DEVELOPMENT OF MICROBIAL FUEL CELL USING SPEEK/CLOISITE 15A MEMBRANE FOR ELECTRICITY GENERATION FROM PALM OIL MILL EFFLUENT

NUR DIANATY BINTI NORDIN

A dissertation submitted in partial fulfilment of the requirement for the award of the degree of Master of Bioprocess Engineering (Mixed Mode)

Faculty of Chemical Engineering
Universiti Teknologi Malaysia

JANUARY 2013
ACKNOWLEDGEMENT

All praises and thanks to Allah, most gracious and most merciful. This thesis would not be completed without His permission and guidance. First and foremost I would like to thank my supervisor Dr Abdul Halim Mohd Yusof for his advice and supervision. I would also like to express my gratitude for his understanding as supervisor and mentor through the course of my research. Secondly, the person that I am most thankfully is En Ya'akop Sabudin, senior technician of biotransformation lab that assists me so much in my experiment preparation over the years. Only Allah could repay the kindness of these people towards me.

It is incomplete to not mention my families that encourage me towards the end of this course. Thank you for being there for me and I am deeply touch by their supports. To helpful and supportive colleagues, Devanai a/p Kannan, Nur Aminatun Naemah and Afiqah Said, truly without your support and encouragement I will not finish this far.

To you that spend the time to read my thesis, thank you very much.
ABSTRACT

A microbial fuel cell (MFC) is a device capable to convert chemical energy to electrical energy by using microorganisms. Typically, microbial fuel cell is recognized with its dual chamber system. In this dual chamber system, the membrane acts as the separator that divides anode and cathode as the cell compartment. One aspect in microbial fuel cell (MFC) development involves the challenge in finding suitable membrane as separator. Excellent membrane should be low in cost, high in proton conductivity, limits substrate and oxygen diffusivity. In this work, a composite membrane constituting a sulfonated poly(ether ether ketone) (SPEEK) and cloisite 15A is studied meanwhile the palm oil mill effluent (POME) waste water was used as the source for electricity generation. The addition of organooclays; cloisite 15A to the SPEEK dope solution during the preparation of the membrane is expected to overcome the limitation imposed by the pure SPEEK and extensively studied membrane Nafion, a sulfonated tetrafluoroethylene. The addition of cloisite 15 A indeed improve the overall membrane properties. The water uptake, mechanical strength and oxygen diffusivity for the SPEEK/Cloisite membrane is 22.6%, 46.2 MPa and 0.36x10-5 cm2 s-1 exceeding the performance of Nafion and pure SPEEK. During MFC operation, the maximum power density was obtained by Nafion with 3.5 mW/m2 slightly higher than SPEEK/Cloisite with power density of 2.8 mW/m2. The assessment on the POME properties shows that the COD values, total ammonia and total nitrogen were reduced in in all three MFCs using SPEEK/Cloisite, SPEEK and Nafion membrane respectively.
Sel bahan api mikrob (MFC) ialah sejenis peranti yang mampu untuk menukar tenaga kimia kepada tenaga elektrik dengan menggunakan mikroorganisma. Biasanya, sel bahan api mikrob ini dikenali dengan sistem dwi kebuk. Dalam sistem dwi kebuk ini, membran bertindak sebagai pemisah yang membagahikan anod dan katod di dalam petak sel. Salah satu aspek dalam pembangunan bahan api mikrob melibatkan cabaran dalam mencari membran yang sesuai sebagai pemisah. Membran yang terbaik mempunyai ciri-ciri seperti kos yang murah, kekonduksian proton yang tinggi, dan mengehadkan kadar kemeresan oksigen dan substrat. Dalam penyelidikan ini, membran komposit yang membentuk poli sulfonated (ketone eter eter) (SPEEK) dan cloisite 15A dijaki manakala sisa kilang kelapa sawit (POME) telah digunakan sebagai sumber untuk penjanaan elektrik. Penambahan organoclays, cloisite 15A dijangka dapat mengatasi keupayaan SPEEK yang tulen dan Nafion, sejenis polimer tetrafluoroethylene sulfonat. Penambahan cloisite 15A sememangnya meningkatkan sifat membrane secara keseluruhan. Penyerapan air, kekuatan mekanikal dan kemeresan oksigen untuk membran SPEEK/Cloisite adalah 22.6%, 46.2 MPa dan 0.36x10-5 cm2 s-1 melebihi keupayaan Nafion dan SPEEK tulen. Semasa operasi MFC, ketumpatan kuasa maksimum telah diperolehi oleh Nafion dengan 3.5 mW/m2 lebih tinggi sedikit daripada SPEEK / Cloisite dengan ketumpatan kuasa sebanyak 2.8 mW/m2. Penilaian ke atas sifat-sifat POME menunjukkan bahawa nilai COD, jumlah ammonia dan nitrogen total telah dikurangkan dalam semua tiga MFCs masing-masing menggunakan membrane SPEEK/Cloisite, SPEEK dan Nafion.
# TABLE OF CONTENT

