SYNTHESIS AND CHARACTERIZATION OF GRAPHENE NANOSHEETS SUPPORTED PLATINUM NANOCOMPOSITE AS CATALYST FOR METHANOL OXIDATION

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DEDICATIONS

To my beloved father and mother,

Allahyarham Hanifah Bin Abdul Karim

&

Puan Hamrah Binti Haron

To my siblings

To my uncles and aunties

To my friends

And

To those who are always gave me the support towards the success of this research.

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In the name of Allah swt, the most gracious, the most merciful.

We glorify Allah swt and ask blessings and salutations of peace for the noble prophet Muhammad (peace be upon him) and his companions and those who follow him in up-holding the cause of the right religion.

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ABSTRACT

Platinum (Pt) is a noble metal catalyst that is most frequently used as the anode catalyst in direct methanol fuel cell (DMFC) because of its superior catalytic activity performance as compared to other metal catalysts. Besides the merit, Pt catalyst is expensive and also contributes to the problem of Pt poisoning by carbon monoxide (CO) during the methanol oxidation which can reduce the performance of DMFC. The use of carbonaceous material which is graphene nanosheets (GNS) as catalyst support for Pt catalyst can reduce the cost and enhance the catalytic property. Since the GNS have large surface area, the Pt nanoparticles can be dispersed uniformly onto the surface of GNS. Therefore, the main objective of this research is to synthesis and characterize the GNS supported Pt catalyst nanocomposite for methanol oxidation in DMFC. The nanocomposite from GNS and Pt catalyst precursor was fabricated by chemical reduction method using sodium borohydride as reducing agent. The physiochemical properties of the prepared graphene oxide nanosheets, GNS and the catalytic activity performance of GNS/Pt nanocomposite catalyst were successfully studied. Extensive characterization of the produced GNS as catalyst support in terms of morphology, structure, thermal stability and electrical conductivity property were conducted. The results showed that the prepared GNS possess high electrical conductivity of 7.65 S cm^{-1} thus indicated a highly potential catalyst support. HRTEM and FESEM analysis showed well-dispersed Pt nanoparticles on the surface of GNS with small average particle size around 3.33 nm obtained. The findings were consistent with the XRD data (~4.47 nm) obtained. The catalytic activities of GNS/Pt nanocomposites were measured by cyclic voltammogram. The electrochemical surface area (ECSA) of GNS/Pt nanocomposite catalyst was 0.36 cm^2 larger than Vulcan XC-72/Pt (0.25 cm^2) and graphite/Pt (0.14 cm^2) catalysts. It has been found that GNS/Pt nanocomposite catalyst has better catalytic activity and high stability than Vulcan XC-72/Pt and graphite/Pt catalysts for methanol oxidation reaction. As a conclusion, the GNS/Pt nanocomposite catalyst fabricated in this study possesses appropriate characteristics to be used as anode catalyst in DMFC system.

