1.0 INTRODUCTION

1.1 Background and Motivation

There is increasing evidence that worldwide production of petroleum, natural gas and other non-renewable fossil resources will undergo a major decline in the future (Riva, 1995; Edwards, 1997; OPEC, 1999). Furthermore, the environmental impact of using these and other non-renewable fuels, such as coal and uranium, present a major obstacle to the continued use of such resources to meet our energy needs. The conventional petroleum-based fuels such as gasoline or diesel, as well as natural gas and coal, all contain carbon. When these fuels are burnt, their carbon recombines with oxygen from the air to form carbon dioxide which is the primary greenhouse gas that causes global warming (Thomas et al., 2006; Davis and Orendovici, 2006). In the same vein, combustion of fossil fuels at the high temperatures and pressures reached inside an internal combustion engine (that powers most vehicles) or in an electric power plant produces other toxic emissions (Pimentel, 1994; Hough et al., 2006; Choung et al., 2006). Carbon monoxide, oxides of nitrogen and sulphur, volatile organic chemicals, and fine particles are all components of air pollution attributable to the refining and combustion of fossil fuels. When released into the atmosphere, many of these compounds cause acid rain or react with sunlight to create ground level smog. Vast ecosystem damage, increased lung disease and cancer are the ultimate price inhabitants pay for consuming these fossil fuels (Pimentel et al., 1994). Therefore, as we enter the new millennium, environmentally friendly energy sources will soon become a necessity due to the threat of global warming and dependence on foreign petroleum reserves. The proton exchange membrane fuel cell (PEMFC) presents a promising solution to these challenges.
Chapter one

Introduction

The PEMFC is an advanced technological device that continuously converts chemical energy in fuels directly into electricity, heat and water without going through any combustion process (Iyuke et al., 2003; Litster and McLean, 2004). It is an alternative energy source that will compete with many other types of energy conversion devices such as the gas turbine in a power plant, the car gasoline engine and even the laptop battery. Combustion engines like the turbine and the gasoline engines burn fuels and use the pressure created to do mechanical work while batteries convert chemical energy into electrical energy. The PEMFC would perform both tasks even more efficiently. It is also fast becoming a popular and direct energy conversion device due to its high environmental benefits, high power density characteristics which include portability, light weight and low operating temperature that allows easy start-up (Wood et al., 1998). These properties as well as its ability to change power output are some of the characteristics that make PEMFC the most suitable device for many engineering applications, especially in automobiles. However, its performance needs to be further optimized to be cost competitive with current energy conversion devices like the internal combustion engine or batteries. Significant strides are being made towards addressing this goal of performance improvement and cost optimization through development of better membranes, improved catalyst layers, fabrication techniques leading to better catalyst utilization and better flow field designs that enhance reactant and product transport within the fuel cell (Gottesfeld and Zawodzinski, 1997).
A significant breakthrough in fuel cell technology was the development of the porous diffusion electrodes that create catalytic effects in the process (Srinivasan et al., 1988). Platinum (Pt) has been identified as the best catalyst for both hydrogen oxidation and oxygen reduction reactions (Baschuk and Li, 2001; Antolini, 2003; Shen and Tian, 2004). This is due to the electrocatalytic activity of platinum particles. This property has made it more important as catalyst composite with carbon nanotubes (CNTs) than many other metals (Maiyalagan et al., 2005; Xie et al., 2006; Onoe et al., 2007). This characteristic of platinum could be attributed to large surface areas and its high dispersion in this material (CNTs). Researchers such as Kim et al., (1998), Rajesh et al., (2002), Iyuke et al., (2003), Matsumoto et al., (2004), Daud et al., (2004), Lister and McLean (2004), Tsai et al., 2006 and Onoe et al., (2007) have also reported many significant findings related to the use of platinum, carbon and CNTs in the design of PEMFC electrodes. The development of a cheap electrode is perhaps the major challenge facing the commercialization of PEMFCs today. Therefore, for sustainability and economic production of a PEMFC on a commercial scale, cost effective and adequate functionality of the individual components especially the electrode, are of paramount importance for significant service operation and optimum output.

