.1)$$

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where σ is the conductivity of electrolyte, t, thickness of sample = 0.41 cm, and A is the area of sample in teflon ring = 2.08 cm^2. This plot is also known as the Nyquist plot.

Table 2.2: Details of conductivity test sample for NH_4CH_3COO.

Sample name	Concentration (M)	Weight (g)
Deionized water	-	-
1.0AA	1.0	1.54
3.0AA	3.0	4.62
5.0AA	5.0	7.71
7.0AA	7.0	10.79

After that, the porous $CA-SiO_2$ membrane with largest average size of pores obtained from Section 2.1 was immersed in the highest conductivity of NH_4CH_3COO electrolyte for 2 days. Later, the conductivity of porous $CA-SiO_2-NH_4CH_3COO$ electrolyte was measured using EIS compared with the conductivity of porous $CA-SiO_2$ before immersed in NH_4CH_3COO electrolyte. The conductivity of both samples can be calculated from R_b using the Equation 2.1. This electrolyte provided proton (H^+) as a source for porous $CA-SiO_2$ membranes.

Both of these samples (porous $CA-SiO_2-NH_4CH_3COO$ and porous $CA-SiO_2$ membranes) were chosen for conductivity measurement at elevated temperature from 25 to 90°C as shown in Figure 2.2.

```
┌─────────────────────────────────────┐
│  Porous CA-SiO₂-NH₄CH₃COO and       │
│     porous CA-SiO₂ membrane         │
└─────────────────────────────────────┘
                   │
                   ▼
┌─────────────────────────────────────┐
│    Conductivity test from 25-90°C   │
└─────────────────────────────────────┘
                   │
                   ▼
┌─────────────────────────────────────┐
│    Calculation of activation energy │
│              values                 │
└─────────────────────────────────────┘
```
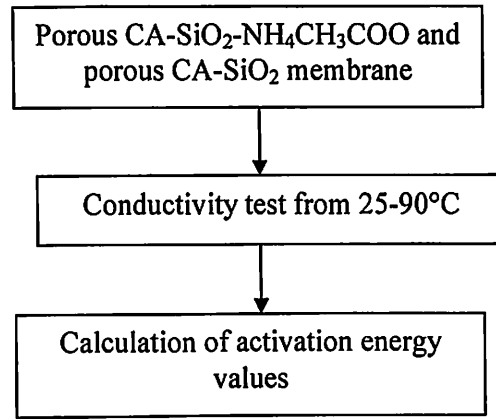
Figure 2.2: Preparation of samples for conductivity test at elevated temperature.

The Arrhenius plot (graph of 1000/T versus log conductivity) were then plotted for both samples. The activation energy values of samples were then calculated based on this graph by using derivation of Equation 2.2-2.8 (Chang, 1998):

$$\sigma = \sigma_0 e^{\frac{-E_a}{kT}} \qquad (2.2)$$

$$\ln \sigma = \ln \sigma_0 e^{\frac{-E_a}{kT}} \qquad (2.3)$$

$$\ln \sigma = \ln \sigma_0 - \frac{E_a}{kT} \qquad (2.4)$$

$$\ln\left(\frac{\sigma}{\sigma_0}\right) = -\frac{E_a}{kT} \qquad (2.5)$$

Since $\ln x = 2.303 \log x$, hence Equation. 2.5 become:-

$$2.303 \log \frac{\sigma}{\sigma_0} = -\frac{E_a}{kT} \qquad (2.6)$$

$$\log \sigma = \left(\frac{-E_a}{2.303k}\right)\left(\frac{1}{T}\right) + \log \sigma_0 \qquad (2.7)$$

where σ is conductivity at 25°C, σ_0 is the pre exponential factor, k is the Boltzmann constant (8.62 x 10^{-5} eV K^{-1}), and T is the absolute temperature in Kelvin (273 K). Equation 2.8 can be rearranged to a linear equation:

$$\log \sigma = \left(\frac{-E_a}{2.303k}\right)\left(\frac{1}{T}\right) + \log \sigma_0 \qquad (2.8)$$

$$\underset{y}{\updownarrow} \quad \underset{m}{\updownarrow} \quad \underset{x}{\updownarrow} + \underset{c}{\updownarrow}$$

Since a plot of 1000/T versus log conductivity gives a straight line whose slope m is equal to $E_a/2.303k$ and intercept c with the ordinate of Y-axis is log σ_0, the values of activation energy were then calculated from $E_a/2.303k$ equal to m.

Linear sweep voltammetry (LSV) for porous CA-SiO_2-NH_4CH_3COO and porous CA-SiO_2 membrane were measured at from 0.0-2.0 V with scan rate of 0.01 V s^{-1}. Meanwhile cyclic voltamettry (CV) was measure from 0.3-3.0 V with scan rate0.05 V s^{-1}. Both of this analysis were measured using Autolab PGSTAT 30 (Eco Chemie B.V.) with NOVA 1.9 software.

2.5 Porous CA-SiO_2-NH_4CH_3COO membrane proton batteries

Proton batteries coin cells were fabricated using the porous CA-SiO_2-NH_4CH_3COO membrane electrolyte in Section 2.4. The anode pellet was prepared with a mixture of Zn powder (particle size <45 μm; Merck), $ZnSO_4.7H_2O$ powder (Univar), Super P powder (specific surface area of 62 m^2 g^{-1}; TIMCAL Graphite & Carbon), and polytetrafluoroethylene (PTFE, Fluka). The cathode pellet was prepared with a mixture of MnO_2 (Aldrich), Super P powder, and PTFE. The current collector, stainless steel mesh (area = 1.8 cm^{-2}), was placed in the middle of both pellets. All materials were combined and fabricated as Zn+$ZnSO_4\cdot 7H_2O$ + Super P +

PTFE ‖ CA-SiO$_2$-NH$_4$CH$_3$COO ‖ MnO$_2$ + Super P + PTFE proton battery. The schematic diagram of coin cell proton battery illustrated in Figure 2.3.
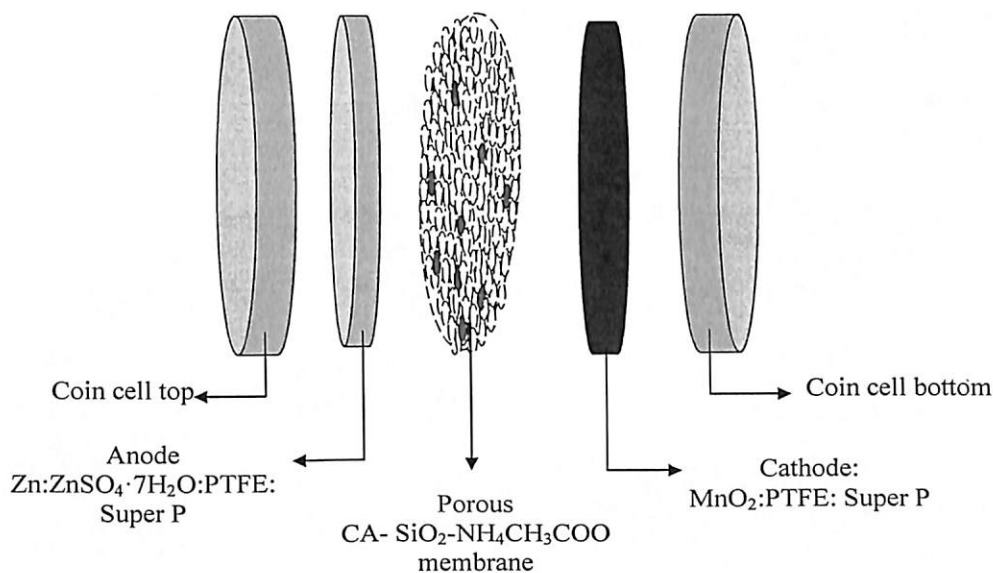
Figure 2.3: Schematic diagram of proton battery coin cell.

Neware BTS was used to characterize the open circuit potential (OCP) and discharge profile at 0.1, 0.2, 0.5 and 1.0 mA of proton batteries. The current voltage (I–V) and current density-power density (J–P) curves were plotted using a discharge current ranging from 20 µA to 100 mA. The average voltage of both batteries was monitored for each current drain after a 10 s operation. This analysis was done using were measured using the galvanostat of Autolab PGSTAT 30 GPES (Eco Chemie B.V.). Figure 2.4 shows the fabrication and characterization test of Zn+ZnSO$_4$·7H$_2$O + Super P + PTFE ‖ CA- SiO$_2$-NH$_4$CH$_3$COO ‖ MnO$_2$ + Super P + PTFE proton battery. The battery was simulated via MULTISIM 11 to ensure that they can operate same with actual applications. All input values were given based on the OCV, discharge profile, and I–V plot results. Afterward, the simulation was compared with the actual performance of the fabricated batteries.

