EFFECT OF CATALYST LOADING IN DIRECT METHANOL FUEL CELL USING SULFONATED-POLY-ETHER-ETHER-KETONE/CHARGED SURFACE MODIFYING MACROMOLECULES MEMBRANES.

SITI ERLYANE BINTI ROSLI

UNIVERSITI TEKNOLOGI MALAYSIA

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SITI ERLYANE BINTI ROSLI

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Specially dedicated to

My beloved parents and brothers,
My family members and friends,
Thanks for their support, encouragement and inspiration.

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ABSTRACT

Direct methanol fuel cell (DMFC) for portable power applications requires high power density and high-energy conversion efficiency which largely depends on membrane and electrocatalyst to achieve high performance. In improving these factors, the first objective of this study was to synthesize and characterize sulfonated-poly-ether-ether-ketone (SPEEK) and SPEEK/ charged surface modifying macromolecules (cSMM). The second objective was to synthesize and characterize Platinum/Ruthenium (Pt/Ru) catalyst for anode and Palladium (Pd) catalyst for cathode. Consequently, the third objective was to test the performance of SPEEK/cSMM using single cell DMFC under different catalyst loadings. In this work, 20 wt %, 30 wt % and 40 wt % Pt/Ru were used as the catalyst for anode while 5 wt % and 10 wt % Pd were used on the cathode, with three different loadings of 2, 4 and 6 mg/cm^2, respectively for each 4 cm^2-electrode. The electrodes were prepared using catalyzed diffusion media (CDM) method, while the membrane electrode assembly (MEAs) was prepared by hot pressing method. The single cell DMFC tests were run at constant condition of 100 ml min^{-1} air flowrate, 1M methanol concentration, 1 ml min^{-1} methanol flowrate and 60°C operating temperature, respectively. In finding the suitable catalyst loading in anode, commercial 40 wt % Pt electrode was used as the cathode. On the anode, it was found that the best result of catalyst loading was 30 wt % Pt/Ru with 4 mg/cm^2, which then was used to get the suitable catalyst loading in cathode for 5 wt % and 10 wt % of Pd/Carbon. On the cathode, the best catalyst loading was 10 wt % Pd with 4 mg/cm^2 loading. By applying the best loading of catalysts, the highest power density of 123 mW/cm^2 was achieved, eventhough its open circuit voltage (OCV) and ohmic voltage yielded the lowest values. This shows that a combination of the best anode and cathode loading were able to generate the highest power density for SPEEK/cSMM electrolyte membrane for DMFC application.

ABSTRAK

Sel bahan api metanol (DMFC) untuk aplikasi mudah alih memerlukan ketumpatan kuasa dan tenaga kecekapan penukaran yang tinggi yang sebahagian besarnya bergantung pada membrane dan pemangkin untuk mencapai prestasi yang tinggi. Dalam meningkatkan faktor-faktor ini, objektif pertama kajian ini ialah untuk sintesis dan mencirikan pengsulfonan poli-eter-eter-ketone (SPEEK) dan SPEEK/ makromolekul pengubah permukaan bercas (cSMM). Objektif kedua ialah untuk sisntesis dan mencirikan pemangkin Platinum/Ruthenium (Pt/Ru) untuk anod dan pemangkin Paladium (Pd) untuk katod. Seterusnya, objektif ketiga ialah untuk menguji prestasi SPEEK/cSMM menggunakan sel tunggal DMFC pada muatan pemangkin yang berbeza. Dalam kerja ini, 20 wt %, 30 wt % dan 40 wt % Pt/Ru digunakan sebagai pemangkin pada bahagian anod manakala 5 wt % dan 10 wt % Pd digunakan pada bahagian katod, dengan tiga muatan berbeza iaitu masing-masing 2, 4 dan 6 mg/cm^2 untuk setiap 4 cm^2 elektrod. Elektrod disediakan dengan menggunakan kaedah media penyebaran pemangkin (CDM) manakala pemasangan membran elektrod (MEA) disediakan dengan kaedah penekanan panas. Sel tunggal DMFC masing-masing diuji pada kadar aliran udara 100 ml min^{-1}, kepekatan metanol 1M, kadar aliran metanol 1 ml min^{-1}dan suhu operasi 60 °C. Dalam mendapatkan pemangkin muatan yang sesuai pada bahagian anod, elektrod komersial 40 wt % Pt digunakan sebagai katod. Pada anod, didapati pemangkin yang terbaik ialah 30 wt % Pt/Ru pada 4 mg/cm^2, yang mana kemudian digunakan untuk mendapatkan pemangkin muatan di katod yang sesuai untuk 5 wt % dan 10 wt % Pd/Karbon. Pada katod, pemangkin muatan yang terbaik dijumpai ialah 10 wt % Pd pada 4 mg/cm^2. Menggunakan pemangkin muatan yang sesuai ini, menghasilkan ketumpatan kuasa yang paling tinggi iaitu 123 mW/cm^2, walaupun voltan litar terbuka (OCV) dan voltan ohmnya menghasilkan nilai terendah. Ini menunjukkan anod dan katod ini berkebolehan untuk menghasilkan ketumpatan kuasa yang paling tinggi untuk membran elektrolit SPEEK/cSSM bagi aplikasi DMFC.