<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DECLARATION</td>
<td>ii</td>
</tr>
<tr>
<td></td>
<td>ACKNOWLEDGEMENTS</td>
<td>iii</td>
</tr>
<tr>
<td></td>
<td>ABSTRACT</td>
<td>iv</td>
</tr>
<tr>
<td></td>
<td>ABSTRAK</td>
<td>v</td>
</tr>
<tr>
<td></td>
<td>TABLE OF CONTENTS</td>
<td>vi</td>
</tr>
<tr>
<td></td>
<td>LIST OF FIGURES</td>
<td>viii</td>
</tr>
<tr>
<td></td>
<td>LIST OF TABLES</td>
<td>ix</td>
</tr>
<tr>
<td></td>
<td>LIST OF SYMBOLS/ABBREVIATIONS</td>
<td>x</td>
</tr>
</tbody>
</table>

1 INTRODUCTION 1

1.1 Background 1
1.2 Problem Statement 4
1.3 Objective 5
1.4 Scope of study 5
1.5 Rationale and Significance 6

2 LITERATURE REVIEW 7

2.1 Microbial Fuel Cell 7

2.1.1 How Microbial Fuel Cell Works? 7

2.2 Components of Microbial Fuel Cell 8
2.2.1 Anode chamber 10
2.2.2 Cathode chamber 10
2.2.3 Electrode 11

2.3 Separator Characteristics 12

2.3.1 Commonly Used Separator 13
2.3.2 Ion Exchange Membrane vs Size 13
    Selective Separator
2.4 Cation Exchange Membrane 14
    2.4.1 Advantages of SPEEK polymer 15
    2.4.2 Disadvantages of SPEEK polymer 16
    2.4.3 Modification of SPEEK 16
        2.4.3.1 Cloisite 15A 18
2.5 Microbial fuel cell application 19
    2.5.1 Wastewater as substrate 19
    2.5.2 Palm Oil mill effluent 20

3 METHODOLOGY 22
3.1 Materials and Chemicals 22
    3.1.1 Polyether ether ketone 22
    3.1.2 Sulfuric acid 23
    3.1.3 N,N-dimethyl acetamide 23
    3.1.4 Cloisite 15A 24
    3.1.5 2,4,6-triaminopyrimidine (TAP) 24
3.2 Flow chart of experimental procedure 26
    3.2.1 Synthesis of SPEEK 27
    3.2.2 Preparation of membrane 27
    3.2.3 Characterization of membrane 28
        3.2.3.1 Water uptake 28
        3.2.3.2 Mechanical strength 28
        3.2.3.3 Dissolved oxygen diffusivity measurement 29
3.3 Collection and characterization of raw 29
    POME
    3.3.1 Cultivation of POME sludge 30
3.4 Configuration of dual chamber MFC 30
    3.4.1 Microbial fuel cell operation 31
3.5 Measurement and analysis 32


