PREPARATION AND PROPERTIES OF REDUCED GRAPHENE OXIDE FOR DIRECT METHANOL FUEL CELL APPLICATION

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I dedicate my thesis for my beloved

♥ *Father, Abdul Halim Mohd Saad*

♥ *Mother, Hamimah Md Dali*

♥ *Siblings*

♥ *Friends*

Thank you for your love and continuous supports.

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ABSTRACT

Reduced graphene oxide has recently attracted great attention due to its unique chemical and physical properties. In this study, reduced graphene oxide is introduced in direct methanol fuel cell application as this system had been delayed by several reasons which are related to the lack of materials with good methanol permeability and conductivity properties. Therefore, the objective of this research is to develop and characterize a high conductive reduced graphene oxide as additive in membrane electrode assembly (MEA). Reduced graphene oxide was prepared using reduction of the oxide with different reducing agents and the degree of reducibility of the reducing agents used was compared in order to determine the alternative reducing agent to replace hydrazine. The reduced graphene oxide was successfully prepared from the pristine graphite by reductive precipitation of graphene oxide aqueous solution using sodium borohydride which acted as the reducing agent for 24 hours reaction time at room temperature. Subsequently, MEA from sulfonated poly (ether ether ketone) (SPEEK) consists of reduced graphene oxide as additive was fabricated for direct methanol fuel cell (DMFC) performance testing. The physicochemical properties of the reduced graphene oxide were characterized by Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), transmission electron microscopy (TEM) and conductivity measurement. The FTIR spectrum of the reduced graphene oxide shows that the carbonyl group was successfully removed and the reduced graphene oxide contains some water. The XRD spectrum shows reduced graphene oxide has hexagonal structured crystal with a sharp peak at $2\theta = 26.4^{o}$ which can be assigned as *002* peak associated with reduced graphene oxide. The exhibited conductivity was in the range of $1.80 \times 10^{3} - 1.30 \times 10^{4}$ S m^{-1}. TEM micrograph showed that reduced graphene oxide has multilayer structures. The DMFC performance of the blended reduced graphene oxide with SPEEK55 exhibited substantial improvement by $5 - 15\%$ of open circuit voltage (OCV), initial voltage, power density, and stabilization period as compared to the commercial nafion membrane. In conclusion, reduced graphene oxide is a potential material as catalyst support in MEA and additive in SPEEK55 membrane to improve the DMFC performance.

ABSTRAK

Sejak kebelakangan ini, grafena oksida terturun telah menarik banyak perhatian kerana sifat kimia dan fiziknya yang unik. Dalam kajian ini, grafena oksida terturun diperkenalkan dalam aplikasi sel bahan api metanol terus kerana sistem ini telah tertangguh disebabkan oleh beberapa sebab yang berkaitan dengan kekurangan bahan dengan kebolehtelapan metanol dan sifat kekonduksian yang baik. Kajian ini bertujuan untuk membangunkan dan mencirikan grafena oksida terturun sebagai tambahan dalam himpunan elektrod membran (MEA). Grafena oksida terturun disediakan dengan menggunakan agen penurunan yang berbeza untuk mengkaji kuasa penurunan dan sebagai satu pendekatan dalam mencari agen penurunan alternatif untuk menggantikan hidrazin. Penghasilan grafena oksida terturun berjaya dilakukan bermula dari grafit tulen dengan pemendakan penurunan grafena oksida oleh natrium borohidrat sebagai agen penurun dengan tindak balas selama 24 jam pada suhu bilik. Selepas itu, MEA oleh sulfonat poli (eter eter keton) (SPEEK) mengandungi grafena oksida terturun telah direka untuk ujian prestasi sel bahan api metanol terus (DMFC). Sifat fizik dan kimia grafena oksida terturun dicirikan menggunakan spektroskopi infra-merah transformasi Fourier (FTIR), pembelauan sinar-X (XRD), mikroskopi penghantaran elektron (TEM) dan pengukuran kekonduksian. Spektrum FTIR yang diperoleh menunjukkan bahawa kumpulan karbonil telah berjaya disingkirkan dan grafena oksida terturun mengandungi air. Spektrum XRD menunjukkan bahawa grafena oksida terturun mempunyai kristal berstruktur heksagon dengan puncak tajam pada $2\theta = 26.4^{o}$ yang boleh ditetapkan sebagai puncak *002* yang dikaitkan dengan grafena oksida terturun. Kekonduksian dipamerkan dalam julat 1.80×10^{3} – 1.30×10^{4} S m^{-1}. Mikrograf TEM menunjukkan bahawa grafena oksida terturun mempunyai struktur berlapis-lapis. Prestasi DMFC campuran grafena oksida terturun dengan SPEEK55 mempamerkan peningkatan yang ketara sebanyak $5 - 15\%$ daripada voltan litar terbuka (OCV), voltan awal, ketumpatan kuasa dan tempoh penstabilan berbanding dengan membran nafion komersial Kesimpulannya, grafena oksida terturun adalah bahan yang berpotensi sebagai tambahan dalam membran SPEEK55 untuk meningkatkan prestasi DMFC.