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LIST OF ABBREVIATIONS

C	-	Carbon
CCM	-	Catalyst-Coated Membrane
CDM	-	Catalyzed Diffusion Media
cSMM	-	Charged Surface Modifying Macromolecules
DMFC	-	Direct Methanol Fuel Cell
DS	-	Degree of Sulfonation
EDX	-	Energy Dispersive X-Ray
GDL	-	Gas Diffusion Layer
H^1NMR	-	Hydrogen-Nuclear Magnetic Resonance
IEC	-	Ion Exchanged Capacity
MEA	-	Membrane Electrode Assembly
MOR	-	Methanol Oxidation Reaction
MPL	-	Microporous Layer
OCV	-	Open Circuit Voltage
ORR	-	Oxygen Reduction Reaction
PEM	-	Polymer Electrolyte Membrane
PEMFC	-	Proton Exchange Membrane Fuel Cell
PEEK	-	Poly (ether ether ketone)
SEM	-	Scanning Electron Microscope
SPEEK	-	Sulfonated Poly (ether ether ketone)

LIST OF SYMBOLS

A	-	Ampere
A/cm^2	-	Area per square centimeter
g	-	Gram
I	-	Current
mg/cm^2	-	Miligram per square centimeter
S	-	Siemens
v	-	Voltage

CHAPTER 1

INTRODUCTION

1.1 Introduction

Fuel cell is an electrochemical device that converts the chemical energy from fuel into electricity through a chemical reaction with oxygen or oxidizing agent. Fuel can run as long as fuel is accessible and no need to recharge. Fuel cells are mainly fitting in power systems because of their energy density, easy to handle, simple in design and inexpensive (Cacciola *et al.*, 2001). Fuel cells have two electrodes which are anode and cathode that are separated by an electrolyte. The anode provides boundary between electrolyte and fuel while the cathode provides boundary between electrolyte and oxygen. Electrolyte is a purposely designed for proton that can surpass through it but filter electrons. The free electrons pass through a wire and produce electric current. The protons pass through to the cathode via the electrolyte and will react with oxygen to create water and carbon dioxide. The most important design in fuel cells are the electrolyte substance which usually defines the type of fuel cell, the anode catalyst that breaks down the fuel into electrons and proton and the cathode catalyst which turns the ion into waste chemicals such as water and carbon dioxide.

There are two types of low-temperature fuel cells which are proton exchange membrane fuel cell (PEMFC) and direct methanol fuel cell (DMFC) (Rao and Trivedi, 2005). Several researchers believed that the DMFC is an appropriate and capable options for portable devices in solving the problem of future energy (Cacciola *et al*., 2001; Segura and Andu, 2009; Verma, 2000). This is because

DMFC can be operated at a low temperature, has high energy-conversion efficiency and produces a low level of pollutants. Moreover, DMFCs using liquid and renewable energy methanol fuel, which is easily stored and transported and simplifies the fuel cell system has been considered to be a favorable option in terms of fuel usage and feed strategies (Wasmus and Ku, 1999) as compared to PEMFC which uses hydrogen gas as fuel. Yet the DMFCs have their own challenges that need to be overcome before they can be massively commercialized. Few of the major problems faced in DMFCs are including methanol crossover, that can overcome by developing improved membranes, meanwhile slow anode and cathode kinetics can be overcame by developing improved anode and cathode catalysts.

The methanol crossover from anode to cathode together with the proton appears to be a part of limitation for DMFCs to become a commercially possible power generator. In order to overcome this problem, many studies are focused on developing new membranes materials that have high proton conductivity but low in methanol crossover. Industry used Nafion® membrane produced commercially by Dupond, has excellent proton conductivity but also possesses very high methanol permeability that limited its advantage in DMFC application.

Most researchers have focused on exploring new anode catalysts that can efficiently enhanced the electro-oxidation of methanol kinetics and looking for new membranes that have a lower methanol crossover (Ding, 2010; Hosseini and Bodaghi, 2011). Several materials have also been studied to discover material of electrode that provides superior catalytic activity to produce lower over potentials towards the methanol oxidation reaction (MOR) and oxygen reduction reaction (ORR).

