PREPARATION AND CHARACTERIZATION OF POROUS CHITOSAN MEMBRANE SOAKED IN AMMONIUM ACETATE ELECTROLYTE FOR PROTON BATTERIES

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by

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

Abbreviation/Symbol	Materials/Compound
CA	Chitosan acetate
DBP	Dibutyl phthalate
DI water	Deionized water
EIS	Electrochemical impedance spectroscopy
EC	Ethylene carbonate
FESEM	Field emission scanning electron microscopy
FTIR	Fourier transform infrared spectroscopy
I-V	Current-voltage
J-P	Current density-power density
KOH	Potassium hydroxide
LED	Light emitting diode
LSV	Linear sweep voltammetry
OCP	Open circuit potential
PEMFC	Polymer electrolyte membrane fuel cell
PTFE	Polytetrafluoroethylene
PVdF-HFP	poly(vinylidene fluoride-*co*-hexafluoropropylene)
Poly(acrylic acid)	PAA
SEM	Scanning electron microscopy
SS	Stainless steel
SHNTs	Sulfonate polyelectrolyte brushes
TGA-DTG	Thermogravimetric-derivative thermogravimetric analysis
XRD	X-ray diffraction

LIST OF SYMBOLS

Symbol	Description
°C	Degree Celsius
σ	Conductivity
E_a	Activation energy
H^+	Proton ion
K	Kelvin
M	Molar
mA	miliAmpere
mA cm^{-2}	miliAmpere per centimeter squared
mA h	miliAmpere hour
mA h g^{-1}	miliAmpere hour per gram
mW cm^{-2}	miliWatt per centimeter squared
n	Number of free mobile
q	Electronic charge
R_b	Bulk resistance
r	Internal resistance
μ	H^+ ions mobility
S cm^{-1}	Siemens per centimeter
T	Temperature
V	Voltage

PENYEDIAAN DAN PENCIRIAN MEMBRAN KITOSAN BERLIANG DIRENDAM DALAM ELEKTROLIT AMMONIUM ASETAT UNTUK BATERI PROTON

ABSTRAK

Membran berliang mendapat banyak perhatian untuk aplikasi bateri kerana keupayaan untuk mengekalkan elektrolit dalam membran. Kesan nisbah berat kitosan:SiO_2 dalam penyediaan membran kitosan berliang telah dikaji dalam kajian ini. Membran kitosan berliang disediakan melalui gabungan ultrasonik dan pengacuan larutan diikuti kaedah fasa balikan dengan nisbah berat SiO_2 penyingkir porogen 0.4-4.0. Membran kitosan berliang dengan nisbah berat kitosan-SiO_2 1:2.0 (PC5) menghasilkan saiz liang optimum 8.5 ± 0.4 μm dengan struktur amorfus, penyerapan air tertinggi 146.4 ± 7.3%, interaksi kimia, kestabilan haba dan sifat tegangan yang baik. Proses rendaman lanjutan membran dalam 5.0 M larutan elektrolit NH_4CH_3COO selama 48 jam (PC5-5A48H) menghasilkan kekonduksian tertinggi $(4.5 \pm 1.7) \times 10^{-3}$, penyerapan elektrolit tertinggi 308.6 ± 15.4%, tenaga pengaktifan terendah 0.04 ± 0.002 eV, voltan pecahan optimum 1.8 V, interaksi kimia, morfologi, struktur amorfus, kestabilan haba dan sifat tegangan yang baik. Fabrikasi sel syiling bateri proton menggunakan PC5-5A48H menunjukkan voltan litar terbuka 1.5 V selama 7 hari, ketumpatan kuasa maksimum 6.7 mW cm^{-2} dan rintangan dalaman yang kecil 0.03 Ω. Kapasiti nyahcas tertentu yang diperolehi dari profil nyahcas meningkat (23.4, 41.0 44.6 and 47.7 mA h g^{-1}) berkadar terus dengan arus nyahcas (0.1, 0.5, 1.0 and 5.0 mA). Voltan keluaran eksperimen dan simulasi dua sel syiling bateri proton yang digabungkan secara sesiri dengan diod pemancar cahaya warna hijau adalah antara 2.0-2.6 V.