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┌─────────────────────────┐        ┌─────────────────────────┐
│ Anode:                  │        │ Cathode:                │
│ Zn:ZnSO₄·7H₂O:PTFE:     │        │ MnO₂:PTFE: Super P      │
│ Super P                 │        │                         │
└─────────────────────────┘        └─────────────────────────┘
```

Anode:
$Zn:ZnSO_4 \cdot 7H_2O:PTFE:$ Super P

Cathode:
$MnO_2:PTFE:$ Super P

Fabrication of cell:
$Zn+ZnSO_4 \cdot 7H_2O$ + Super P + PTFE || CA-SiO_2-NH_4CH_3COO || MnO_2 + Super P + PTFE

Proton battery characterization
- Open circuit potential
- Discharge
- *I-V* and *J-P*
- Simulation using MULTISM 11
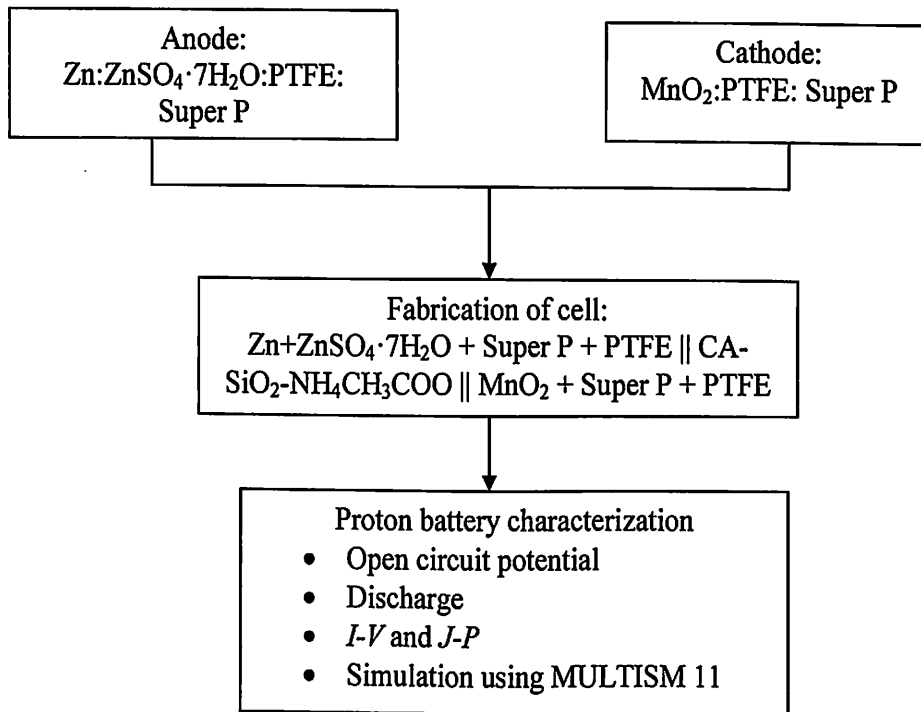
Figure 2.4: Fabrication and characterization test of $Zn+ZnSO_4 \cdot 7H_2O$ + Super P + PTFE || CA-SiO_2-NH_4CH_3COO || MnO_2 + Super P + PTFE proton battery.

CHAPTER 3

RESULTS AND DISCUSSIONS

3.1   Introduction

In this chapter, the properties of porous chitosan acetate-silica membranes, porous chitosan acetate-silica-ammonium acetate electrolyte and fabrication of the properties of $Zn+ZnSO_4 \cdot 7H_2O$/porous chitosan acetate-silica-ammonium acetate membranes/MnO_2 proton battery coin cell. The discussion of current results will be related to the theoretical equation as mentioned earlier in Chapter 2. This chapter will be divided into three sections.

a) The first section will focus on the results of the porous chitosan acetate-silica membranes:

   i)   Field emission scanning electron microscopy analysis (FESEM), energy dispersive X-ray spectroscopy (EDX) and average of pore sizes.

   ii) X-ray diffraction analysis (XRD) and crystallite size

   iii) Fourier transform infrared analysis (FTIR)

   iv) Thermogravimetric analysis (TGA) and Differential scanning calorimetry (DSC)

b) The second section will highlight the porous chitosan acetate-silica-ammonium

acetate electrolyte electrochemical results including:

    i)   Nyquist and conductivity plot at room and elevated temperature

    ii) Temperature dependence and activation energy (E_a) plot

    iii) Linear sweep voltammetry (LSV) and cyclic voltammetry (CV)

b) The third section will highlight the properties of $Zn+ZnSO_4 \cdot 7H_2O$/porous

chitosan acetate-silica-ammonium acetate membranes/MnO_2 proton battery coin cell

including:

    i)   Open circuit potential (OCP) of proton battery

    ii) Discharge profile of proton battery

    iii) Current voltage ($I-V$) and current density-power density ($J-P$) curves

    iv) Simulation of proton battery via MULTISIM 11 compared with the actual

        performance of the fabricated batteries.

3.2 Porous CA-SiO₂ Membranes Properties

3.2.1 Morphology and Pore Sizes Analysis

The micrographs of chitosan powder, chitosan acetate (CA) and porous CA-SiO_2

membranes are shown in Figure 3.1. Normally, chitosan powder with bulky surface is

shown in Figure 3.1a. The cross section of CA membrane was clear and dense (Figure

3.1b). Figure 3.1c depicted the dense and jagged fleck cross section of CA4S before

immersed in NaOH. Meanwhile, the cross section of CA-SiO_2 membranes turned into

porous membranes with different pores shape after SiO_2 was dissolved in different

concentrations of NaOH (Figure 3.1d-g). The pores of membranes were crumple at

first (CA4S1.3N) and growth little by little (CA4S3.0N, CA4S5.0N and CA4S8.0N).

The pores shapes of porous SiO$_2$-CA membranes were highly dependent on the concentration of NaOH.
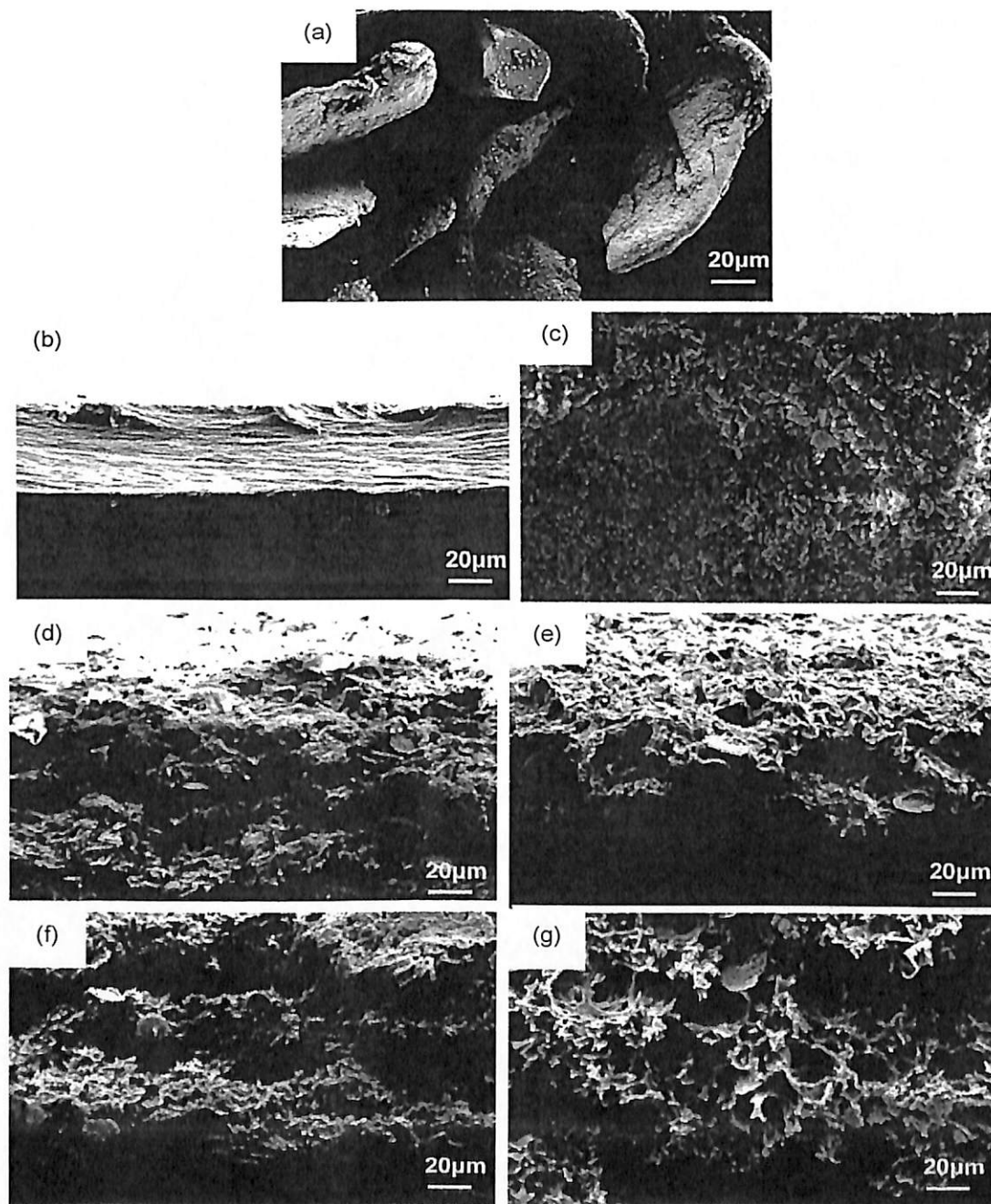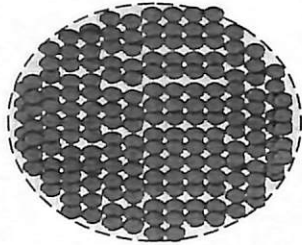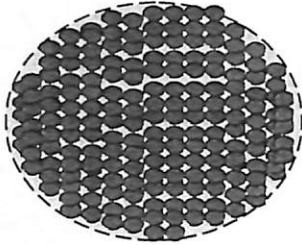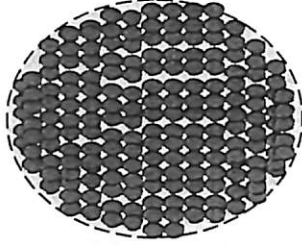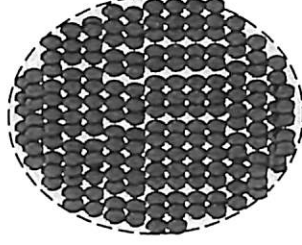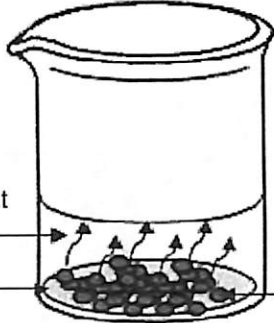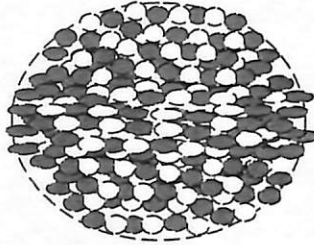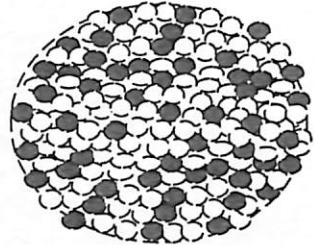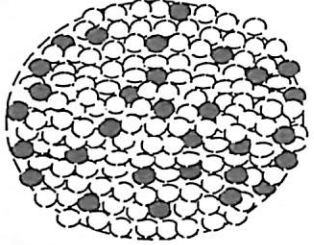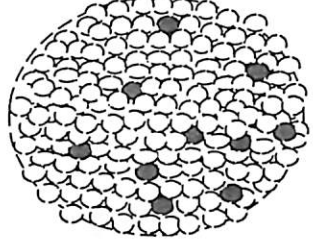
Figure 3.1: Surface morphology of (a) chitosan powder, (b) cross section image of chitosan acetate membrane, porous chitosan-SiO$_2$ membrane with ratio 1:4 after (c) before and after immerse in (d) 1.3, (e) 3.0, (f) 5.0 and (g) 8.0 M NaOH.

Further discussion on removal SiO_2 particles from membrane process is illustrated in Table 3.1. The pore shapes of CA4S1.3N, CA4S3.0N and CA4S5.0N membranes were not uniform and agglomeration still occurred after immersed in low concentration of NaOH. Herein, SiO_2 was not fully dissolved and still trapped inside membrane (grey colour of particles). The SiO_2 particles attempted to disslove in NaOH. When NaOH concentration was up to 8.0 M, the SiO_2 dissolved well in NaOH. This is because a sufficient concentration of NaOH can pull out SiO_2 from membranes and dissolved in NaOH. Hence, the porous membranes with uniform pore shape were produced.

The element analysis by EDX represents in Figure 3.2, it showed the different composition of chitosan powder, CA membrane and porous SiO_2-CA membranes tables inside). The composition of Si decreased when increasing concentrations of NaOH same circumstances as clarified in Table 3.2.

Table 3.1: Illustration of removal SiO$_2$ from porous SiO$_2$-chitosan membrane.

Samples	CA4S1.3N	CA4S3.0N	CA4S5.0N	CA4S8.0N
Before immerse in NaOH				
During immerse in NaOH	SiO$_2$ particles dissolved in different NaOH concentration (1.3, 3.0, 5.0 and 8.0 M)			
After immerse in NaOH				

NaOH solution at different concentrations

SiO$_2$-chitosan membrane

SiO$_2$ particles

● SiO$_2$ particles before chitosan membrane immerse in NaOH
○ Pores after SiO$_2$ particles dissolve in NaOH from chitosan membrane
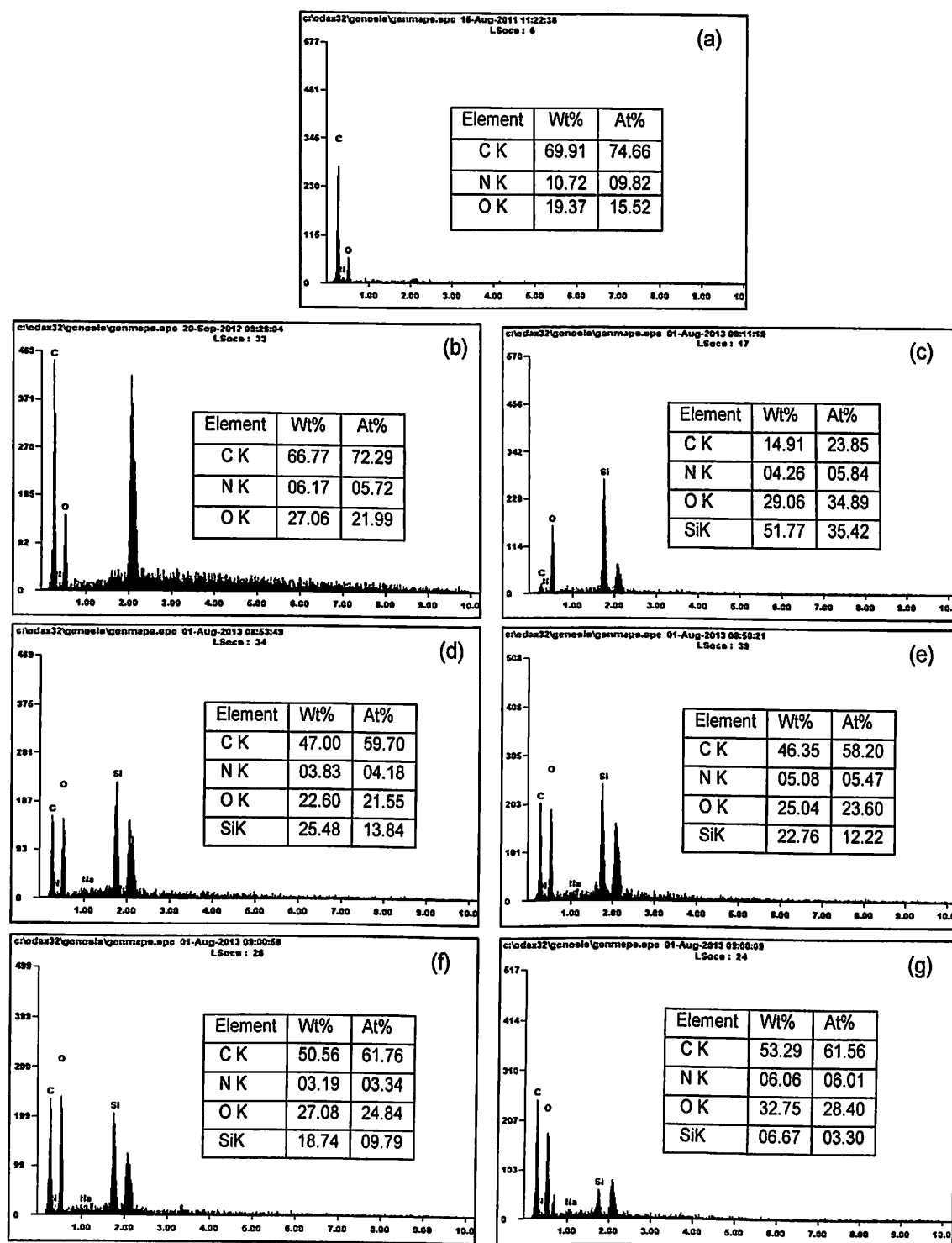
Figure 3.2: EDX of (a) chitosan powder, (b) chitosan acetate membrane (c) CA4S, (d) CA4S1.3N, (e) CA4S3.0N, (f) CA4S5.0N and (g) CA4S8.0N.

(a)

Element	Wt%	At%
C K	69.91	74.66
N K	10.72	09.82
O K	19.37	15.52

(b)

Element	Wt%	At%
C K	66.77	72.29
N K	06.17	05.72
O K	27.06	21.99

(c)

Element	Wt%	At%
C K	14.91	23.85
N K	04.26	05.84
O K	29.06	34.89
SiK	51.77	35.42

(d)

Element	Wt%	At%
C K	47.00	59.70
N K	03.83	04.18
O K	22.60	21.55
SiK	25.48	13.84

(e)

Element	Wt%	At%
C K	46.35	58.20
N K	05.08	05.47
O K	25.04	23.60
SiK	22.76	12.22

(f)

Element	Wt%	At%
C K	50.56	61.76
N K	03.19	03.34
O K	27.08	24.84
SiK	18.74	09.79

(g)

Element	Wt%	At%
C K	53.29	61.56
N K	06.06	06.01