**LIST OF FIGURES**

<table>
<thead>
<tr>
<th>FIGURE NO</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Schematic diagram of a microbial fuel cell</td>
<td>2</td>
</tr>
<tr>
<td>2.1</td>
<td>Components of microbial fuel cell</td>
<td>9</td>
</tr>
<tr>
<td>3.1</td>
<td>Experimental procedure flow chart</td>
<td>26</td>
</tr>
<tr>
<td>4.1</td>
<td>Chemical structure of SPEEK, Nafion, Cloisite 15A and TAP</td>
<td>35</td>
</tr>
<tr>
<td>4.2</td>
<td>Illustration of proton hopping system according to Grotthuss mechanisms</td>
<td>35</td>
</tr>
<tr>
<td>4.3</td>
<td>Illustration of oxygen transport across the three membranes</td>
<td>39</td>
</tr>
<tr>
<td>4.4</td>
<td>The surface image of membrane at magnification range from 2500 X where (a) SPEEK, (b) SPEEK/Cloisite15A and (c) Nafion112</td>
<td>41</td>
</tr>
<tr>
<td>4.5</td>
<td>The cross-section of membrane at magnification 600 and 2500 X where (a) SPEEK,(b) SPEEK/Cloisite15A® and (c) Nafion112</td>
<td>42</td>
</tr>
<tr>
<td>4.6</td>
<td>Polarization curves of the different membranes</td>
<td>43</td>
</tr>
<tr>
<td>4.7</td>
<td>Power curves of different membrane during MFC operation</td>
<td>44</td>
</tr>
</tbody>
</table>
# LIST OF TABLES

<table>
<thead>
<tr>
<th>TABLE NO</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Approaches for the development of cation exchange membranes for MFC (modified from Kerres, 2004)</td>
<td>17</td>
</tr>
<tr>
<td>2.2</td>
<td>List of wastewaters used in microbial fuel cell system</td>
<td>20</td>
</tr>
<tr>
<td>3.1</td>
<td>The properties of polyether ether ketone (PEEK)</td>
<td>22</td>
</tr>
<tr>
<td>3.2</td>
<td>The properties of sulfuric acid</td>
<td>23</td>
</tr>
<tr>
<td>3.3</td>
<td>The properties of N,N-dimethylacetamide</td>
<td>24</td>
</tr>
<tr>
<td>3.4</td>
<td>The properties of Cloisite 15A</td>
<td>24</td>
</tr>
<tr>
<td>3.5</td>
<td>The properties of TAP</td>
<td>25</td>
</tr>
<tr>
<td>3.6</td>
<td>List of parameters for POME characterization</td>
<td>30</td>
</tr>
<tr>
<td>4.1</td>
<td>Water uptake of different membranes</td>
<td>34</td>
</tr>
<tr>
<td>4.2</td>
<td>Tensile strength of different membranes</td>
<td>37</td>
</tr>
<tr>
<td>4.3</td>
<td>Mass transfer coefficients and diffusivities of oxygen for various membranes tested in double chamber MFC set up</td>
<td>38</td>
</tr>
<tr>
<td>4.4</td>
<td>Palm oil mill effluent wastewaters before and after feeding the MFC for different membranes</td>
<td>46</td>
</tr>
</tbody>
</table>
## LIST OF SYMBOLS/ABBREVIATIONS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>percentage</td>
</tr>
<tr>
<td>°C</td>
<td>celcius</td>
</tr>
<tr>
<td>A</td>
<td>ampere</td>
</tr>
<tr>
<td>A</td>
<td>Area</td>
</tr>
<tr>
<td>cm</td>
<td>centimetre</td>
</tr>
<tr>
<td>$D_O$</td>
<td>Oxygen diffusion coefficient</td>
</tr>
<tr>
<td>E</td>
<td>voltage</td>
</tr>
<tr>
<td>g</td>
<td>gram</td>
</tr>
<tr>
<td>$H^+$</td>
<td>hydrogen ion</td>
</tr>
<tr>
<td>I</td>
<td>current</td>
</tr>
<tr>
<td>kg</td>
<td>kilogram</td>
</tr>
<tr>
<td>$K_O$</td>
<td>Mass transfer coefficient</td>
</tr>
<tr>
<td>L</td>
<td>Litre</td>
</tr>
<tr>
<td>$L_t$</td>
<td>membrane thickness</td>
</tr>
<tr>
<td>m</td>
<td>mili</td>
</tr>
<tr>
<td>M</td>
<td>molar</td>
</tr>
<tr>
<td>ml</td>
<td>mililitre</td>
</tr>
<tr>
<td>mmHG</td>
<td>milimetre mercury</td>
</tr>
<tr>
<td>MPa</td>
<td>Megapascal</td>
</tr>
<tr>
<td>mW</td>
<td>miliwatt</td>
</tr>
<tr>
<td>P</td>
<td>Power density</td>
</tr>
<tr>
<td>R</td>
<td>Resistance</td>
</tr>
<tr>
<td>s</td>
<td>seconds</td>
</tr>
<tr>
<td>V</td>
<td>volume</td>
</tr>
<tr>
<td>wt</td>
<td>weight</td>
</tr>
<tr>
<td>$\Omega$</td>
<td>ohm</td>
</tr>
</tbody>
</table>
AEM - Anion exchange membrane
CEM - Cation exchange membrane
COD - Chemical oxygen demand
DMAc - N,N- dimethylacetamide
DMFC - Direct methanol fuel cell
MFC - Microbial fuel cell
OCV - open circuit voltage
PEEK - Polyether ether ketone
POME - palm oil mill effluent
SPEEK - Sulfonated poly (ether ether ketone)
TAP - 2,4,6-triaminopyrimidine
TN - total nitrogen
TSS - Total suspended solids
CHAPTER 1