ABSTRAK

Platinum (Pt) adalah mangkin logam yang paling kerap digunakan sebagai pemangkin anod dalam sel bahan api metanol terus (DMFC) kerana keunggulan prestasi aktiviti pemangkin berbanding mangkin logam yang lain. Selain daripada merit tersebut, mangkin Pt adalah mahal dan ia juga menyumbang kepada masalah keracunan Pt dengan karbon monoksida (CO) semasa pengoksidaan metanol yang boleh mengurangkan prestasi DMFC. Penggunaan bahan berasaskan karbon iaitu kepingan nano grafena (GNS) sebagai penyokong untuk mangkin Pt boleh mengurangkan kos dan meningkatkan aktiviti pemangkin. Oleh kerana GNS mempunyai luas permukaan yang besar, maka zarah nano Pt boleh tersebar secara sekata pada keseluruhan permukaan GNS. Oleh itu, objektif utama penyelidikan ini adalah untuk mensintesis dan mencirikan komposit nano mangkin Pt yang disokong oleh GNS bagi pengoksidaan metanol dalam DMFC. Komposit nano daripada GNS dan bahan pemula mangkin Pt difabrikasikan melalui kaedah penurunan kimia menggunakan natrium borohidrida sebagai agen penurun. Sifat fisiokimia kepingan nano grafena oksida, GNS dan prestasi aktiviti pemangkin daripada komposit nano GNS/Pt telah berjaya dikaji. Pencirian secara menyeluruh ke atas GNS yang dihasilkan sebagai penyokong mangkin daripada segi morfologi, struktur, kestabilan terma dan sifat kekonduksian elektrik telah dijalankan. Hasil kajian menunjukkan bahawa GNS yang disediakan memiliki kekonduksian elektrik yang tinggi iaitu 7.65 S cm^{-1} dan ini menunjukkan potensi yang tinggi sebagai penyokong mangkin. Analisis HRTEM dan FESEM menunjukkan penyebaran zarah nano Pt secara sekata pada permukaan GNS dengan purata saiz zarah yang kecil sekitar 3.33 nm telah diperolehi. Penemuan ini selaras dengan data XRD (~4.47 nm) yang diperolehi. Aktiviti pemangkin komposit nano GNS/Pt telah diukur melalui voltamogram berkitar. Luas permukaan elektrokimia (ECSA) mangkin komposit nano GNS/ Pt adalah 0.36 cm^2 lebih besar daripada mangkin Vulkan XC-72/ Pt (0.25 cm^2) dan grafit/ Pt (0.14 cm^2). Mangkin komposit nano GNS/ Pt didapati mempunyai aktiviti pemangkin yang lebih baik dan kestabilan yang lebih tinggi berbanding dengan mangkin Vulkan XC-72/Pt dan mangkin grafit/Pt untuk tindak balas pengoksidaan metanol. Kesimpulannya, mangkin komposit nano GNS/Pt yang telah difabrikasi dalam kajian ini mempunyai ciri-ciri yang sesuai untuk digunakan sebagai mangkin anod dalam sistem DMFC.

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LIST OF ABBREVIATIONS

^{13}C NMR	-	^{13}Carbon Nuclear Magnetic Resonance
2D	-	2-Dimensional
3D	-	3-Dimensional
AFC	-	Alkaline fuel cell
C/O	-	Carbon to Oxygen ratio
CB	-	Carbon Black
CNF	-	Carbon Nanofiber
CNT	-	Carbon nanotube
CO	-	Carbon monoxide
CV	-	Cyclic Voltammogram
CVD	-	Chemical Vapor Deposition
DC-PECVD	-	Direct Current Plasma-Enhanced Chemical Vapor Deposition
DMFC	-	Direct methanol fuel cell
DWCNT	-	Di-Wall Carbon Nanotube
ECSA	-	Electrochemical Active Surface Area
EDX	-	Energy Dispersive X-ray
FC	-	Fuel Cell
FESEM	-	Field emission scanning electron microscopy
FTIR	-	Fourier transform infrared
GNF	-	Graphitic Nanocarbon
GNS	-	Graphene nanosheets
GO	-	Graphene oxide Nanosheets
HRTEM	-	High resolution - transmission electron microscopy

MCFC	-	Molten carbonate fuel cell
MOR	-	Methanol Oxidation Reaction
MWCNT	-	Multi-Wall Carbon Nanotube
NASA	-	National Aeronautics and Space Administration
OAD	-	Oblique Angle Deposition
PAFC	-	Phosphoric acid fuel cell
PC	-	Personal Computer
PECVD	-	Plasma-Enhanced Chemical Vapor Deposition
PEMFC	-	Proton exchange membrane fuel cell
PFI	-	Perfluorinated Ionic
POM	-	Polyoxometalates
Pt	-	Platinum
Pt-Ru	-	Platinum-Ruthenium
rGO	-	reduced Graphene Oxide
RT	-	Room Temperature
SOFC	-	Solid oxide fuel cell
SWCNT	-	Single Wall Carbon Nanotube
TCF	-	Transparent Conductive Films
TEM	-	Transmission electron microscopy
TGA	-	Thermogravimetric Analysis
UV-Vis Spectrophotometry	-	Ultra Violet -Visible Spectrophotometry
VGCNF	-	Vapor Grown Carbon Nanofiber
XPS	-	X-Ray Photoelectron Spectroscopy
XRD	-	X-Ray Diffractometer

LIST OF SYMBOLS

d	-	Average particle size
π	-	Mathematical constant (~3.142)
θ	-	Angle
λ	-	Wavelength
$\beta_{1/2}$	-	Width of the peak at half height in radians
ρ	-	Resistivity
σ	-	Conductivity