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LIST OF ABBREVATIONS

AFC	-	Alkaline Fuel Cell
BSA	-	Bovine Serum Albumin
C	-	Carbon
CMG	-	Chemically Modified Graphene
CNT	-	Carbon Nanotube
CV	-	Cyclic Voltammetric
CVD	-	Chemical Vapour Deposition
DMFC	-	Direct Methanol Fuel Cell
DS	-	Degree of Sulfonation
FC	-	Fuel Cell
FESEM	-	Field Emission Scanning Electron Microscope
FET	-	Field Effect Transistors
G	-	Graphene
GNS	-	Graphene Nano Sheet
GO	-	Graphene Oxide
g/mol	-	Gram per mol
H^1NMR	-	Hydrogen-Nucleur Magnetic Resonance
MCFC	-	Molten Carbonate Fuel Cell
MEA	-	Membrane Electrode Assembly
$NaBH_4$	-	Sodium Borohydride
NaOH	-	Sodium Hydroxide
NMP	-	N-methylprrolidone
OCV	-	Open Circuit Voltage
PAFC	-	Phosphoric Acid Fuel Cell
PEM	-	Polymer Electrolyte Membrane
PEMFC	-	Proton Exchange Membrane Fuel Cell
PEEK	-	Poly (ether ether ketone)

PFI   -   Perfluorinated

SEM   -   Scanning Electron Microscope

SOFC   -   Solid Oxide Fuel Cell

SPEEK   -   Sulfonated Poly (ether ether ketone)

SPEEK/G   -   Graphene Sulfonated Poly (ether ether ketone)

TEM   -   Transmission Electron Microscopy

TGA   -   Thermal Gravimetric Analysis

XRD   -   X-Ray Diffraction

LIST OF SYMBOLS

Å	-	Angstroms
A	-	Ampere
A/ cm^2	-	Area per square centimeter
g	-	Gram
g/mol	-	Gram per mol
i	-	Current
L	-	Liter
m	-	Meter
mL	-	Mililiter
nm	-	Nanometer
ppm	-	Part per million
W/ cm^2	-	Watts per square centimeter
V	-	Voltage
R	-	Resistance
θ	-	Theta
λ	-	Wavelength
ρ	-	Resistivity
σ	-	Conductivity
Ω	-	Ohm
S	-	Siemens

CHAPTER 1

INTRODUCTION

1.1 Background of Study

At present, the development of batteries and fuel cells has been growing rapidly all around the world, especially in the United States, Germany and Japan. Malaysia however, is lagging behind as electronic sectors such as fuel cell are still relatively new. Greater effects and emphasis would have to be done by our country in order to keep up with the progress of the other countries in scientific research, electric and electronic field.

In developing new world energy from eco-friendly energy sources, fuel cell, which offers a very low production of harmful greenhouse gases is a remarkable improvement. As the by-products from an operating fuel, i.e heat and water, are environmentally, fuel cell has attracted substantial attention for an assortment of applications (Hou *et al.*, 2011). In fuel cells system, combustion, moving part and recharging are not required as long as fuel is supplied. Furthermore, this system works by converting energy into electricity using the electrochemical process concept. This concept generates significant efficiencies using the theory of waste heat for regeneration. The others advantages of fuel cells include producing electricity with higher energy density, easy system design, light weight and greater efficiency than other conventional systems. These benefits has further extends the utilization of fuel cells as a new power and energy resources (Sharma *and Pollet,* 2012; Kang *et al.*, 2012).

As there are many other uses for fuel cell in research and development, many works recently have been focussed on commercialization of fuel cells. The demands for of electronic devices has also been increasingly popular, hence there are enormous efforts to accelerate researches on fuel cells. In general, fuel cells are distinguished by different operating temperatures, type of electrolyte and catalysts. There are six commercial main types of fuel cells, namely alkaline fuel cell (AFC), molten carbonate fuel cell (MFCF), phosphoric acid fuel cell (PAFC), solid oxide fuel Cell (SOFC), direct methanol fuel cell (DMFC) and proton exchange membrane fuel Cell (PEMFC) (complement to DMFC) (Jaafar, 2006; Sharma and Pollet, 2012). As of today, the PEMFC and DMFC are two of the most favoured fuel cells for further advanced studies attributable to current commercial applications.