1.2 Problem Statement

The limiting factors in achieving high performance of DMFC relate to membrane and electrodes. These factors in DMFC need to be overcome before they can be massively commercialized. Sulfonated poly (ether ether ketone) (SPEEK) is getting more attention as Nafion competitor in DMFC application (Jaafar et al., 2009; Jones and Roziere, 2001; Jung and Park, 2009; Yang, 2008). The membrane surface of SPEEK which is more hydrophilic tends to favor water uptake and enhance proton conductivity. The proton conductivity of the membrane can be enhanced if the hydrophilicity of the membrane is improved. Moreover, SPEEK also provides a tortuous pathway towards methanol that reduce methanol crossover through the membrane. Furthermore, the previous work by Norddin *et al*. (2008) has shown that the performance in DMFC has improved further by modification of SPEEK with cSMM polymer. The overall membrane performance of SPEEK/cSMM was better than Nafion while their open circuit voltage (OCV) and power density is comparable to Nafion. Therefore, SPEEK/cSMM has the potential to compete with Nafion, if the appropriate condition of catalyst loading for SPEEK/cSMM is determined.

Low power density in DMFC system is caused by poor kinetics of the catalyst reactions (Baldauf and Preidel, 1999). Catalyst loading in electrode is an important parameter to be controlled because it influences the cell performance. Even though high catalyst loading is required in DMFCs to accomplish high power density but it also contributes to poor DMFC performance since it can 'poison' the electrode. Generally, platinum (Pt) is used at the cathode and an alloyed platinum-ruthenium (Pt-Ru) at the anode. Natter *et al*. (2003) synthesized electrodes of Pt-Ru for DMFC and it turned out to be most active for the methanol electro oxidation at about 50 % Ru. On the other hand, Palladium (Pd) is showing a potential as cathode catalyst sine its reactivity towards ORR is only second to Platinum. In advantage, Pd has better resistance to mass transfer loss than Pt. In this study, the cathode catalyst of Pt is replaced by another catalyst material which is Pd, and will be tested with different anode and cathode catalyst loading to achieve higher power density.

1.3 Objectives

The general aim of this study is to find the best catalyst loading combination of anode and cathode electrode for SPEEK/cSMM membrane in order to produce higher power density. The specific objectives of this study are listed as follows;

i. To synthesize and characterize SPEEK and SPEEK/cSMM.
ii. To synthesize and characterize Pt/Ru and Pd for anode and cathode as catalyst for DMFC.
iii. To test the performance of SPEEK/cSMM using single cell DMFC under different catalyst loading.

1.4 Scope

In order to achieve the objectives of this study, the following scopes have been drawn:

i. Preparing SPEEK and SPEEK/cSMM membrane via intercalation method.
ii. Characterizing SPEEK and SPEEK/cSMM on water uptake, methanol permeability and proton conductivity.
iii. Preparing the electrode consisting of 2, 4 and 6 mg/cm^2 catalyst loading for 20, 30 and 40 weight % of Pt/Ru as well as for 5 and 10 weight % of Pd.
iv. Preparing membrane electrode assembly (MEA) with SPEEK/cSMM membrane, anode and cathode using hot pressed method.
v. Characterizing the electrode on scanning electron microscopy (SEM) and energy-dispersive x-ray (EDX).
vi. Testing the MEA on single cell DMFC performance to compare the results of OCV and power density.

1.6 Thesis Organization

Chapter 1 describes a general fuel cell technology in terms of electrode structure. Optimizing catalyst loading in electrode is an important parameter to be controlled in order to commercialize it for future energy solution. This chapter also presents the background of fuel cell, problem statement, objectives and scope of the study.

Chapter 2 provides an overview of direct methanol fuel cell technology with the basic components of DMFC. This chapter also provides information about DMFC performance related to methanol oxidation and oxygen reduction reaction as the literature review of the matter understudy.

Chapter 3 explains the methodology of the experiments in this research. It also describes all the characterization methods of the electrode structure in DMFC. The workflow of the study is included to give an overview of the overall structure of the research. Steps of the membrane preparation are described in detail in this chapter.

Chapter 4 presents the performance of DMFC by using different catalyst loading on the anode and cathode. It explains the effect of each catalyst loading on these performances. This chapter also describes the characterization of catalyst layer using scanning electron microscopy and energy dispersive x-ray. These details were used to further explain the relationship between catalyst loading, electrode and PEM performance.

Chapter 5 concludes the overall performance of DMFC and presented some future improvement to the fuel cell development. It gives the general conclusion from this research and some recommendation for future works.

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