PREPARATION AND CHARACTERIZATION OF POROUS CHITOSAN MEMBRANE SOAKED IN AMMONIUM ACETATE ELECTROLYTE FOR PROTON BATTERIES

ABSTRACT

Porous membrane received much attention for batteries application due to the ability to retain electrolyte inside membrane. The effects of chitosan:SiO_2 weight ratio in preparation of porous chitosan-SiO_2 membranes were investigated in this study. Porous chitosan membranes were prepared via ultrasonic mix solution-cast and phase inversion method using different SiO_2 porogen removal weight ratio from 0.4-4.0. Porous chitosan membrane with chitosan:SiO_2 weight ratio 1:2.0 (PC5) produced optimum pores with size of 8.5 ± 0.4 μm, as well as with an amorphous structure, the highest water uptake of (146.4 ± 7.3) %, good chemical interaction, thermal stability and tensile properties. Further soaking this membrane in 5.0 M NH_4CH_3COO electrolyte solution for 48 hours (PC5-5A48H) produced the highest conductivity ($(4.5 \pm 1.7) \times 10^{-3}$), highest electrolyte uptake (308.6 ± 15.4 %), lowest activation energy (0.04 ± 0.002 eV), optimum breakdown voltage (1.8 V), good chemical interaction, morphology, amorphicity, thermal stability and tensile properties. Fabrication of coin cell proton battery using PC5-5A48H displayed an open circuit potential of 1.5 V for 7 days, maximum power density (6.7 mW cm^{-2}), and small current resistance (0.03 Ω). Specific discharge capacities were obtained from discharge profile increment (23.4, 41.0, 44.6, and 47.7 mA h g^{-1}) as the discharge currents increased (0.1, 0.5, 1.0, and 5.0 mA). The output voltage of experimental and simulation of the two coin cell proton batteries combined in series connected with green light emitting diode was between 2.0-2.6 V.

CHAPTER 1

INTRODUCTION

1.1 Background

Chitosan is a linear polysaccharide that is composed of randomly distributed β-(1-4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine derived from deacetylation of chitin [1]. It has high hydrophilicity and good for proton conducting application attributed by the hydroxyl (–OH), ether (C–O–C), and primary amine (NH_2) group on its backbone that can attach with oxygen from the water molecule to produce hydrogen bond ($CH_2OH–OH_2$, $OH–OH_2$ and $NH_2–H_2O$) [2,3]. Hence, modification of proton-conducting membrane based on chitosan has received much attention by many researchers aiming for environmental-friendly materials as green materials for electrochemical application [1,4-8].

Inert ceramic oxides fillers, such as silica (SiO_2), alumina (Al_2O_3), copper oxide (CuO), or titanium oxide (TiO_2) have been used to produce porous membrane [9-12]. This porous membrane has been widely utilized in various applications, such as dehumidification processes [13], medical purposes [14], and electrochemical sensors [15]. Among these inert ceramic oxides, SiO_2 has excellent properties as a porogen agent to produce porous membrane via phase inversion technique [14,16-18]. In this method, SiO_2 particles are soluble in alkaline sodium hydroxide (NaOH) solutions [14,16,19]. The dissolution of SiO_2 particles in NaOH can generate porous chitosan membrane.

The proton batteries consist of three major components, which are zinc (Zn) anode; electrolyte that can be in liquid, gel, or solid form; as well as manganese (IV) oxide (MnO_2) cathode. Normally, the proton-conducting electrolyte based on chitosan mixed with salt, such as ammonium acetate (NH_4CH_3COO) [4], ammonium nitrate (NH_4NO_3) [20], and ammonium chloride (NH_4Cl) [21], is involved in the transportation of proton charge carriers, such as H^+ and NH_4^+, as a source of electric energy via direct conversion of chemical energy. Besides, the existence of uniform pores inside the membrane can be enhanced in charge carriers transportation through the pores and increase conductivity values together with segmental motion of polymer [22].