INTRODUCTION

1.1 Background

Microbial fuel cell has received wide attention from the researchers in the past few years. Regards as promising new source of energy, the application of microbial fuel cell does not limit only to the energy area. Most of the studies done, apply microbial fuel cell as the solution to the untreated waste and limited research is done on constructing the MFC as the true source of energy. Microbial fuel cell as oppose to chemical fuel cell utilize bacteria as the catalyst to convert the organic and inorganic compound available by oxidation and generate power (Logan et al., 2006). In other word, microbial fuel cell convert the chemical energy obtain from the bacterial reaction and turns it into electricity. Theoretically, any organic compound can be used as a substrate in microbial fuel cell. Then bacteria will feed on the substrate and produce electrons along the metabolic pathways. These electrons are then transferred to the anode and flowed through the cathode and create electric potential (Rodrigo et al., 2007). Figure 1 illustrates the concept of microbial fuel cell.
In the research area of microbial fuel cell, the focus of the study revolves around the microbial fuel cell design and operation, construction material for parts in the microbial fuel cell system and also the application of it. Furthermore, studies are also done on the type of microbial consortia that can be used as the electron provider. Most of the time, the focus had been on using species that does not require electron mediator to extract the electrons out from the microbe bodies. Such species include *Shewanella putrefaciens* which can be grown anaerobically and eliminates the use of any electron mediators by directly transferring electrons to the electrodes (Kim et al., 2002). On the other hand, though the use of such anodic biocatalyst is desirable to obtain higher power generation, microbial fuel cell is still inefficient. The next move had been focusing on the use of wastewaters. Wastewaters had the advantages; the microbes needed and organic nutrient to feed the microbes. Moreover, simultaneous degradation of the pollutant inside the wastewater and electricity
generation can be achieved with the use of wastewaters as the anodic substrate (Cha et al., 2010).

In order to overcome the limiting factor in the microbial fuel cell system, many aspects in the device had been studied. One of the aspects that are at interest is in the design of the microbial fuel cell. MFC can take shape in a dual chamber system or single chamber system (Pant et al., 2010). Various testing and modification are done to the use of materials. With different configuration, different materials can be tested in order to achieve efficient power generation. Specifically, in dual chamber configuration, the immediate part that needs attention is the type of separator used. The separator may originate from many materials from salt solution, ultrafiltration membrane to proton exchange membrane (Li et al., 2010). Most importantly, the separator being used are able to fulfill the need of the system configuration and able to increase the performance of the microbial fuel cell system (Zhang et al., 2009).

Generally, ion exchange membrane provides better isolation of the substrate and oxygen in anode chamber as compare to most size selective separators (Kim et al., 2007a). Ion exchange membrane also offers excellent proton conductivity as in the case of commonly used perfluorinated ionomer membrane such as Nafion (Rozendal et al., 2008). However, expensive price of Nafion makes the development of other type of membranes attractive. One type of polymer that receives attention is non-fluorinated polymers due to the excellent proton conductivity they possessed. Improvement such as incorporation of inorganic materials to increase the barrier properties hence reducing the substrate and oxygen crossover across the membrane is attempted to the membrane.
1.2 Problem Statement