O K	32.75	28.40
SiK	06.67	03.30

Table 3.2: Composition of all membranes after immersed in 1.3, 3.0, 5.0 and 8.0 M NaOH.

Sample	Si		O	
	(Wt %)	(At %)	(Wt %)	(At %)
CA4S	51.77	35.42	29.06	34.89
CA4S 1.3N	25.48	13.84	22.60	21.55
CA4S 3.0N	22.76	12.22	25.04	23.60
CA4S 5.0N	18.74	09.79	27.08	24.84
CA4S 8.0N	06.67	03.30	32.75	28.40

Figure 3.3 shows the average pore size of porous $CA-SiO_2$ membranes calculated from FESEM results. The pores started to form when membranes were immersed in NaOH. The pore sizes for all membranes were increased gradually especially for CA4S1.3N, CA4S3.0N and CA4S5.0N. However, as mention earlier (Figure 3.1 and Table 3.1) the formation of pore accordingly with SiO_2 shape, which is not uniform and agglomerate. Generally, agglomeration of these particles is caused by the high surface energy of ceramics. This is a common problem that weaken the efficiency of the ceramic filler (Liu et al., 2003). Therefore, this would affect the average pore size of porous $CA-SiO_2$ membranes. For these samples, the low concentrations of NaOH solution lower the ability of SiO_2 to dissolve in NaOH. Most of SiO_2 in deep membrane cannot be reached by NaOH solution. Thus, the pores size much smaller in a range between 4.7 to 5.0 µm.

Nevertheless, after immersed CA4S8.0N membrane in 8.0 M NaOH, porous membranes with largest average pore sizes (5.9 µm) and uniform pore shape were produced. The higher concentration of NaOH may dissolve large amount of SiO_2 particles in NaOH. Only a small amount of SiO_2 still trapped in deep membrane and not significantly affected the porous structure of membrane. The results are almost similar with previous studies on removal SiO_2 particles from chitosan membrane using NaOH as porogen removal solution based on morphology, removal SiO_2

3.2.2 Structural and Degree of Crystallinity Analysis

The XRD pattern of chitosan powder, CA, SiO_2, CA4S, CA4S1.3N, CA4S3.0N, CA4S5.0N and CA4S8.0N membranes are shown in Figure 3.4. The broad peak at $2\theta = 20°$ is the signature of pure chitosan powder. However, the peak vanished after chitosan powder dissolve in acetic acid. Meanwhile, there is a small peak at $2\theta = 22°$ for SiO_2. When SiO_2 were dispersed in CA solution, the peak at $2\theta = 20$ and $22°$ become broad. After CA-SiO_2 membranes immersed in NaOH, the intensity of $2\theta = 22°$ continue to increase slowly. Only broad peak at $2\theta = 20°$ can be seen for CA4S8.0N.
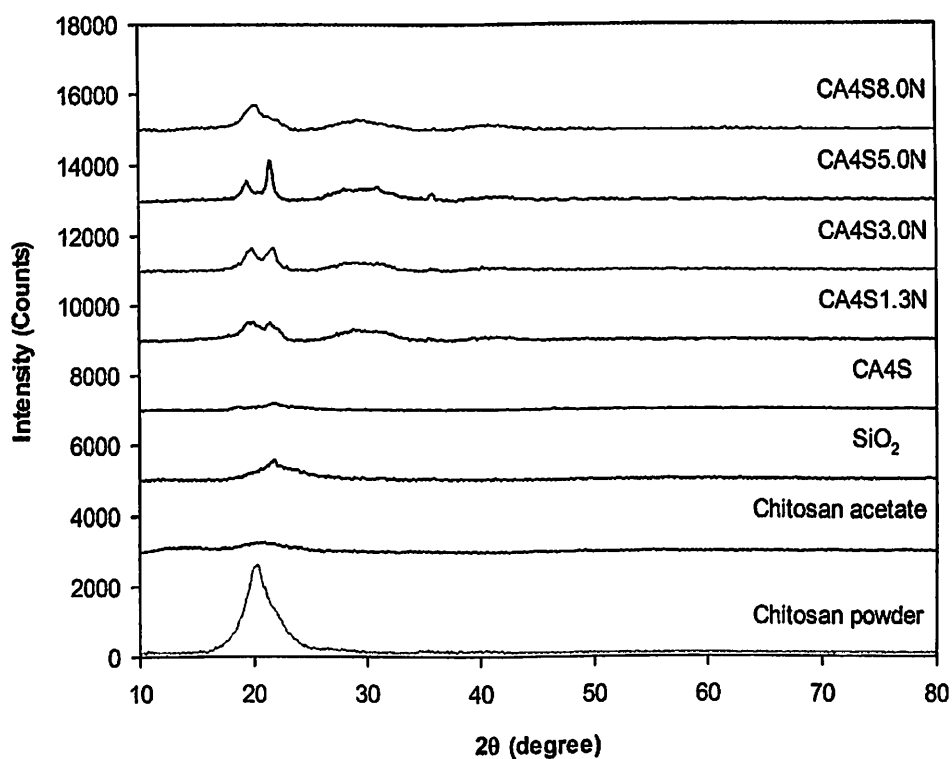
Figure 3.4: XRD of chitosan powder, chitosan acetate membrane, SiO_2, CA4S, CA4S1.3N, CA4S3.0N, CA4S5.0N and CA4S8.0N.

The deconvolution of XRD for chitosan powder, CA membrane, SiO_2, CA4S, CA4S1.3N, CA4S3.0N, CA4S5.0N and CA4S8.0N (Figure 3.5) provides the details changing of membranes crystalline structure showed in Figure 3.4. The highly crystalline of chitosan powder turn into amorphous structure after dissolve in acetic acid for CA membrane (Figure 3.5a and b). This can be seen by the decreasing intensity peak at $2\theta = 20°$ and broad peak at $2\theta = 15°$ of CA membrane. Figure 3.5c shows the SiO_2 is highly crystalline based on the high intensity peak at $2\theta = 22°$ similar with previous study on structural analysis of SiO_2 (Bu et al., 2014). When SiO_2-CA membranes immersed in NaOH, the intensity of $2\theta = 22°$ were slightly increase, but not too notable since the whole XRD peaks for CA4S1.3N, CA4S3.0N and CA4S5.0N still broad (Figure 3.5d-f). In addition, the intensity of humps at $2\theta = 20, 30$ and $40°$ for these three samples maintain at same range and broad. This endorses the fact that these membranes still had amorphous structure. However, Figure 3.5e shows only broad peak at $2\theta = 20, 30$ and $40°$ appeared for CA4S8.0N. The shifting of all peaks demonstrated that structure of membrane has been changed.

After immersed in 8.0 M NaOH, the crystallinity of membrane decreased, increased its amorphous structure compared with membranes immersed in lower concentration of NaOH (1.3, 3.0 and 5.0 M). Normally, the formation of amorphous polymer phases at the surface can be brought by the ceramic filler (Liu et al., 2003). In this study, the sufficient concentration of NaOH will attract more SiO_2 particles to dissolve into NaOH solution. Hence, produce amorphous membrane. Insufficient concentration of NaOH will cause insolubility of SiO_2. Thus, the membranes were not fully amorphous since some parts contained high crystalline of SiO_2 ceramic filler.

The degrees of crystallinity for chitosan powder, CA and porous SiO_2-CA membranes are further determined from XRD analysis as seen in Figure 3.6. The chitosan powder had the highest crystalinity. Meanwhile, the crystallinity for CA decreased to 44 %. Furthermore, the crystalinity of porous SiO_2-CA membranes increased rapidly after mixed SiO_2. The crystalinity increased gradually after immersed in different concentration of NaOH. However, the crystallinity decreased when porous SiO_2-CA membrane was immersed in 8.0 M NaOH. Table 3.3 listed the degree of crystallinity all membranes after immersed in 1.3, 3.0, 5.0 and 8.0 M NaOH.
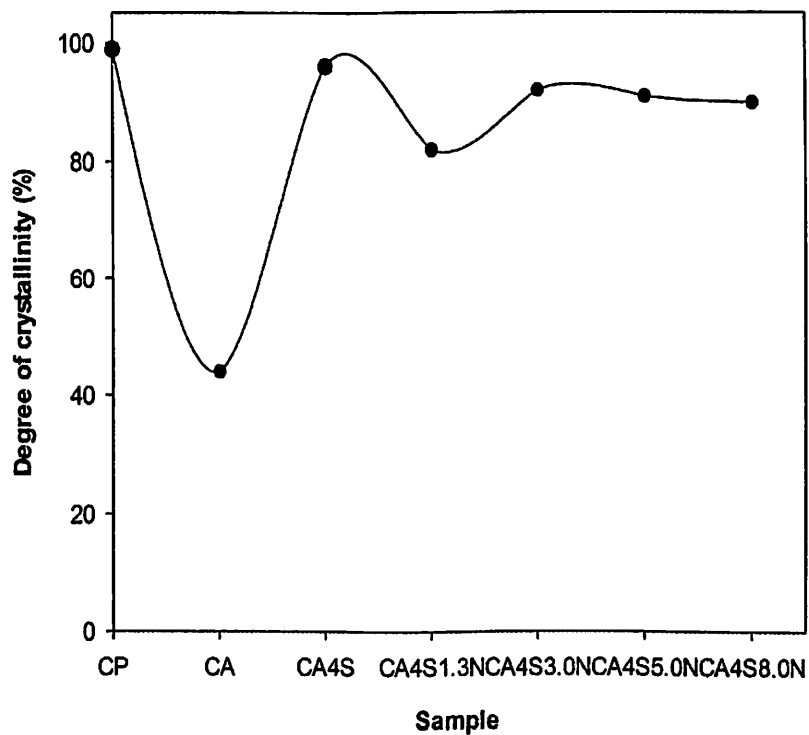
Figure 3.6: Degree crystallinity of chitosan powder, chitosan acetate membrane, SiO_2, CA4S, CA4S1.3N, CA4S3.0N, CA4S5.0N and CA4S8.0N.

Table 3.3: Degree of crystallinity all membranes after immersed in 1.3, 3.0, 5.0 and 8.0 M NaOH.

Sample	Degree of crystallinity (%)
Chitosan powder (CP)	99
Chitosan acetate (CA)	44
CA4S	96
CA4S 1.3N	82
CA4S 3.0N	92
CA4S 5.0N	91
CA4S 8.0N	90

The decreasing crystallinity of CA membrane is due to the changing of high crystalline chitosan powder to amorphous structure after dissolve in CH_3COOH. Normally, polymers are not 100 % crystalline since too difficult for polymers to align the chains. Therefore, the dominant amorphous structure of CA membrane decreased the crystallinity. When high crystalline of SiO_2 was mixed to the CA membrane, the crystallinity of membranes increased. This attributed by the shifting of membrane molecular chains after immersed in 1.3, 3.0 and 5.0 M of NaOH. The poor condition for SiO_2 to dissolve affected the structure of membranes. Nevertheless, the cystallinity of porous SiO_2-CA membrane slightly decreased after immersed in 8.0 M NaOH. This proved that at the sufficient concentration of porogen removal solution, the SiO_2 will dissolve in NaOH (Zeng and Ruckenstein, 1996; Santos et al., 2008). Thus, the crystallinity of membranes decreased.