1.2 Problem statement

Most of prior studies have used chitosan proton conducting polymer electrolyte in solid form. The drawback is the ability of solid chitosan electrolyte to absorb water lower (~ 95 %) compared with porous chitosan (~173 %) [14]. This is due to the dense and rough surface morphology of solid chitosan electrolyte since the salt was complexed with chitosan during preparation process [6,23-27]. In contrast, the porous chitosan membrane has pores on surface and cross-section. Santos et al. [14] found the size of pores inside the porous chitosan membrane was in a range between 4 to 20 μm, while Clasen et al. [16] obtained the size of pores in a range of 40 to 63 μm. The existence of pores inside the membrane shows the potential of porous membrane to soak in electrolyte compared with solid polymer electrolyte. However, the analyses of porous chitosan membrane in prior studies still lack on several characterization techniques such as chemical interaction, structural and thermal stability and tensile properties.

Various types of ammonium salts were used to increase the conductivity of chitosan [28-33]. The NH_4CH_3COO is one of type of salt that has been mixed with chitosan and achieved the conductivity up to 10^{-4} S cm^{-1} [34]. However, in previous study, NH_4CH_3COO was complexed with chitosan solid polymer electrolyte during sample preparation. The using of porous chitosan membrane has potential to absorb extra H^+ ions during soaking in electrolyte and increase conductivity. This is due to the existence of pores inside membrane compared with solid polymer electrolyte. However, the effect of soaking chitosan membrane in NH_4CH_3COO electrolyte to improve conductivity values and electrolyte uptake still has not been looked into.

Prior studies on proton batteries based on chitosan solid polymer electrolyte have shown that the discharge capacity was in the range of 9.0 to 17.0 mA h by using discharge current between 0.6 and 1.0 mA [26,35]. In these studies, the solid polymer electrolytes have been chosen based on the highest conductivity and good electrochemical properties. Since the porous chitosan membrane have the ability to absorb extra H^+ ions during soaking in electrolyte, hence, it has potential in improving the electrochemical properties and increase the discharge capacity of proton batteries. However, the previous studies on porous chitosan membrane were mainly focused on fuel cell application and performance [36-38].

Moreover, there was no previous studies had been done in comparing the real circuit and simulation of proton batteries performance. The value of proton batteries performance obtained from simulation result is important in comparing with the real performance after being connected with load. For instance, Wu et al. [39] simulated the discharge behaviors of batteries in series and parallel-connected battery pack.

However, this simulation was focused on lithium-ion batteries. Meanwhile, Mohamad et al. [40] connected three cells in series to turn on a digital watch, but it was not supported by numerical analysis.

1.3 Objectives

This work mainly focused on the following objectives:

i. To characterize the morphology, pores size, structural, water uptake, chemical interaction, thermal stability and tensile properties of porous chitosan membranes prepared via phase inversion method and as SiO_2 porogen agent.

ii. To improve the conductivity of porous chitosan membrane-NH_4CH_3COO electrolyte with optimum electrolyte uptake, high breakdown voltage, good chemical interaction, morphological, structural, thermal stability, and tensile properties.

iii. To fabricate and characterize the properties of $Zn+ZnSO_4 \cdot 7H_2O$ || porous chitosan membrane-NH_4CH_3COO electrolyte || MnO_2 coin cell proton battery, and simulate using MULTISIM.

1.4 Thesis outline

This chapter presents an introduction to the thesis with a brief explanation on the problems and the objectives of the present study. Meanwhile, Chapter 2 reviews the fundamental principle of polymer electrolyte, recent progress, and improvement of the proton-conducting membrane properties based on chitosan, as well as the use of SiO_2 as a porogen agent to produce porous membrane. The basic mechanism and the performance of proton batteries are also discussed. Next, Chapter 3 explains all