Great concerns to the environment had resulted in interest to develop new technique or process in treating waste to reduce the cost of the treatment and at the same time obtain value added products. Microbial fuel cell is believed to be the alternative to the readily available treatment of wastewater combine with energy generation (Durruty et al., 2011). In order to obtain high power generation, the MFC should work efficiently. One of the essential items in MFC design beside anode and cathode is the separator commonly used to physically divide the anode and cathode chamber. In a dual chamber system of microbial fuel cell, the use of efficient separator in microbial fuel cell is believed to increase the performance of MFC and generate higher power. Specifically, the most commonly used and studied is classified in the ion exchange membrane type. Size selective membrane like microfiltration and ultrafiltration membrane are also applied by others (Tang et al., 2010, Hou et al., 2011, Huang et al., 2011). However, ion exchange membrane provides better separation and promotes proton transfer (Xu, 2005). The most extensively used ion exchange membrane in microbial fuel cell is Nafion, a proton exchange membrane. The lack of cheap and effective membrane limits the potential of MFC to be widely utilized. Major drawback in Nafion utilization is the high cost of the membrane. On the other hand, usage of Nafion in microbial fuel cells permits high oxygen diffusion risking anaerobic condition maintained at the anode chamber (Chae et al., 2007). Therefore it is at great interest to produce cheaper membrane with lower oxygen diffusivity and good proton conductivity. Low cost cation exchange membrane can be produced from inexpensive material through sulfonation of functionalized polymer (Yee et al., 2012). SPEEK provides the desired characteristic to replace Nafion. Moreover, the use of SPEEK based polymers in microbial fuel cell has not been studied as compared to other polymeric membranes. (Ayyaru and Dharmalingam, 2011). SPEEK polymers had been extensively used by direct methanol fuel cell (DMFC) researchers. In order to improve SPEEK properties on oxygen diffusivity, organoclays is added to the membrane preparation previously used in DMFC to reduce methanol permeability rate (Jaafar et al., 2009). On the other hand, the operation of MFC is not limited to obtaining electricity generation. In this case, simultaneous treatment of waste is desirable with the use of wastewater as
substrate. The ability of microbial fuel cell to provide waste treatment will make it more attractive as an alternative green energy.

1.3 **Objective of Study**

The research was studied to achieve the following objectives:

1. To prepare pure sulfonated poly (ether ether ketone) and composite sulfonated poly (ether ether ketone) membrane with addition of Cloisite 15A and TAP.
2. To characterize the prepared membrane by conducting water uptake test, dissolve oxygen permeability test and mechanical strength test and compared it to pure SPEEK membrane and Nafion.
3. To conduct electrochemical performance assessment of the membranes by using palm oil mill effluent (POME) as substrate.

1.4 **Scope of study**

In order to achieve the objectives, the following scopes had been identified:

1. Dual chamber microbial fuel cell was designed and used in this experiment
2. Preparation of the SPEEK membrane was done at 60° C
3. Cultivation of POME was achieved using anaerobic sludge
4. Three types of membrane were prepared and studied which is pure SPEEK, SPEEK added with Cloisite 15A and Nafion.
1.5 Rationale and Significance

The study of a suitable and feasible membrane to act as a separator will create opportunity to scale up microbial fuel cell to be use economically. The constraint of a low cost and effective separator had prevented the use of microbial fuel cell widely. If a low cost separator can be adapted in the use of microbial fuel cell, a new alternative source of energy will be created. The application of this new energy is very wide. In addition it is also environmental friendly. This research seeks to find the efficiency of using POME as a substrate to the microbial fuel cell (MFC) for electricity generation with simultaneous accomplishment of wastewater treatment. Thus, anaerobic sludge is employed in the anode chamber in order to investigate its ability to replenish electrons. The culture is used to inoculate the bottom chamber of the MFC while POME is used as the substrate in the MFC. The treatment efficiency of the MFC system is measured through the removal of chemical oxygen demand (COD) and the characterization of the effluent. In the end, the energy recovered on the basis of electricity generation and the treatment efficiency based on the composition of the wastewater before and after treatment is obtained. The result will show the microbial fuel cell performance with different membranes and feasibility of this technique in wastewater treatment and electricity generation.
REFERENCES


wastewater and its treatment in activated sludge based microbial fuel cell and analysis of developed microbial community in the anode chamber. *Bioresource Technology*, 100, 5132-5139.