3.2.3 Chemical Interaction Analysis

The FTIR analysis and chemical interaction of chitosan powder, CA, porous CA4S1.3N, CA4S3.0N, CA4S5.0N, CA4S8.0N membranes and SiO_2 are illustrated in Figure 3.7. The broad peak at 3550-3050 cm^{-1} in Region 1 could be assigned to the axial stretching vibration of O–H superposed to the N–H stretching band and chitosan inter-hydrogen bonds (Enescu et al., 2009).

The small peak at 2990-2830 cm^{-1} in Region 2 is denoted as two bands for CH_2 group for all samples except CA4S membrane and SiO_2. This is attributed by the high amount of SiO_2 in CA4S membrane before immersed in NaOH. Meanwhile, the peak of 1650-1550 cm^{-1} in Region 3 refer to the symmetry of C=O stretch peak (Tran et al., 2013). Herein, the cation of CH_3COOH solution interacted with the nitrogen atom of NH_2 in chitosan. Consequently, NH_2 and other bands shifted for CA membrane. However, this peak became smaller proportional with NaOH concentration used to immerse porous membranes. This is due to the effect of inclusion and removal of SiO_2 in CA2.0S30N membrane.

In Region 4, a few peaks exhibits in a range 1450-1250 cm^{-1} presented the existence of C-O stretch or OH deformation and C-C(O)-C stretch (acetates). The O–H band at 1400 cm^{-1} is referred to CA after dissolve in CH_3COOH solution. Moreover, the C–O stretch at 1269 cm^{-1} is also denoted to CA after dissolve in CH_3COOH solution. Both of these peaks disappeared in all membranes after porogen removal of SiO_2 occurred in NaOH solutions.

Another small peak in a range of 1200-1150 cm^{-1} is shown in Region 5 could be assigned to C-N stretch of chitosan powder CA, and all porous membranes. In Region 6, there are several functional group appeared in a range 1080-920 cm^{-1} which are C-O-H deformation, C-NH_2 and C-OH deformation of chitosan powder

CA and Si-O-Si, Si-O-C of porous CA4S1.3N, CA4S3.0N, CA4S5.0N, CA4S8.0N membranes and SiO_2 (Pattnaik et al., 2011; Ramesh and Liew, 2012).

The peak of 895-620 cm^{-1} presented in Region 7 could be assigned to the Si-O-Si, Si-CH_3, N-H bend and O-C=O of chitosan powder, CA, SiO_2 and porous CA4S1.3N, CA4S3.0N, CA4S5.0N, CA4S8.0N membranes (Pattnaik et al., 2011; Ramesh and Liew, 2012). The shifting of peak for Si-O-Si, Si-O-C for all porous membranes proved that after immersed in NaOH, the SiO_2 particles removed from membrane. As a result, the intensity of these peaks also decreased.
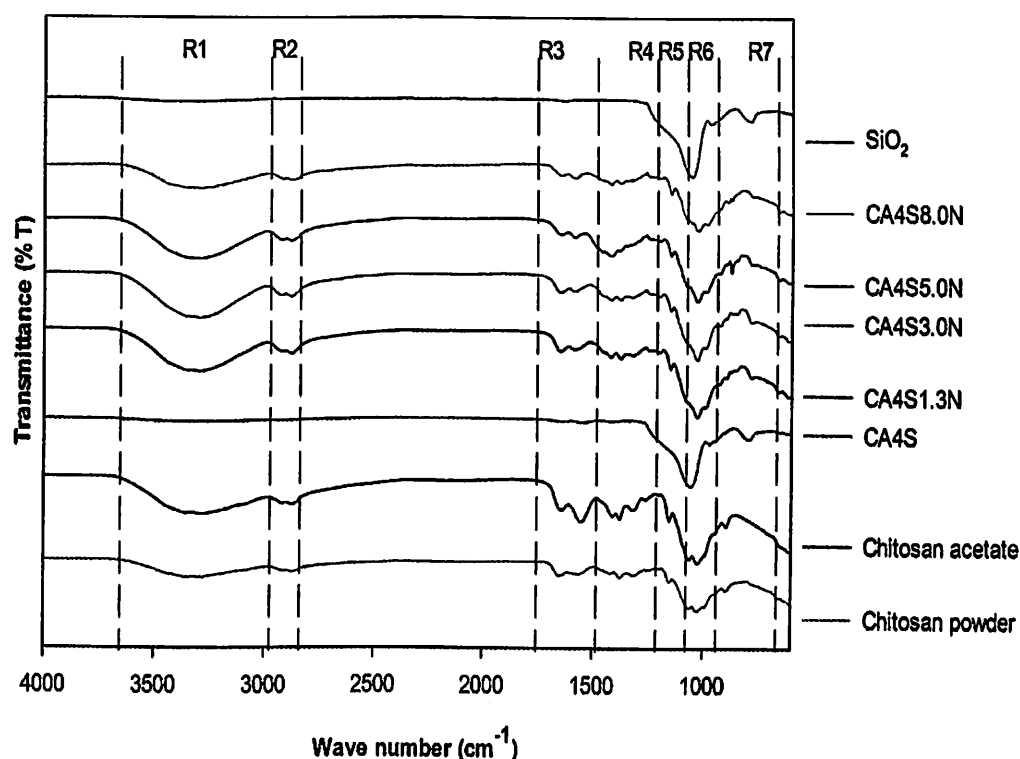
Figure 3.7: FTIR of chitosan powder, chitosan acetate, CA4S1.3N, CA4S3.0N, CA4S5.0N, CA4S8.0N membranes and SiO_2.

All the chemical interaction between chitosan powder, acetic acid and SiO_2 occurred in this study is illustrated in Figure 3.8. After immersed in NaOH, the functional group of porous CA2.0S30N membrane shifted. This showed that SiO_2

particles were removed easily from membrane at optimum concentration of NaOH porogen removal solution (Zeng and Ruckenstein, 1996; Clasen et al., 2006; Santos et al., 2008; Mei et al., 2012). The functional group of all membranes are listed in Table 3.7.
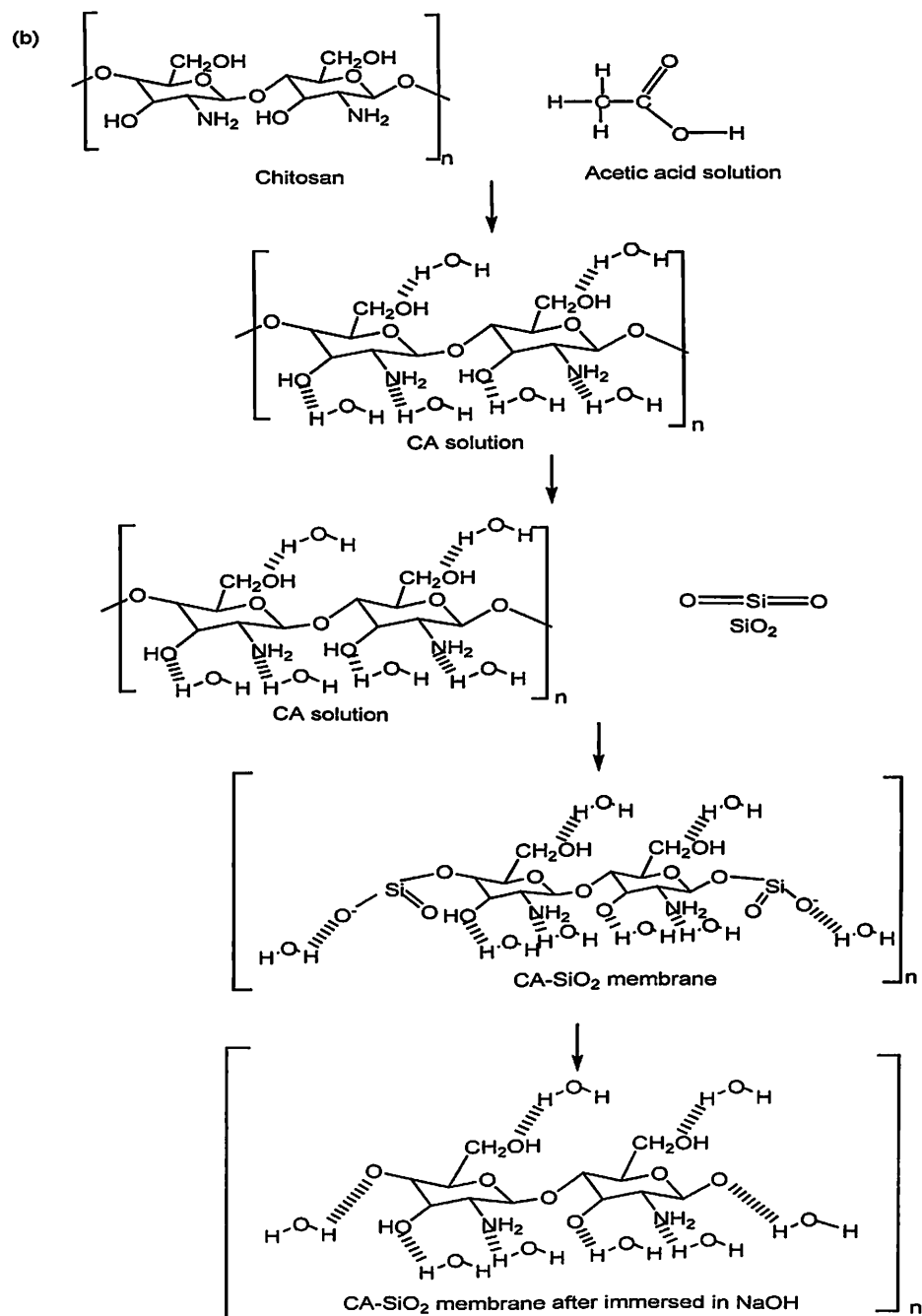
Figure 3.8: Chemical interaction between chitosan powder, acetic acid and SiO_2.

Table 3.4: Functional group of all membranes.

Region	Wavenumber (cm^{-1})	Functional group
R 1	3550-3050	Stretching vibration of N-H and O-H
R 2	2990-2830	Two bands for CH_2 group
R 3	1650-1550	C=O stretch
		N-H bend
R 4	1450-1250	C-O stretch / OH deformation
		C-C(O)-C stretch (acetates)
R 5	1200-1150	C-N stretch
R 6	1080-920	C-O-H deformation
		Si-O-Si
		Si-O-C
		$C-NH_2$
		C-OH deformation
R7	895-620	$Si-CH_3$
		N-H bend
		$R-NH_2$
		O-C=O

3.2.4 Porous CA-SiO₂ Membrane: Thermal analysis

The percentage of chitosan powder, chitosan acetate, CA4S1.3N, CA4S3.0N, CA4S5.0N and CA4S8.0N membranes weight loss was determined from thermogravimetric analysis (TGA). The first phase is desorption process followed by total decomposition. The desorption process for all samples were occurred in a range 100-120°C, with a steady weight loss about 10-15 %. This water desorption process range of temperature and percentage of weight loss is in agreement with previous study on chitosan film thermal properties (Matet et al., 2013). The total decomposition began in the region between 200-300°C with rapid weight loss in a range between 20-60 % . This percentage of weight loss increase after immersed in NaOH porogen removal solution.
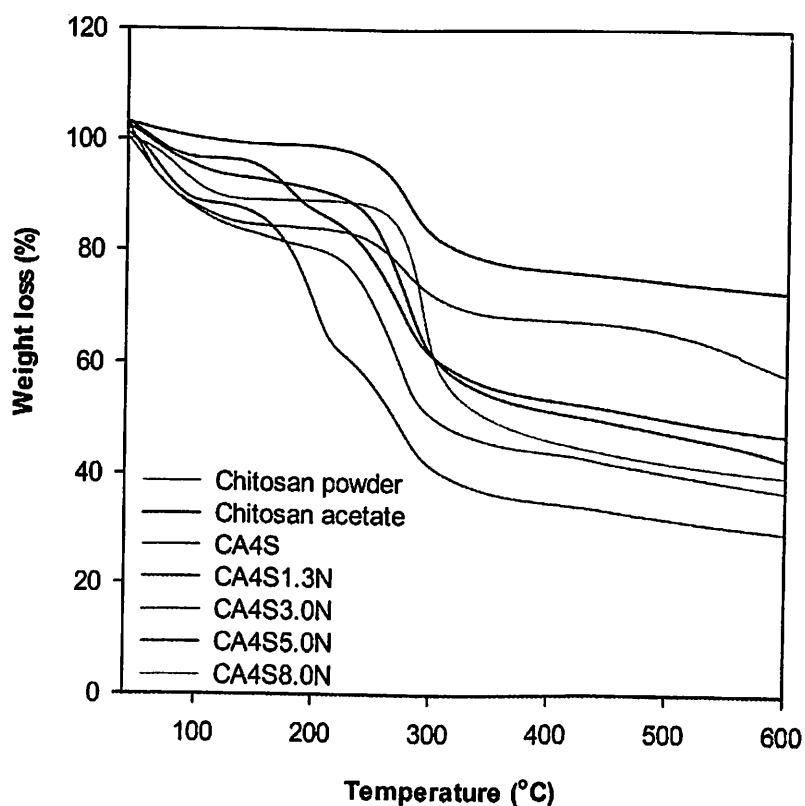
Figure 3.9: TGA thermograms of chitosan powder, chitosan acetate, CA4S1.3N, CA4S3.0N, CA4S5.0N and CA4S8.0N membranes.

The differential scanning calorimetry (DSC) shows the chitosan powder, chitosan acetate, CA4S1.3N, CA4S3.0N, CA4S5.0N and CA4S8.0N membranes are shown in Figure 3.10. The noticeable endothermic peak emerged in a range between 120-130°C, which represents the melting of chitosan membrane crystallinity. The melting peak of CA4S membrane much higher since this membrane was not immersed in NaOH and still contain higher amount of SiO_2. However, this peak started to decrease after immersed in NaOH. The melting point range obtained in this study is almost similar with previous study on poly(lactic acid)/starch/chitosan blended matrix (Bie et al., 2013).
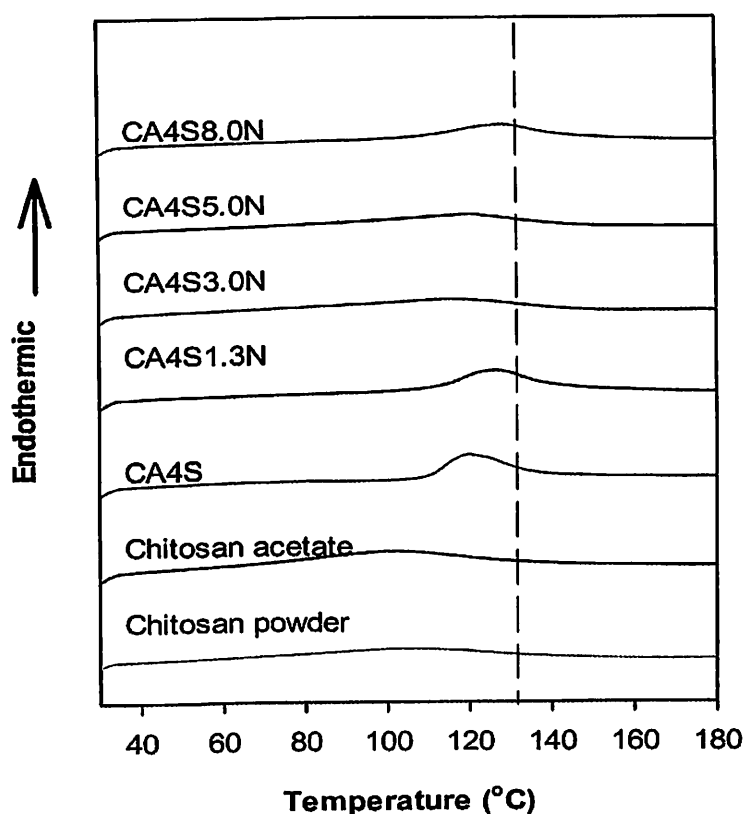
Figure 3.10: DSC of chitosan powder, chitosan acetate, CA4S1.3N, CA4S3.0N, CA4S5.0N and CA4S8.0N membranes.

was obtained in 5.0AA. No existing capacitance component can be seen. However, the R_b increased for 7.0AA due to the high resistance in NH_4CH_3COO solution. All the samples show only resistive component which is attributed to the addition concentrations of NH_4CH_3COO into the system. The bulk resistance values of NH_4CH_3COO were listed in Table 3.5.

Table 3.5: The bulk resistance values of NH_4CH_3COO at different concentrations.

Sample name	Concentration of NH_4CH_3COO (M)	Weight of NH_4CH_3COO (g)	Amount of deionized water (ml)	Bulk resistance, R_b (Ω)
Deionized water	-	-	20	6530.0
1.0AA	1.0	1.54	20	5.5
3.0AA	3.0	4.62	20	3.9
5.0AA	5.0	7.71	20	2.7
7.0AA	7.0	10.79	20	3.0