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Fuel cells have received much attention as the most promising alternative energy sources. Based on 'reverse electrolysis' concept of converting a fuel directly into electrical energy, fuel cells have several advantages such as high efficiency, low environmental impact and flexible application. Therefore, the great efforts to develop and design fuel cells as new power sources have been devoted due to the increasing concern of environmental issues and the depletion of fossil fuels for the last few decades (Sundmacher, 2010). The basic principal of a fuel cell is to directly convert the chemical energy into electricity and heat. Among the type of fuel cells, direct methanol fuel cell (DMFC) is one of the most promising fuel cell for the environmentally friendly energy conversion system. DMFC is a promising alternative to rechargeable batteries due to the high energy density of 6.1 kWh kg^{-1} of the methanol fuel used in the DMFC (McGrath *et al.*,2004) and high efficiency of the fuel cell system itself (Li and Faghri, 2012). In general, DMFC consists of a proton exchange membrane or polymer electrolyte membrane in between catalyst layer and diffusion layer at either side of anode and cathode which porous electro-catalytic electrodes are attached.

DMFC have been extensively studied and persistent attention in recent years due to some advantages such as ease of handling liquid fuels (McGrath *et al.*,2004), low pollutant emission, high energy conversion efficiency and low operating temperature (Basri *et al.,* 2010). These advantages are important for portable electronic devices such as laptop, computers, smart phones and MP3 players since it has been developed at rapid pace and demanding ever-increasing energy and power density in rechargeable batteries (Li and Faghri, 2012). However, the commercialization of DMFCs is still inhibited by some critical barriers such as the high cost of Platinum (Pt) electrocatalyst (Cheng *et al.,* 2013), the poisoning of the electrocatalyst by CO-like species at the anode and the slow electrooxidation kinetics of methanol at relatively low temperatures (Huang *et al.,* 2012). According to Huang *et al.*,(2012), the development of a novel class of electocatalyst with higher poison tolerance and greater methanol oxidation activity is the best ideal to overcome the problems as stated above. Many attempts have been carried out in order to enhance the electrocatalytic activity and CO tolerance of catalysts such as preparing alloying metal catalyst (Tian *et al.,* 2007) and preparing Pt and its alloy with different morphology (Chen *et al.,* 2004; Liang *et al.,* 2004).

Nowadays, the adoption of novel carbon materials as the catalyst support arises great interest to achieve high catalytic activity toward methanol oxidation reaction such as multi-wall carbon nanotube (Jha *et al.,* 2008), carbon nanofiber (Guo *et al.,* 2006) and graphene (Dong *et al.,* 2010). According to Han *et al.*,(2003), the performance and stability of DMFCs are strongly dependent on the characteristics of carbon support as well as catalytic active species. A significant enhancement in DMFCs performance have been brought by using carbon materials with a desirable characteristics such as good crystallinity and high surface area. Therefore, the fabrication of catalyst supports together with a low platinum loading is an attractive goal in DMFC technology.

1.2 Problem Statement

Platinum (Pt) is a noble metal catalyst that most frequently used as the anode electro-catalyst in DMFC application because of its superiority catalytic activity performance. However, the high cost of Pt issue is the major obstacle in the commercial application of DMFC (Liu *et al*., 2012). In addition, the efficiency of Pt-based electro-catalyst in DMFC is limited with the consequence of highly Pt poisoning by carbon monoxide (CO). CO is an intermediate product produced during the oxidation process of methanol or impurities (Bambagioni *et al*., 2009). This intermediate causes the slow of electro-oxidation kinetic due to its adsorption to the active site of Pt catalyst. Thus causes a significant loss in DMFC performance.

Based on these drawbacks, many researchers have made some efforts to produce alternative catalyst via modification of Pt to another metal with the decrease of Pt content. The most Pt-based alloy used as anode catalyst in DMFC is Pt-Ru. Pt–Ru is the predominant binary electro-catalyst since it has the capability to exhibit significant activity for methanol electro-oxidation as well as the removal of the poisoning CO or CHO species. However, previous studies have shown that the use of Pt-Ru catalyst still requires high loading which is lead to high cost and the durability issue is one of the serious problems due to the dissolution of Ru under fuel cell conditions (Kanninen *et al*., 2012).

