

ELECTEROCHEMICAL STUDY OF SOLFONATED POLY ETHER ETHER
KETONE NANOCOMPOSITE MEMBRANE AT MODERATE TEMPERATURE FOR
DIRECT METHANOL FUEL CELL APPLICATION

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ABSTRACT

High methanol permeability and expensive price of current commercial Nafion[®] membrane for direct methanol fuel cell (DMFC) have encouraged researchers to modify proton exchange membrane (PEM). Sulfonated poly ether ether ketone (SPEEK) is a polymer which attracted a lot of attention recently. This study aimed to test the DMFC performance of nanocomposite SPEEK membrane filled with Cloisite 15A[®] clay by introducing 2,4,6 triaminopyrimidine (TAP) as a compatibilizer as electrolyte membrane at room temperature to 80°C and compare with Nafion 117. SPEEK polymer was made at 60°C in order to obtain the degree of sulfonation of 60%. According to the results, the SPEEK nanocomposite with the following composition SP60/CL2.5/TAP5.0 showed higher proton conductivity and methanol permeability than of Nafion 117 at various temperatures because of the presence of CL and TAP addition. Furthermore the highest overall performance (membrane selectivity) was allocated to the SP60/CL2.5/TAP5.0 at 60°C while the lowest one was for Nafion 117 at 80°C. In addition DMFC performance results showed the OCV for the nanocomposite membrane increase when the temperature increase. In addition voltage and power density increase with temperature increment due to catalyst high activity on electrode surface, and higher proton conductivity, clearly the maximum power density at 60°C was 54.93 (mWcm⁻²).

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Fuel cells are the devices that produce electricity from chemical energy with high efficiency and low pollutant. During the recent decades fuel cells have been magnetized high interest because of high-energy request, fossil fuel shortage, and environmental treatments (Liu *et al.*, 2006). In general, fuel cells are known as “alternative battery” as they have some similarity to batteries but do not follow the thermodynamic Carnot cycle energy conversion due to their different mechanism. Their pollutions are very lower than most of the environmental standards (Othman, 2009).

Different types of fuel cell are recognized by the electrolyte material. This clarifies: 1) kind of chemical reactions occur inside the cell, 2) kind of catalyst needed, 3) the temperature range of operation, 4) types of fuels used and other factors. Table 1.1 shows several types of fuel cells being used (Othman, 2009).

Table 1. 1 Types of fuel cells

Type	Electrolyte	Fuel/ Oxidant	Operating Temperature (°C)	Application
Molten Carbonate (MCFC)	Carbonate (Lithium Potassium Mixture)	Salt & Carbonate	H ₂ /O ₂ ~ 650	Stationary
Phosphoric Acid (PAFC)	Pottasium hydroxide solution	H ₂ /O ₂	~ 220	Stationary
Solid Oxide (SAFC)	Solid Ceramic	H ₂ /O ₂	~ 1000	Vehicle Stationary
Alkaline (AFC)	Potassium Hydroxide Solution	H ₂ /O ₂	60-120	Vehicle Spatial
Polymer Electrolyte (PEMFC)	Solid Ion Exchange Membrane	H ₂ /O ₂	50-100	Vehicle Stationary Portable Power
Direct Methanol (DMFC)	Solid Ion Exchange Membrane	CH ₃ OH/ O ₂	50-120	Vehicle Portable Power

Proton exchange membrane (PEM) fuel cells or polymer electrolyte membrane fuel cells have magnetized more attention amongst different types of fuel cells during recent decade, due to their excellent performance in stationary and portable devices. These types of fuel cells applied solid polymer membranes as the electrolyte. The advantages of PEM can be listed as follows: 1) absence of corrosive liquid reduces corrosion; 2) Operation in low temperature let prepare instant response to any alter in power demand and 3) Can produce high power densities with lower weight, cost and compact (Libby *et al.*, 2003).

Basically there are two types of PEM fuel cells, including the hydrogen PEM fuel cell and direct methanol fuel cell (DMFC), both are excellent for substituting the electricity generators (Othman, 2009). Hydrogen PEMFC mainly applied in automotive and residential applications; however DMFCs are more suitable for portable electronic devices because of their low cost, low temperature and pressure operation, rapid refueling and compact cell design (Ge and Liu, 2005). Generally, there are two main problems when employing DMFC: 1) slow oxidation kinetics of the fuel 2) methanol crossover through membrane that due to depolarization of the cell, decrease fuel efficiency and reduction in OCV (open circuit voltage) (Hasani-Sadrabadi *et al.*, 2010).