Figure 3.12 shows the conductivity of NH_4CH_3COO at different concentrations. The conductivity was calculated based on the R_b values Equation 2.1. The conductivity increased inversely proportional with R_b values. The highest conductivity of $(7.0 \pm 0.2) \times 10^{-2}$ S cm^{-1} was obtained with 5.0 M of NH_4CH_3COO electrolyte solution. However, the conductivity decreased at 7.0 M NH_4CH_3COO electrolyte solution. At high concentrations of NH_4CH_3COO, reassociation (ion pairing) of H^+ took place, which decreased conductivity. The conductivity of NH_4CH_3COO at different concentrations is tabulated in Table 3.6.
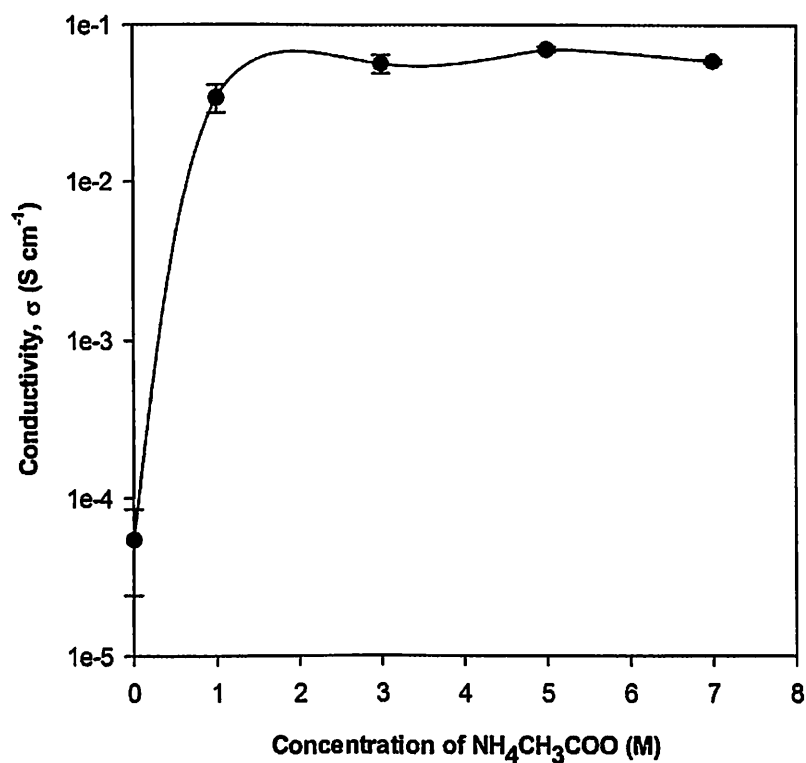
Figure 3.12: Conductivity of NH_4CH_3COO at different concentrations.

Table 3.6: The conductivity of NH_4CH_3COO at different concentrations.

Sample name	Concentration of NH_4CH_3COO (M)	Weight of NH_4CH_3COO (g)	Amount of deionized water (ml)	Bulk resistance, R_b (Ω)
Deionized water	-	-	20	6530.0
1.0AA	1.0	1.54	20	5.5
3.0AA	3.0	4.62	20	3.9
5.0AA	5.0	7.71	20	2.7
7.0AA	7.0	10.79	20	3.0

Since CA4S8.0N membrane shows good morphology, structural, thermal and chemical properties, this membrane has been chosen to immerse in 5.0 M NH_4CH_3COO electrolyte solution. The Nyquist plot of CA4S8.0N and CA4S8.0N after immersed in NH_4CH_3COO electrolyte solution for 2 days (designated as

The temperature dependence for CA4S8.0N and CA4S8.0N5AA-2D were performed within a range of 25 to 90°C as represented in Figure 3.14. The dependencies for both samples can be fitted reasonably by linear lines in this temperature range with correlation coefficients (R^2) of ~0.9. The conductivity of samples increased proportionally with the temperature and showed Arrhenius type relation. Similar to previous conductivity values at room temperature, the conductivity also increased for CA4S8.0N5AA-2D after immersed in NH_4CH_3COO electrolyte solution for 2 days.

The free volume model can be described the behavior of conductivity enhancement with temperature (Rajendran and Uma, 2000). This free volume can expand easily proportional with increasing temperature for CA4S8.0N5AA-2D compared with CA4S8.0N. When the temperature increased, the overall mobility of H^+ ions, solvated molecules and potato starch segments can move into the expansion of free volume. This conducts in increasing of H^+ ions mobility and segmental mobility that will assist H^+ ion transport and almost balance for the hindering effect of H^+ ion clouds. In contrast, there is no existence H^+ ion in CA4S8.0N. Even the free volume expanded at high temperature, but the free volume could not contribute to increase conductivity.

The activation energy for CA4S8.0N and CA4S8.0N5AA-2D were calculated based on Equation 2.2-2.8. The activation energy for CA4S8.0N and CA4S8.0N5AA-2D were 0.2 and 0.03 eV, respectively. The sufficient amount of H^+ ions is utterly assisted to lower activation energy. The energy needed for H^+ ions to hop together on the coordinating site of CA4S8.0N5AA-2D was lower compared with CA4S8.0N (membrane without H^+ ion).
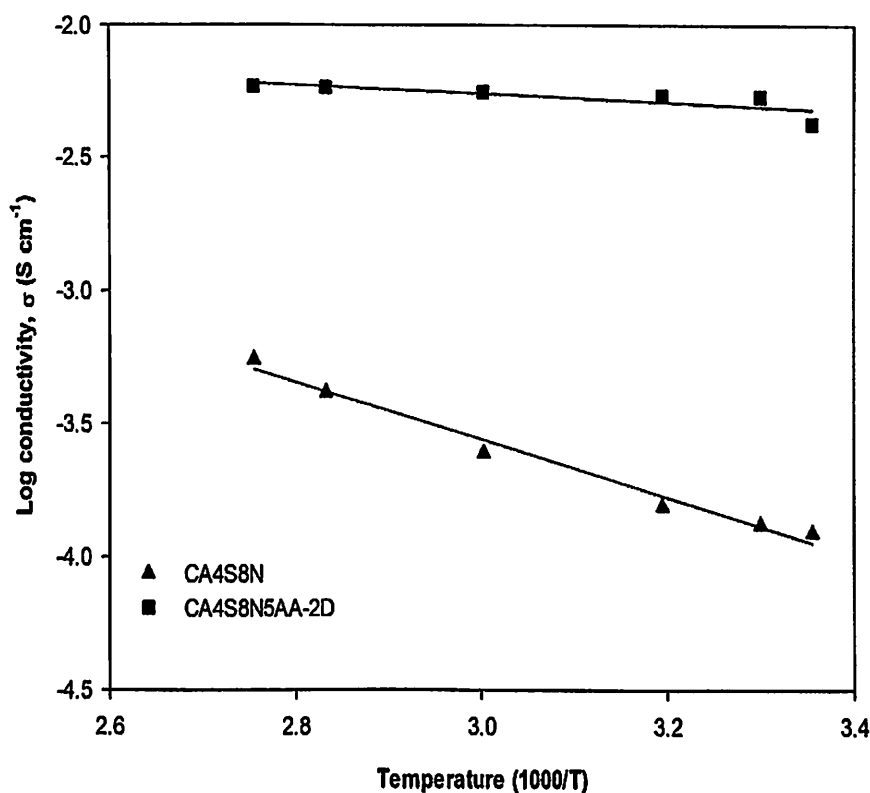
Figure 3.14: The temperature dependence of CA4S8.0N and CA4S8.0N5AA-2D.

3.3.2 Linear Sweep Voltammetry

The linear sweep voltammetry (LSV) of CA4S8.0N and CA4S8.0N5AA-2D are presented in Figure 3.15. The breakdown voltages can be determined by the extrapolating of the straight line from LSV curves. The LSV curve has a breakdown voltage of 1.5 V for CA4S8.0N (Figure 3.15a). Meanwhile the LSV curve has a breakdown voltage of 1.8 V for CA4S8.0N5AA-2D (Figure 3.15b). Generally, the optimal value of breakdown voltage for electrolyte added with other materials such as salts is in between 1.84-1.89 V (Koh et al., 2011). Hence, the LSV value of CA4S8.0N5AA-2D obtained in this study is almost similar with optimal value of breakdown voltage for electrolyte.
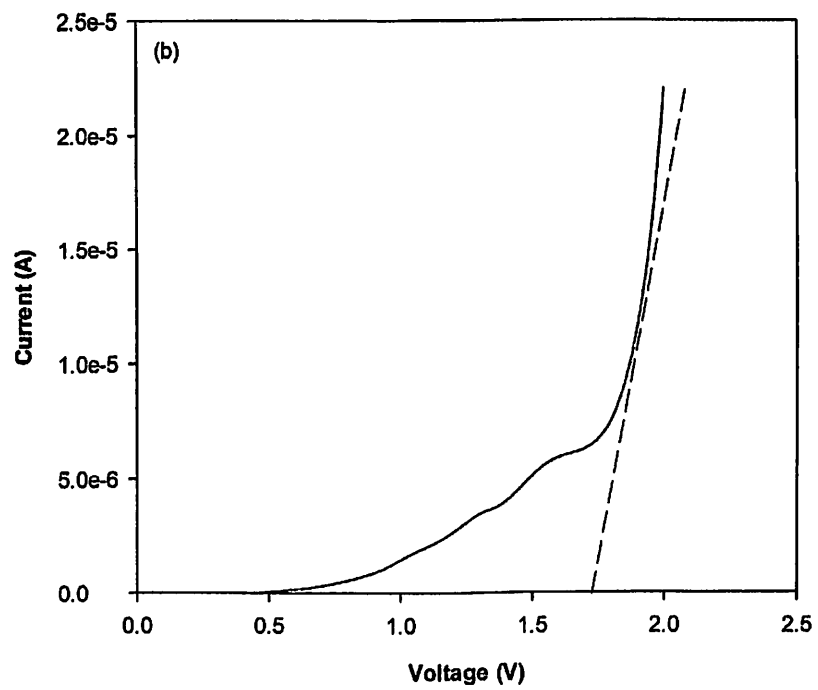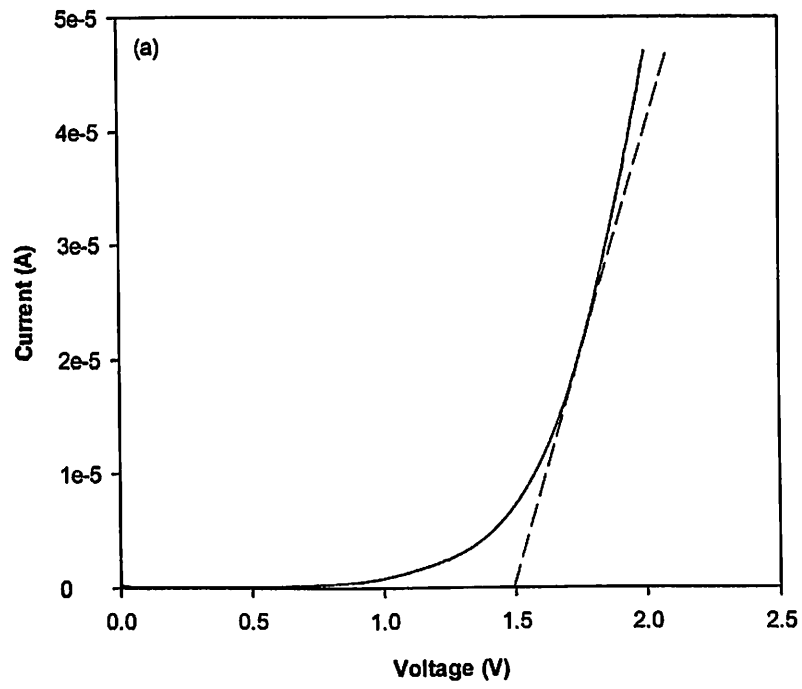
Figure 3.15: Linear sweep voltammetry curves of (a) CA4S8.0N and (b) CA4S8.0N5AA-2D.

3.3.3 Cyclic Voltammetry

The CA4S8.0N5AA-2D was further analyzed using cyclic voltammetry (CV) as shown in Figure 3.16 in order to determine its window stability. The window stability of CA4S8.0N5AA-2D was 3.2 V. When the value of window stability is more than 2.4 V, it can be see that the increasing of currents is due to the increased flow of oxygen gas is evolved. Hydrogen gas is also evolved as the ability to more than -2.8 V. The production of hydrogen and oxygen gas proved that CA4S8.0N5AA-2D membrane suffered to degrade when excess capacity range of 3.2 V at 25°C. In addition, the potential difference of CA4S8.0N5AA-2D (3.2 V) is greater than the stability window of water (1.23 V).
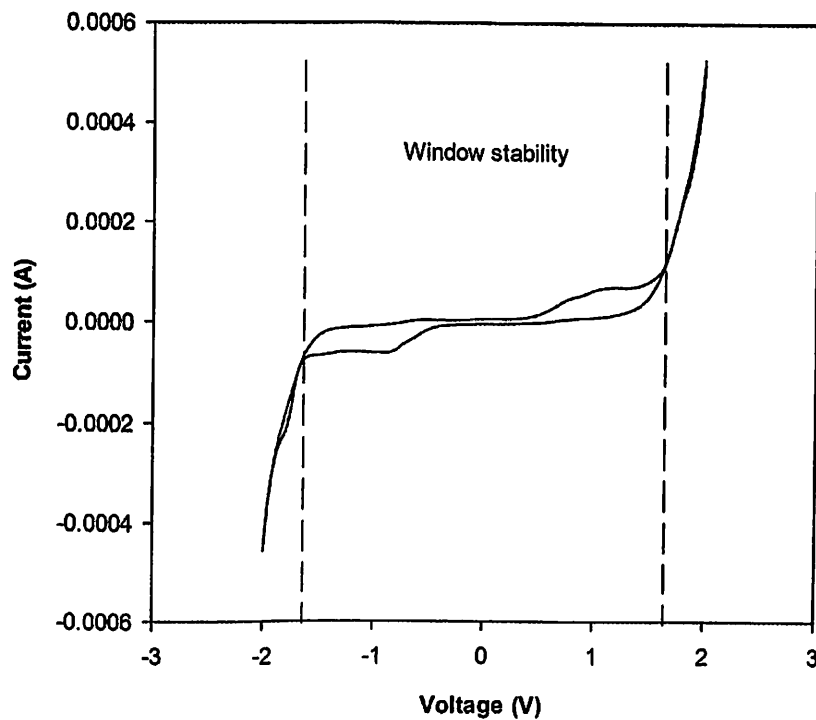
Figure 3.16: Cyclic voltammetry of CA4S8.0N5AA-2D

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3.4 Porous CA-SiO$_2$-NH$_4$CH$_3$COO Membrane: Proton Batteries Properties

3.4.1 Discharge Profile

The discharge profile of Zn+ZnSO$_4$·7H$_2$O ‖ CA4S8.0N5AA-2D ‖ MnO$_2$ coin cell at 0.1, 0.2, 0.5 and 1.0 mA are depicted in Figure 3.17. The discharge profile properties are summarized in Table 3.7. The specific discharge capacities increased as the discharge current increased. The specific discharge capacities obtained in this study higher compared with discharge capacities obtained in previous works on proton batteries discharge capacities which were 17.0 mAh (Ng and Mohamad, 2006), 14.7 mAh (Yap and Mohamad, 2007) and 42.7 mAh (Ng and Mohamad, 2008).
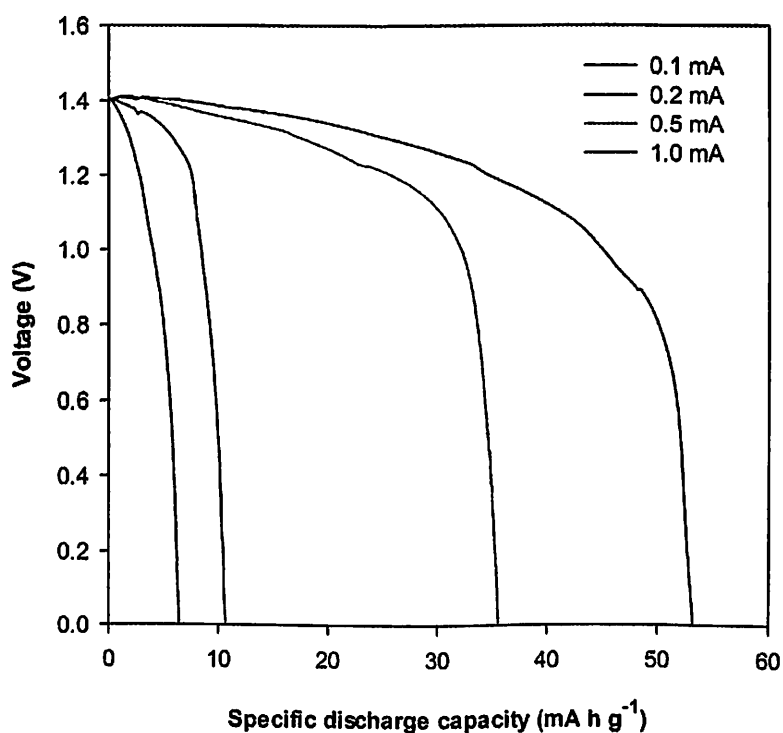
Figure 3.17: The Zn+ZnSO$_4$·7H$_2$O ‖ CA4S8.0N5AA-2D ‖ MnO$_2$ coin cell discharge profile at 0.1, 0.2, 0.5 and 1.0 mA.

Table 3.7: Discharge profile properties at 0.1, 0.2, 0.5 and 1.0 mA.

Discharge current (mA)	Initial voltage (V)	Cutoff voltage (V)	Specific discharge capacity ($mAh\ g^{-1}$)
0.1	1.4	0.0009	6.4
0.2	1.4	0.0083	10.7
0.5	1.4	0.0027	35.6
1.0	1.4	0.0018	53.3

3.4.2 I-V and J-P Plot

The characteristics of I-V and J-P of $Zn+ZnSO_4 \cdot 7H_2O$ || CA4S8.0N5AA-2D || MnO_2 coin cell is shown in Figure 3.18 using current drains ranging from 5.0 μA to 80.0 mA. The voltage dropped from 1.5 V to 0.1 V. The internal resistance (r) value was calculated from the gradient of the I-V plot, which was 0.02 Ω. The I-V curves for both batteries were linear. This result showed that the ohmic contribution was mainly controlled for the polarization of the electrode. The r value much lower compared with previous works on proton batteries which were 29.8 Ω (Ng and Mohamad, 2006), 8.5 Ω (Yap and Mohamad, 2007) and 16.8 Ω (Ng and Mohamad, 2008).