Therefore, in order to reduce the cost and improve the activity of electro catalyst, there is a need to develop the platinum-based catalyst with conductive support usually carbon black which can greatly influence to enhance the dispersion, activation and stability of metal catalyst, electrochemical behavior as well as increasing the electro-conductivity (Liu *et al*., 2012). Carbon black is a carbon-based materials that are the most widely used in anode electrocatalyst support. Typically, carbon blacks are always found in commercial electrocatalyst for DMFC. This is because carbon black has the high electrical conductivity (Hall *et al.*, 2004).

Unfortunately, there are some disadvantages of using carbon black in which related to pore size distribution and surface chemistry affects (Liu *et al.,* 2012).

Nowadays, many of the new and novel carbon-based nanomaterials have been developed to replace carbon black as electrocatalyst supports such as carbon nanotubes (Song *et al.,* 2010), carbon nanofibers (Sebastian *et al*., 2012) and graphene (Ji *et al.,* 2012). In recent years, graphene as electrocatalyst support has given a rise attention in fuel cell application and shown a great promising material due to its unique characteristics such as high surface area, high stability and large surface to volume ratio (Geim and Novoselov, 2007), strong mechanical property (Lee *et al*., 2008), electrical conductivity (Service, 2009) and thermal conductivity (Balandin *et al*., 2008). Graphite powder can be used as the raw material to produce graphene through the formation of graphene oxide by oxidation with acid using modified Hummer's method and subsequently chemical reduction process. According to Liu *et al*., (2012), the stability and dispersion of electrocatalyst is greatly influenced by the physicochemical properties of the electrocatalyst support, the highly distributed of small size catalyst nanoparticles and narrow distribution due to the large surface-to-volume ratios. Therefore, the development of highly disperse electrocatalyst onto the support is still a great challenge.

In the present work, the fabrication of the graphene nanosheets supported Pt nanocomposite catalyst (GNS/Pt) via the impregnation and chemical reduction method by using sodium borohydride as reducing agent for methanol oxidation reaction at the anode electrode in DMFC was investigated. This Pt electrocatalyst incorporation with graphene nanosheets as the electrocatalyst support has the capability to enhance the electrocatalytic activity for methanol oxidation reaction at the anode in DMFC (Qian *et al.,* 2011).

1.3 Significance of Study

The significance of this study lies in the fact that the fabrication of this Pt nanocomposite catalyst can increase the rate of methanol oxidation reaction at the anode electrode in DMFC. Furthermore, the method used to fabricate the nanocomposite catalysts are very simple, clean, easy to handle and no time consuming. Therefore, the fabrication of this GNS/Pt nanocomposites catalyst can contribute to the significance benefits in term of processing method and the performance of DMFC.

1.4 Objective of study

Based on the aforementioned research background and problem statement identified, the main objective of this study is to develop the Pt-based catalyst by incorporating with graphene nanosheets as catalyst support with improved catalytic properties. Thus, the specific objectives include the following:

i. To synthesis and characterize the graphene oxide nanosheets and graphene nanosheets.
ii. To fabricate and characterize the GNS/Pt nanocomposite catalyst.
iii. To evaluate the catalytic performance of GNS/Pt nanocomposite catalyst for methanol oxidation reaction at the anode.

1.5 Scopes of the study

In order to achieve the aforementioned objectives, the following scopes are drawn:

i. Preparing graphene oxide nanosheets (GO) via modified Hummers' method.

ii. Preparing graphene nanosheets via chemical reduction process using sodium oxalate ($Na_2C_2O_4$) as the reducing agent at 95^{o}C with varying the reduction time for 30 minutes, 1 hour and 2 hours.

iii. Characterizing of GO and GNS by using XRD, TEM, HRTEM, UV-Vis Spectrophotometry, FTIR, XPS, Raman Spectroscopy, solid ^{13}C NMR and TGA.

iv. The electrical conductivity characterization of GO and GNS using Four Point Probe measurement method.

v. Preparing GNS/Pt nanocomposite catalyst via impregnation and chemical reduction method simultaneously using sodium borohydride as reducing agent at 85 ^{o}C with the reduction time for 3 hours.

vi. The GNS/Pt nanocomposite catalyst characterization using XRD, HRTEM, FESEM, EDX, Raman spectrometer and XPS.

vii. Testing the electrocatalytic properties of GNS/Pt nanocomposite catalyst via cyclic voltammogram.

viii. Preparing Vulcan XC-72/Pt catalyst and graphite/Pt catalyst as control sample for comparison in term of catalytic performance with GNS/Pt nanocomposite catalyst.

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