Nonetheless, according to fuel cell system, there are several difficulties. For instance, the well-known commercialization for transportation and stationary application has been delayed by various reasons which are related to the search for materials with good chemical resistance and high conductivity (Cao *et al.*, 2011). In addition, existence of perfluorinated ionomers, like nafion membranes, in DMFC caused the complexity of high methanol permeability throughout electrolyte membranes at which the fuel wastage has resulted in loss of cathode performance and tendency for catalyst poisoning to occur due to the absence of appropriate proton conducting membranes (Lin *et al.*, 2013; Zhang *et al.*, 2008). Therefore, these matters have opened eyes of researchers and have attracted interest to enhance and replace the perfluorinated membrane to overcome the weaknesses.

A good material as additive should have the characteristic of high electrical conductivity, high surface area, mesoporous structure for easy electron transport and easy recovery of the catalyst. Previous research has shown that the catalyst with support material had improved stability and obtained higher activity compared to unsupported catalyst (Sharma and Pollet, 2012).

Reduced graphene oxide, a carbon based materials, has unique structural characteristic which possesses large surface area, high conductivity, high durability and low cost (Li *et al.*, 2008). It is a promising alternative for numerous crucial fuel cell materials which is suitable to be used as inorganic filler. Besides that, because of its extraordinary characteristic, reduced graphene oxide has been widely used in many applications such as electrode in batteries, supercapacitor and semiconductor, sensor, transparent conductive films, in biomedical for drug and many more. Based on its promising properties, reduced graphene oxide is highly recommended to be utilized as the additive in polymer membrane for direct methanol fuel cell. As alternative on substituting nafion membrane, it is suggested to perform sulfonation poly (ether ether ketone) (SPEEK) membrane incorporated with synthesized reduced graphene oxide

1.2 Statement of Problems

Fuel cell produces electricity by the reaction between an anode (fuel) and cathode (an oxidant), where there a variety of material combinations of the fuel and oxidant. This combination could be used in this system as long as the fuel cell performance not distracted (Huang *et al.*, 2008). However, commercialization of fuel cell has been hindered due to the cost and durability issues related to the catalysts material in fuel cells (Hou *et al.*, 2011; Kang *et al.*, 2012). Moreover, for DMFC, its suffers low performance of electrode due to low kinetic and efficiency of anodic catalyst, expensive perfluorinated membranes, and high methanol permeability with perfluorinated (PFI) proton exchange membrane through electrolyte membrane (Li et al., 2003; Lee *et al.*, 2011; Fu *et al.*, 2008; Ji *et al.*, 2012). High methanol permeability led to DMFC performance limitations, which are oxygen consumption that cause performance loss at cathode (loss fuel cell power), flooding possibility in the electrodes by excessive water production, low fuel efficiency in system, and tend to circuit poisoning of catalysts. (Jaafar, 2006; Lin *et al.*, 2013).

Numerous researchers have come with new ideas in order to increase fuel cells performance and reduce the cost. Among them are by decreasing electrocatalyst

nanoparticle's size, reducing the electrocatalyst's loading at electrodes, improving performance of carbonaceous catalyst support, and development of MEA (Hermann *et al.*, 2005). In focussing to MEA's development related to alternative PEM, a few avenues of DMFC improvements by introducing new non-fluorinated polymers, sulfonation process applied at different polymers and lastly integration of inorganic filler materials into polymer matrices have been carried out (Jung et al., 2009; Ma *et al.,* 2003; Arico *et al.*, 2003).

Therefore, to overcome these problems, the introduction of newly synthesized reduced graphene oxide into SPEEK55 membrane as an alternative on substituting perfluorinated membrane for DMFC was performed. Previous works had investigated reduced graphene oxide based material's performance as polymer composites due to its excellent electrical, mechanical, and thermal properties (Park *et al.*, 2009; Geim *et al.*, 2007). Reduced graphene oxide have a better distribution particle than graphene oxide that lead to low absorption of methanol in membrane (Cai *et al*., 2011) and literature stated that carbonaceous material is important electrode assembling in maximizing the performance of fuel cell (Seger *et al.*, 2009). Modification of graphene oxide into nafion membrane had resulted 70% lower methanol permeability than Nafion115 membranes, which is effective in reducing methanol crossover (Lin *et al.*, 2013).