The J-P curves of of $Zn+ZnSO_4 \cdot 7H_2O$ || CA4S8.0N5AA-2D || MnO_2 coin cell is illustrated in Figure 3.19. Based on the J-P curves, the maximum power density was 11.0 mW cm^{-2}. The maximum power densities attained for both batteries were comparable compared with those in previous studies (Yap and Mohamad, 2007; Ng and Mohamad, 2008).
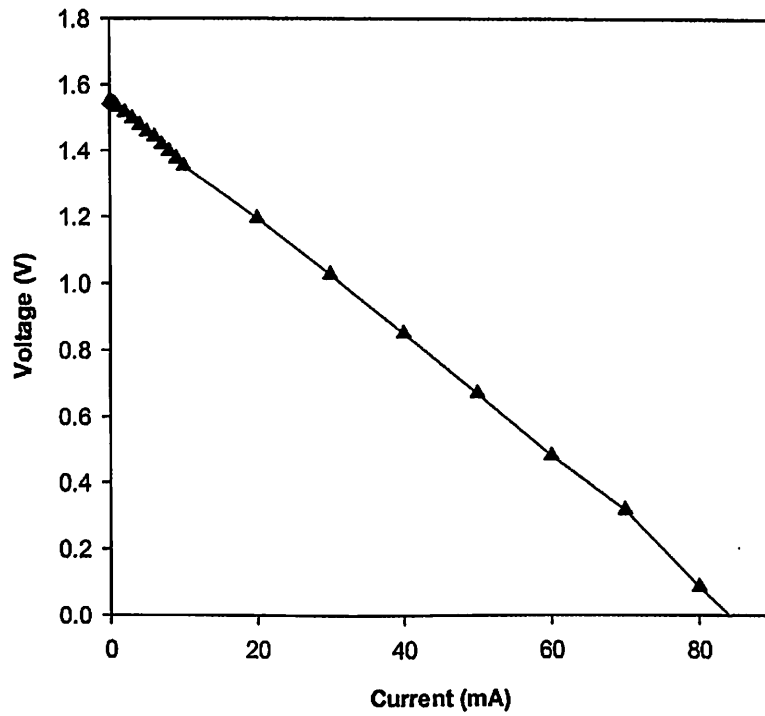
Figure 3.18: Plot of $I-V$ for Zn+ZnSO$_4$·7H$_2$O || CA4S8.0N5AA-2D || MnO$_2$ coin cell.
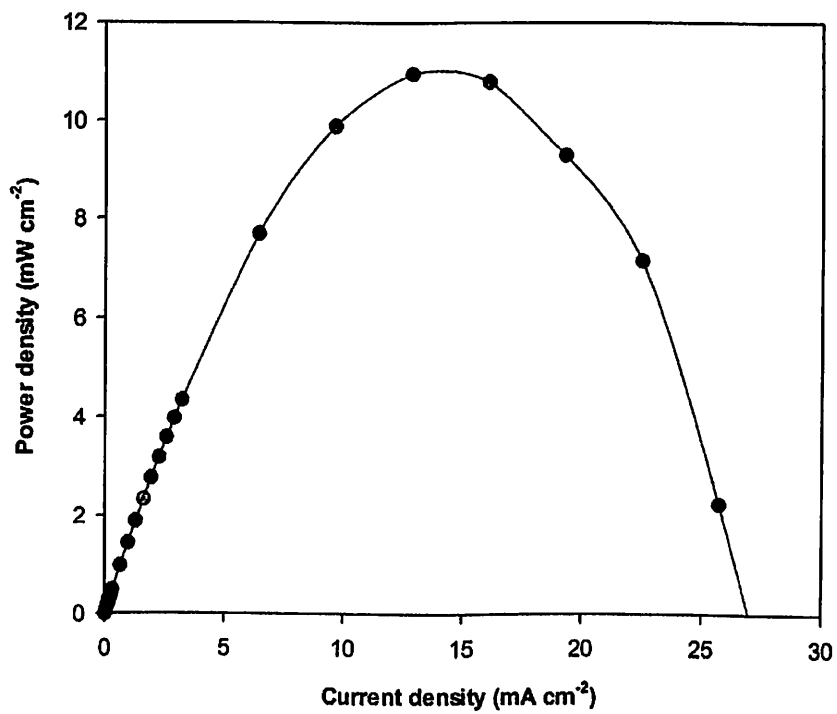
Figure 3.19: Plot of $J-P$ for Zn+ZnSO$_4$·7H$_2$O || CA4S8.0N5AA-2D || MnO$_2$ coin cell.

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3.4.3 Open Circuit Potential

The OCP of $Zn+ZnSO_4 \cdot 7H_2O \parallel CA4S8.0N5AA-2D \parallel MnO_2$ coin cell is presented in Figure 3.20. The OCP of the proton battery was 1.5 V for 8 days. The chemical reaction that probably took place in the proton battery was as follows (Weast, 1977):

At the negative (anode) electrode, Zn was oxidized with the release of two electrons. $ZnSO_4 \cdot 7H_2O$ provided the source of H^+ ions as follows:

$$Zn \rightarrow Zn^{2+} +2e^- \qquad\qquad E^\circ_{ox} = 0.76 \text{ V} \qquad (3.1)$$

$$ZnSO_4 \cdot 7H_2O \rightarrow 7H^+ + 7OH^- + ZnSO_4 \qquad E^\circ_{ox} = -0.82 \text{ V} \qquad (3.2)$$
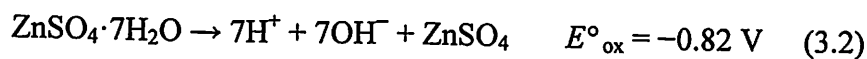
At the positive (cathode) electrode, MnO_2 was reduced with the acceptance of two electrons as follows:

$$MnO_2 +2e^- +4H^+ \rightarrow Mn^{2+} + 2H_2O \qquad E^\circ_{red} = 1.22 \text{ V} \qquad (3.3)$$
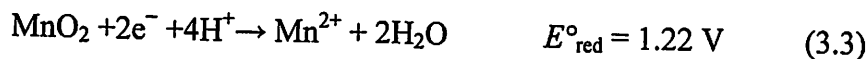
The overall proton battery reaction was calculated based on the standard electrode potential (the oxidation potential is the negative value of the reduction potential) as follows (Linden, 2002):

$$E^\circ_{ox} + E^\circ_{red} = E^\circ_{cell}$$

$$Zn + ZnSO_4 \cdot 7H_2O + MnO_2 +2e^- +4H^+ \rightarrow Zn^{2+} + 7H^+ + 7OH^- + ZnSO_4 + Mn^{2+} +$$

$$2H_2O$$
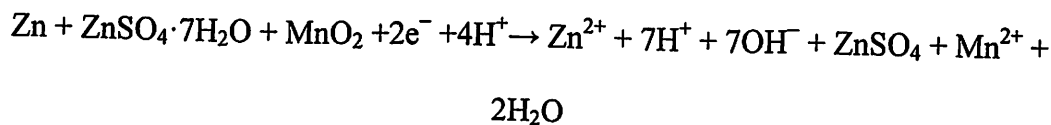
$$-(0.76 - 0.82) \text{ V} +1.22 \text{ V} = 1.28 \text{ V} \qquad (3.4)$$

The overall reaction should provide the cell with E°_{cell} of 1.28 V. However, the E°_{cells} of both batteries from the current work was 1.5 V. Thus, Equations (3.1) to (3.4) are possible because the fabrication of both batteries achieved higher OCP values than those obtained through theoretical calculation. In the present study, the high conductivity of H^+ improved the OCP of the coin cells.
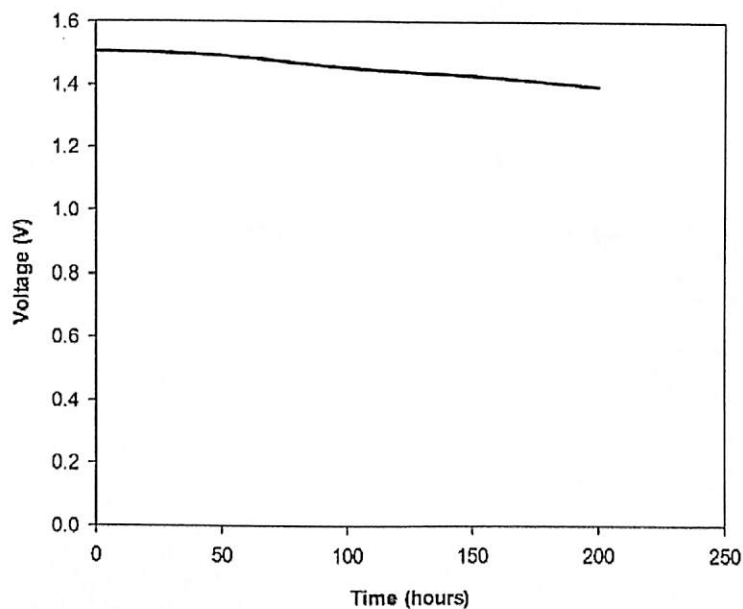
Figure 3.20: The $Zn+ZnSO_4\cdot 7H_2O$ || CA67S8N5A || MnO_2 coin cell open circuit potential.

3.4.4 Application of Proton Batteries

Figure 3.21 shows the virtual and actual combination of two $Zn+ZnSO_4\cdot 7H_2O$ || CA67S8N5A || MnO_2 coin cell to turn on the green light-emitting diode (LED). After 40 hours, the LED was switched off and the voltage dropped from 2.5 to 2.0 V (Figure 3.22).
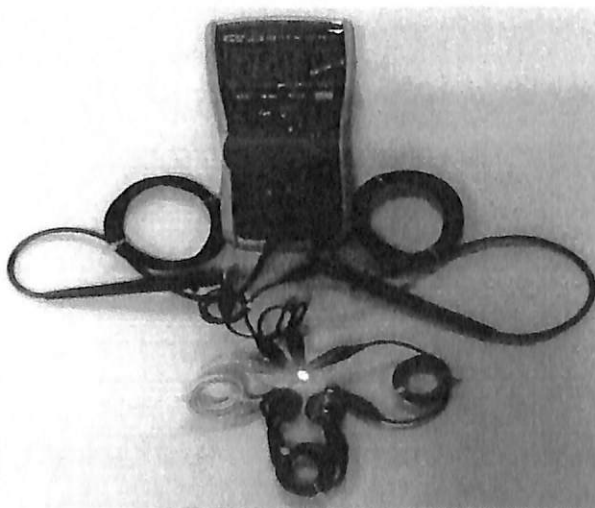
Figure 3.21: The $Zn+ZnSO_4\cdot 7H_2O$ || CA67S8N5A || MnO_2 coin cells actual application with green LED.

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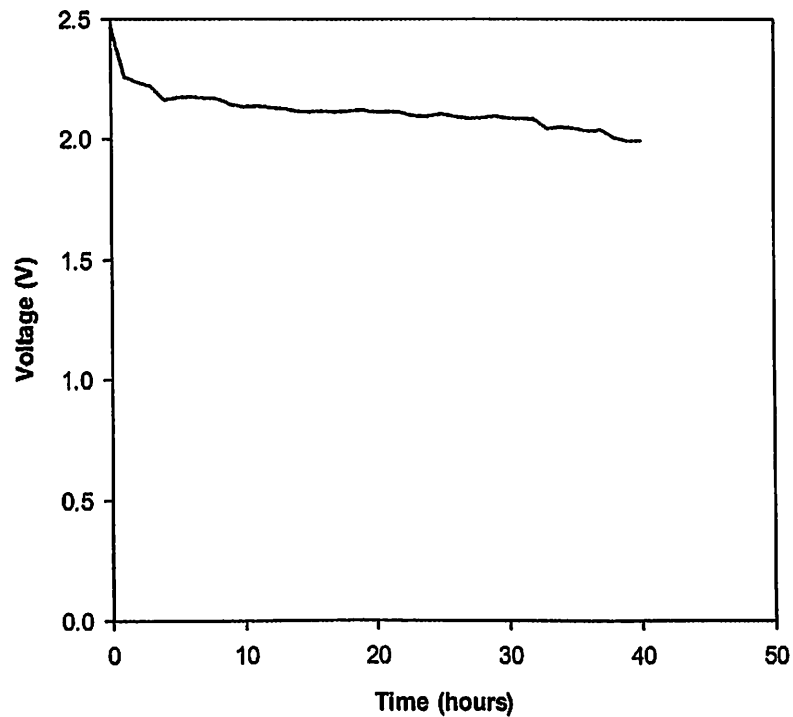
Figure 3.22: The $Zn+ZnSO_4 \cdot 7H_2O$ || CA67S8N5A || MnO_2 coin cells open circuit potential with green LED.

The virtual analysis is important in order to compare with actual application of proton batteries (Figure 3.23). All the parameters configured in virtual analysis were selected based on OCV, discharge and I-V analyses. The OCP values (1.5 V), r (0.02 Ω), and discharge capacity (26.7 mAh). The circuit was simulated and analyzed virtually via transient analysis of MULTISIM, as illustrated in Figure 3.24-3.25. Both of actual and virtual analyses confirmed the proton batteries were functional in both simulation and actual applications.

(a)
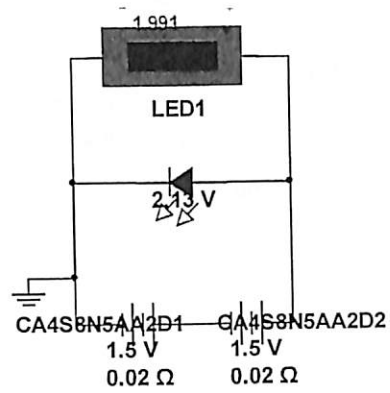
(b)
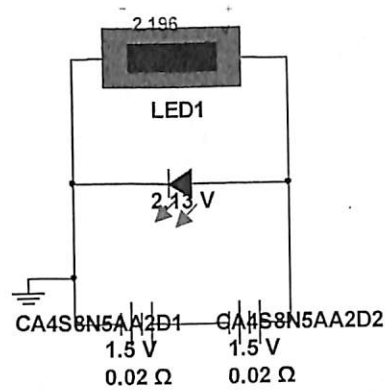
(c)
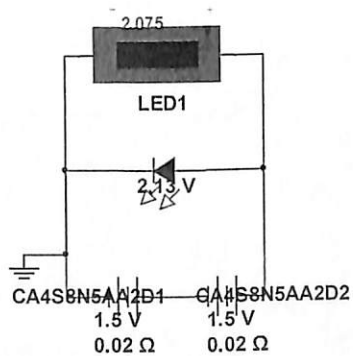
Figure 3.23: Simulation of $Zn+ZnSO_4 \cdot 7H_2O \parallel CA67S8N5A \parallel MnO_2$ coin cells using MULTISM (a) circuit components including virtual coin cells and LED, (b) during switch on and (c) after switch off.

Transient Analysis of Proton Batteries
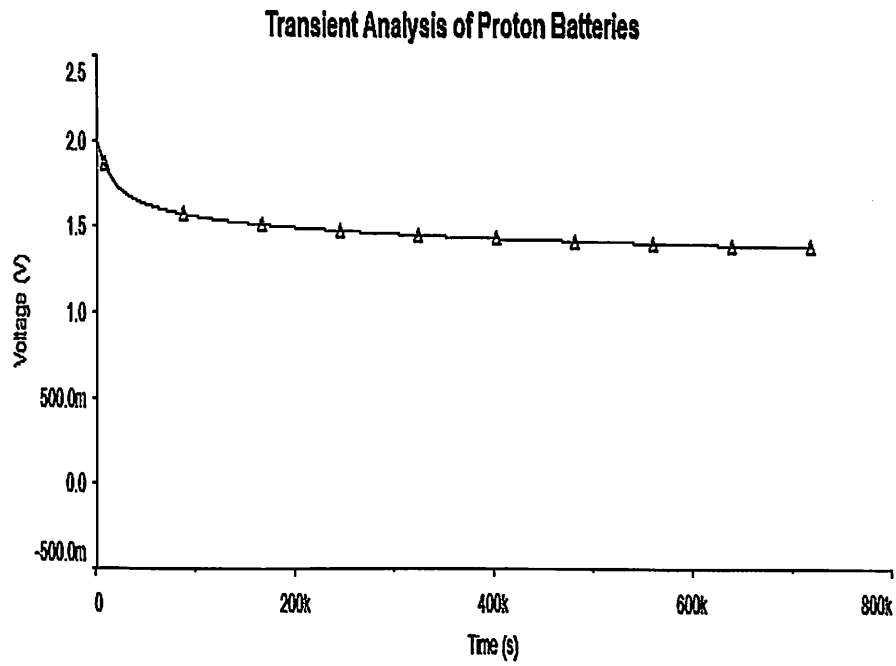
Figure 3.24: Transient analysis of Zn+ZnSO$_4$·7H$_2$O || CA67S8N5A || MnO$_2$ coin cells using MULTISM.

CHAPTER 4

CONCLUSION AND SUGGESTION

5.0 Conclusion

In this study, the porous chitosan acetate-silica membranes have been successfully prepared using inverse porogen/polymer solubility technique. The optimum chitosan to silica ratio for producing largest macroporous membrane was 1:4. The optimum average pore size and degree of crystallinity of 5.9 μm and 90%, respectively were obtained. Fourier transform infrared analysis showed the interaction between chitosan, acetic acid and silica have been occurred based on the shifting of several functional group peaks intensity. The melting point of the membrane obtained from differential scanning calorimetry was 130°C. Thermogravimetry analysis shows the decomposition of the total of the membrane begins at a temperature of 200°C.

The membrane had the higher conductivity of $(4.7 \pm 1.1) \times 10^{-2}$ S cm^{-1} after two-day immersion in 5.0 M ammonium acetate electrolyte solution compared with the membrane before immersed in ammonium acetate electrolyte $(6.0 \pm 0.1) \times 10^{-8}$ S cm^{-1}. The activation energy for membranes before and after immersed in 5.0 M ammonium acetate electrolyte solution were were 0.2 and 0.03 eV, respectively. The breakdown voltage and window stability obtained from linear sweep voltammetry and cyclic voltammetry were 1.5 and 1.8 V, respectively.

The proton batteries displayed an open circuit potential of 1.5 V for 8 days and turned on LED for 40 hours. The internal current resistance of batteries was 0.02 Ω and maximum power density of 11.0 mW cm^{-2}. The specific discharge capacities of

proton batteries were 6.4, 10.7, 35.6 and 53.3 mA h g^{-1} for 0.1, 0.2, 0.5 and 1.0 mA discharge current, respectively.