Therefore recent researches concentrate on the modification of membranes to achieve more proton conductivity at higher temperatures, prepare a sufficient water supply and decrease methanol crossover rate. During former decade, Scientists produced novel polymers with non-fluorinated backbones, and introducing different types of inorganic fillers into polymeric matrices, including montmorillonite, titanium dioxide, zirconium phosphate silica and zeolites (Hasani-Sadrabadi, *et al.*, 2010). The latter system is known as polymer nanocomposites.

Polymer nanocomposites can be categorized into hybrid systems consisting of high surface area nanostructure components. The exclusive properties of polymer-clay nanocomposites come from nanoscale spreading of clay layers into the polymeric matrix, which robustly depends on interfacial characteristics. Amongst non-fluorinated hydrocarbons, poly ether ether ketone (PEEK), was presented to be sufficient for fuel cells, due to its cheaper price, better film developing properties, and good thermal, mechanical and chemical resistance (Hasani-Sadrabadi, *et al.*, 2010).

1.2 Problem Statement

There are two main problems normally encountered during the applications of direct methanol fuel cells (Gaowen and Zhentao, 2005): first is the slow oxidation rate of methanol and secondly the excessive methanol permeation through the membranes. Nafion[®] (Dupont), Flemion[®] (Asahi Glass Company), Aciplex[®] (Asahi Chem.) perfluorinated ionomer (PFI) membranes are usually developed as electrolytes, due to their good resistance during cell operation and high proton conductivity. On the other hand the methanol cross over is still high in these types of membranes that undesirable for DMFC performance (Norddin *et al.*, 2009).

Since recent decade, a number of researchers had attempted to solve PFI's weaknesses. There were three main techniques employed to minimize the weakness of PFI's: 1) development of PFI membranes, 2) modification of other fluoropolymer membranes, and 3) improvement of non- fluorinated polymer membranes (Jaafar *et al.*, 2009).

Because of the high proton conductivity of non- fluorinated polymers, several attempts have been done to develop the membrane performance by reducing methanol crossover through the membrane and even enhanced proton conductivity for DMFC application, by applying inorganic materials such as clay. Amongst natural clays, smectites, which are family of either montmorillonite (MMT) or hectorites, are a suitable material for DMFC application because of their excellent proton conductivity, proper surface area, high surface reactivity, and low methanol permeability (Kathleen, 2000) .

Although the MMT has advantages, but there are still some weaknesses of MMT because of its chemical microstructure properties. Due to hydrophilic properties of silicate clays and low attraction for hydrophobic polymers, an organic development on the clay surface must be done in order to improve their compatibility with polymeric materials (Lin *et al.*, 2007).

The adjustment of inorganic clays to organoclays is the popular method to modify the compatibility properties of MMT clay. Cloisite15A[®] is one of the developed MMT clays that has desirable advantages such as high interlayer distance (~31.5 Å) and high aspect ratio (70- 150), which is donate to good proton conductivity and also low methanol crossover (Jaafar *et al.*, 2011).

Jaafar et al. (2011) presented the SP63/2.5Cl/5.0TAP polymer-clay nanocomposites membrane as a substitute proton exchange membrane (PEM) for DMFCs with better DMFC performance than Nafion[®] 112. It has been reported that the new membrane has high proton conductivity ($16.3 \times 10^{-4} \text{ mScm}^{-1}$), low methanol permeability ($1.3 \times 10^{-1} \text{ cm}^2 \text{ s}^{-1}$) and also high mechanical stability at room temperature and 100%RH (Jaafar, *et al.*, 2011). To the best of our knowledge, the performance of mentioned membrane at different operating parameters such as temperature, has never been studied before.

1.3 Research Objective

Based on the background of the study and the problem statement addressed, therefore the objectives of this study is to study the performance of SP63/2.5Cl/5.0TAP membrane in direct methanol fuel cell at different operating temperatures.

1.4 Research Scope

In order to achieve the above objectives, the following scopes of work have been drawn:

- i. Preparing the SP60/2.5 Cl/ 5.0 TAP proton exchange membrane.
- ii. Measuring the, methanol permeability of SPEEK nanocomposite membrane and Nafion 117 at the temperature range of room temperature to 80°C.
- iii. Measuring the proton conductivity of SPEEK nanocomposite membrane and Nafion 117, at the temperature range of room temperature to 80°C.
- iv. Preparing the Membrane Electrode Assembly (MEA) from the SP60/2.5 Cl/ 5.0 TAP membrane
- v. Studying the performance of SP60/2.5 Cl/ 5.0 TAP membrane in DMFC single cell in terms of voltage and power density at different temperatures

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