To synthesis of reduce graphene oxide involved reduction process that removes superfluous functional groups. Numerous researchers had used a variety of reducing agents to remove carbonyl and C-O bond, such as strong alkaline (Fan *et al.*, 2008), hydrazine (Wang *et al.*, 2008; Wu *et al.*, 2010), bovine serum albumin (BSA) (Liu *et al.*, 2010), and hydriodic acid (Pei *et al.*, 2010). The reducing agent is the most vital part because it will affect the production of reduced graphene oxide. Among these reductants, hydrazine is normally selected due to its ability to store high conductivity. Hydrazine generally is toxic, difficult to handle and produce graphene in a large size. Therefore, this study focusing on using the chemical reduction process as convenient method to synthesize reduced graphene oxide since it is possible to produce small size structure and economical production process. Investigation of different reducing agents like sodium borohydride, oxalic acid and formic acid are also introduced as alternative in replacing hazardous reducing agents.

1.3   Objectives

The objectives of this research are:

1.3.1   To synthesis and characterize the reduced graphene oxide from pure graphite

1.3.2   To examine the effects of temperature, reaction time and reducing agent used on the degree of reducibility of the reduced graphene oxide production.

1.3.3   To determine the performance of sulfonated poly (ether ether ketone) polymer (SPEEK)-reduced graphene oxide composite membrane in direct methanol fuel cell (DMFC).

1.4   Scope of Study

The scope of study of this research is focussed on the preparation of reduced graphene oxide using chemical reduction process. Many studies employed hydrazine hydrate as the reducing agent. However, its high toxicity and harmful effect has limit its application. Therefore, this study investigated the effect of using various types of reducing agent with less toxicity and hazardous such as sodium borohydride, formic acid and oxalic acid. Historically these reductants are utilized in previous researches in reduction process, degradation of metal solution and bleaching process (Gaylort. 1957; Garron *et al.*, 2005). The consumption effect of different reducing agent are been studied. In reduction process of synthesis reduced graphene oxide, the variables involved are temperature and reaction time of graphene oxide. The temperatures chosen are 27 $^{\circ}$C, 50 $^{\circ}$C and 80 $^{\circ}$C for one hour to study the degree of reducibility. These temperatures were selected due to the operating working temperature in direct methanol fuel cell is from 60 $^{\circ}$C to 90 $^{\circ}$C. The reaction time was examined in 6, 18, and 24 hours due to the standard operating working hours of fuel cells. For the preparation of reduced graphene oxide with small size and amount, the maximum

reaction time of 24 hours is longer time of real size in operating membrane system. Ethanol and deionized water were used to remove impurities. The products were characterized by Fourier transform infrared (FTIR), X-ray diffraction (XRD), transmission electron microscopy (TEM), and conductivity measurement.

Membrane Electrode Assembly (MEA) from reduced graphene oxide as inorganic filler for sulfonation poly (ether ether ketone) (SPEEK) polymer base membrane for DMFC performance testing was fabricated. NMP is the solvent been used as medium for synthesizing graphene SPEEK solution for flat sheet membrane module. In this study, SPEEK55 was employed as the membrane shown desirable physic-chemical, thermal and mechanical properties for DMFC application (Jaafar, 2006; Lim et al., 2012). SPEEK55 was prepared at the temperature of 60 °C for 3 hours. SPEEK55 polymer was identified through Fourier transform infrared (FTIR). The performance of the reduced graphene oxide with SPEEK55 (SPEEK55/rGO) membrane was evaluated by single DMFC system with 1M and 2M of methanol concentrations. The methanol concentrations of below 3M were used as the previous studies reported that the tendency for methanol crossover to occur is high and this will consequently reduce the DMFC performance (Norddin, 2010; Jiang et al., 2013).

1.5   Significance of study

A numbers of research reported that the use of fluorinated-based electrolyte membrane in fuel cells give an average performance with high potential of drawbacks. The introduction of reduced graphene oxide, a carbonaceous-based material is believed able to enhance the performance SPEEK for DMFC application. The synthesized membrane is more environmental-friendly with non fluorinated base. This research can hopefully contribute towards developing new supporting materials and polymer that are able to be used as an additive in fuel cells.

The other significance of this study is a new approach in identifying the optimum conditions in term of the temperature and reaction time to synthesize reduced graphene oxide by sodium borohydride as the reducing agent. The best conditions and product were identified by properties characterization analyses. FTIR was used to observe the relationship between the time, temperature and reduced peak. The performance study of the products was measured by conductivity measurement. These results are evidences and supports in proving that the products are suitable as inorganic filler in the membrane could have high surface area and good distribution.

Another aspect is to investigate the reducibility properties of certain reducing agent in removing C-O and C=O bond in graphene oxide. Here, the ability of each reductants to reduces desired groups and the discussion on the properties are reported. These results are hopefully able to contribute in finding other reducing agent to replace hydrazine and giving preferable conditions for control reduction process. In addition, these reducing agents are more environmentally safe and less time consuming as the chemicals used are less toxic and hazardous compared to commercial reducing agent.

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