5.1 Suggestion

It suggested that future research work should focus on producing porous chitosan membrane using other simple technique such as ultrasonicator. This is because this technique will reduce the duration of sample preparation besides can produce uniform pore size and shape.

Other kind of salt such as ammonium nitrate, ammonium bromide can be used to replace ammonium acetate. Different kind of salts can give various results in term of electrochemical properties. Besides that, all the electrochemical properties can be investigated at high temperature. The analysis of fabricated proton batteries can be focus on elevated temperatures to find the resistance of batteries besides focus on failure analysis of batteries.

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LIST OF PUBLICATIONS

Articles

1. Alias, N. and Mohamad, A. A. *Morphology study of electrodeposited zinc from zinc sulfate solutions as anode for zinc-air and zinc-carbon batteries.* Journal of King Saud University - Engineering Sciences (Article in press).

2. Masri, M. N., Nazeri, M. F. M., Ng, C. Y. and Mohamad, A. A. *Tapioca binder for porous zinc anodes electrode in zinc–air batteries.* Journal of King Saud University - Engineering Sciences (Article in press).

3. Siti Salwa Alias, Siew Mian Chee, A.A. Mohamad. *Chitosan-ammonium acetate-ethylene carbonate Membrane for Proton Batteries,* Arabian Journal of Chemistry, 2014 minor correction.

Book

1. Siti Salwa Alias, Ahmad Azmin Mohamad. *Synthesis of Zinc Oxide by Sol-Gel Method for Photoelectrochemical Cell,* SpringerBriefs in Materials (2014).

Conference Proceeding

1. S. S. Alias and A. A. Mohamad. *Preparation and Characterization of Porous Chitosan Membrane for Proton Battery.* Proceeding International Conference on Materials for Advanced Technologies (ICMAT 2013), page 34.

2. Siti Salwa Alias, Zulkifli Mohamad Ariff, and Ahmad Azmin Mohamad. *Preparation and Characterization of Porous Silica-Chitosan Membrane for Proton Batteries.* Proceeding Asia-Pacific Conference on Electrochemical Energy Storage and Conversion (APEnergy2014).

APPENDIXES

ORIGINAL ARTICLE

Morphology study of electrodeposited zinc from zinc sulfate solutions as anode for zinc-air and zinc-carbon batteries

Nurhaswani Alias, Ahmad Azmin Mohamad *

School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia

Abstract The morphology of Zinc (Zn) deposits was investigated as anode for aqueous batteries. The Zn was deposited from zinc sulfate solution in direct current conditions on a copper surface at different current densities. The morphology characterization of Zn deposits was performed via field emission scanning electron microscopy. The Zn deposits transformed from a dense and compact structure to dendritic form with increasing current density. The electrodeposition of Zn with a current density of 0.02 A cm^{-2} exhibited good morphology with a high charge efficiency that reached up to 95.2%. The Zn deposits were applied as the anode in zinc–air and zinc–carbon batteries, which gave specific discharge capacities of 460 and 300 mA h g^{-1}, respectively.

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1. Introduction

Zinc (Zn) is a promising anode candidate for secondary alkaline batteries because of its abundance, relatively low cost, compatibility with aqueous electrolytes, and low-toxic element (Hilder et al., 2012). In secondary alkaline batteries, the anode should be efficient as a reducing agent and must have a high coulombic output, good conductivity, ease of fabrication, and low cost (Linden, 2001). The applications of Zn as an anode tremendously increased because Zn possesses these favor-

able properties. Furthermore, Zn has a large overpotential for hydrogen gas evolution, which allows Zn to operate at lower potentials than the window stability of water (Abe and Miyazaki, 2012). A Zn anode is generally fabricated by various methods such as electrodeposition (Gomes and da Silva Pereira, 2006; Popov et al., 1978) and paste drying (Masri and Mohamad, 2009).

Recent investigations have highlighted electrodeposition as an attractive approach that not only provides a cost-effective intensive method that does not require any equipment, but also has the advantage to control the shape and grain size of the deposit and can provide a high surface area (Bunshah, 1994; Leung et al., 2011; Lehr and Saidman, 2012). Bicelli et al. (2008) also reported that interdiffusion or chemical reactions can be minimized using a low processing temperature (room temperature) during the electrodeposition process. Therefore, various studies on the electrodeposition of Zn were performed in different operating conditions to improve the

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ORIGINAL ARTICLE

Tapioca binder for porous zinc anodes electrode in zinc–air batteries

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Abstract Tapioca was used as a binder for porous Zn anodes in an electrochemical zinc-air (Zn-air) battery system. The tapioca binder concentrations varied to find the optimum composition. The effect of the discharge rate at 100 mA on the constant current, current–potential and current density–power density of the Zn-air battery was measured and analyzed. At concentrations of 60–80 mg cm^{-3}, the tapioca binder exhibited the optimum discharge capability, with a specific capacity of approximately 500 mA h g^{-1} and a power density of 17 mW cm^{-2}. A morphological analysis proved that at this concentration, the binder is able to provide excellent binding between the Zn powders. Moreover, the structure of Zn as the active material was not affected by the addition of tapioca as the binder, as shown by the X-ray diffraction analysis. Furthermore, the conversion of Zn into ZnO represents the full utilization of the active material, which is a good indication that tapioca can be used as the binder.

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1. Introduction

Tapioca is a common plant that can be found in almost every tropical country. Its biodegradable starch is an important source of carbohydrates (Atichokudomchai and Varavinit, 2003; Blagbrough et al., 2010; Breuninger et al., 2009). In general, the starch of tapioca is made up of two major macromolecular components, which can be identified as amylose and

amylopectin (Breuninger et al., 2009; Chung and Liu, 2009; Pérez et al., 2009). Amylose is a linear component polymer that is primarily composed of (1 → 4)-linked α-glucan (Fig. 1a). The degree of polymerization of this polymer can be as high as 600. In tapioca starch, the amylose content can vary from 17% to 20%. Alternatively, amylopectin is the major component of tapioca starch (Fig. 1b). This polymer is made up of α(1 → 4)–linked α-glucan with an α-(1 → 6) branch point. Amylopectin is significantly different than amylose because amylopectin contains approximately 5% branch points (Chung and Liu, 2009; Pérez et al., 2009).

When tapioca starch is heated in excess water, an irreversible structure transition takes place, which is known as starch gelatinization or pasting. The granules of tapioca starch lose their birefringence and crystallinity as more water is absorbed. Upon cooling, tapioca starch experiences an increase in

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The Zn–air battery clearly had better performance with a high discharge capacity compared with the Zn–carbon battery even when similar Zn deposit samples were used as anode for both systems. This result is due to the fact that the Zn–air battery directly used oxygen from the atmosphere, which results in unlimited capacity and high energy density.

4. Conclusions

Zn was successfully deposited via the direct current electrode-position process in $ZnSO_4$ solution without the presence of additives. Electrodeposition of pure Zn at a current density of 0.02 A cm^{-2} produced fine morphology with a high current efficiency without the presence of dendrites. Electrochemical results show that the Zn deposits achieved good specific capacity and stability during the discharge process for the Zn–air and Zn–carbon battery systems. Therefore, a good morphology of Zn deposits can be applied as anode materials in aqueous battery cells.

Acknowledgment

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Chitosan-ammonium acetate-ethylene carbonate Membrane for Proton Batteries

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Abstract

Proton-conducting membranes were prepared using solution-casting technique. The highest membrane conductivity of $(3.83 \pm 0.73) \times 10^{-3}$ S cm^{-1} was achieved in chitosan acetate–50 wt.% ammonium acetate–70 wt.% ethylene carbonate. The batteries were fabricated with a configuration of Zn+ZnSO$_4$·7H$_2$O ‖ chitosan membrane ‖ MnO$_2$ and Zn+ZnSO$_4$·7H$_2$O ‖ chitosan membrane ‖ V$_2$O$_5$. The cathode materials produced open circuit voltages of 1.60 and 1.27 V using manganese (IV) oxide (MnO$_2$) and vanadium (IV) oxide (V$_2$O$_5$), respectively. The discharge capacities of the batteries were 45.0 and 34.7 mAh using MnO$_2$ and V$_2$O$_5$ cathode at 1.0 mA, respectively. The maximum power densities were 1.83 mW cm^{-2} for the battery with MnO$_2$ and 1.36 mW cm^{-2} for the battery with V$_2$O$_5$ cathode.

Siti Salwa Alias
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Synthesis of Zinc Oxide by Sol– Gel Method for Photoelectro- chemical Cells

Acknowledgments

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Preparation and Characterization of Porous Chitosan Membrane for Proton Battery

S. S. Alias and *A. A. Mohamad

Abstract

The porous chitosan membrane has been prepared by using the ultrasonic and solution-cast technique. The chitosan acetate membrane is mixed with various amount of silica from 17-80 wt. %. All the membrane has been immersed in 8 M sodium hydroxide at 60 °C for 1 day to produce porous chitosan acetate-silica membrane. The porous chitosan acetate membrane contain with 67 wt. % silica had the highest pores size of 8.47 μm. This membrane had the highest conductivity of $(8.61 \pm 1.44) \times 10^{-4}$ S cm^{-1} after immersed in 5 M ammonium acetate salt solution for two days. The battery has been fabricated with a configuration of $Zn+ZnSO_4 \cdot 7H_2O$ || chitosan acetate-67 wt. % silica-5 M ammonium acetate electrolyte || MnO_2 gave the open circuit voltage of 1.60 V and can sustain up to 8 days.
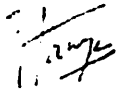
Keywords: Porous chitosan; Membrane; Silica; Ammonium acetate; Proton batteries

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Looking forward to meeting you and wish you a productive and successful workshop in MSI, UniKL

Thank you for your consideration and cooperation.

Yours faithfully,

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Dear Professor,

Invitation for Mendeley and EndNote Workshop

On behalf of Universiti Kuala Lumpur Malaysia Spanish Institute (UniKL MSI) we would like to invite you as a speaker for the workshop on Mendeley and EndNote.

Details are as follows:

      Date   : 20th November 2013

      Time   : 8 am to 5 pm.

      Venue : Al-Farabi Meeting Room

The participants for this workshop will involves 30 lecturers from UniKL MSI. It would be a great pleasure if you accept this invitation and reply to me at your earliest convenience.

Please do not hesitate to contact me who will ensure you are set up with the facilities and assistance needed.

Preparation and Characterization of Porous Silica-Chitosan Membrane for Proton Batteries

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Abstract

Porous chitosan membranes were prepared by stirring mixed solution-cast method. Different concentration of sodium hydroxide porogen removal solution was used to dissolve silica from chitosan acetate membrane. The morphology and structural properties were determined using FESEM and XRD. The optimum average pore size and degree of crystallinity of 5.9 μm and 90%, respectively were obtained. The chemical interations of membranes were detected using FTIR. The membrane exhibited its highest conductivity at $(4.7 \pm 1.1) \times 10^{-3}$ S cm^{-1} after two days immersion in 5.0 M NH$_4$CH$_3$COO electrolyte solution. The membrane had good electrochemical properties based on cyclic voltametry. Fabricated proton batteries displayed an open circuit potential of 1.4 V for 6 days. The specific discharge capacities of proton batteries was 12.0 mA h g^{-1} for 1.0 mA discharge current.

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