Carbon is a critical material in the preparation of fuel cell electrodes (Auer et al., 1998; Dicks, 2006) and carbon nanotubes have been promising in this sort of application due to its corrosion resistant property, and electronic, electrical and thermal conductivity. The peculiar electronic, adsorption, mechanical and thermal properties of carbon also suggest
that CNTs are suitable materials for electrocatalytic supports in the PEMFC (Lordi et al., 2001; Li et al., 2002; Li et al., 2004).

CNTs are made of bundles of layers of cylindrical graphite sheets with outside diameters ranging from 0.4 – 100 nm and lengths ranging from several microns to millimeters (Hoenlein et al., 2003; Kenneth et al., 2003). Based on their discovery, CNTs are classified into two groups namely: single walled carbon nanotubes (SWCNTs) and multi walled carbon nanotubes (MWCNTs). Due to their nanometre scale and interesting properties, they have undergone numerous theoretical and experimental studies and they are also of great interest for many applications such as in batteries (Che et al., 1999; Li et al., 2006), flat panel displays (Wildoer et al., 1998), chemical sensors (Kong et al., 2000), bulky paper (Kulesza et al., 2006), field emission displays (Xinghui et al., 2005; Zeng et al., 2006) and composites (Shaffer, 2004).

Electrodes, which are integral parts of a PEMFC, are sites where energy conversion reactions take place for energy generation. In the last few decades, platinum has proved to be the most active catalyst for use in the PEMFC (Yi et al., 2002; Xue et al., 2005). It is therefore anticipated that a platinum electrode on a CNT support will be developed to enhance the stability and electrocatalytic properties in PEMFC production. This study is therefore aimed at preparing and developing an alternative and locally made CNT supported platinum electrode for the fabrication of a membrane electrode assembly (MEA) which is often referred to as the heart of proton exchange membrane (PEM) fuel cell.
1.2 Research Problems/Questions

The ultimate goal of nanotechnology is the creation and utilization of functional materials, devices, and systems with unique properties that are obtained through the control of matter at the nanoscale (Yinzhong et al., 2003; Mamalis et al., 2004). Therefore, this research, which uses nanotechnology as its base, is set to answer the following questions on the preparation of electrocatalytic CNT/platinum electrodes for PEM fuel cells. These questions are:

- What are the limiting factors in the current methods of production that could be overcome?
- Can electrocatalytic electrodes for PEMFCs be produced from locally sourced platinum materials?
- Are the properties of the locally produced electrodes comparable to those of commercially available ones?
- What are the inherent merits of the locally produced CNT/platinum electrodes over the existing ones?

1.3 Aim and Objectives

The primary aim of this research work is to synthesize and characterize CNT/platinum electrocatalytic electrodes for the fabrication of a MEA using locally available materials. This aim will be achieved through the following objectives:

a. Synthesis of MWCNTs from an acetylene carbon source, ferrocene or/and iron–cobalt catalysts using chemical vapour deposition methods.
b. Purification and functionalization of synthesized MWCNTs using a mixture of concentrated HNO₃ and H₂SO₄ acids.

c. Preparation of a CNT/platinum catalyst using platinum precursor salt and the purified/functionalized MWCNTs and determination of platinum loading in the prepared catalysts.

d. Characterization of the CNT/platinum electrocatalyst, specifically its thermal, electrical and chemical properties.

e. Preparation of electrocatalytic electrodes using the synthesized CNT/platinum and carbon cloth/paper.

f. Fabrication of a single membrane electrode assembly (MEA) using the prepared electrodes and a locally prepared sulphonated membrane by a hot pressing technique.

g. Testing and analysis of the fabricated MEA in a single PEM fuel cell to investigate properties such as voltage, power density, current density with respect to platinum loading on the electrodes.

1.4 Scope of the Research

The scope of the research encompasses the synthesis, purification, and characterization of CNTs for the production of CNT/platinum catalyst to make electrocatalytic electrodes with carbon paper for the fabrication of a Membrane Electrode Assembly. It also involved testing of the fabricated MEA to analyze and compare its properties with the commercially available ones.
1.5 Contribution to Knowledge

The research studies of the development of carbon nanotubes/platinum electrodes for PEM fuel cells using the proposed methodology are expected to:

a. Produce MEAs that could achieve better quality than the commercially available ones.

b. Develop an optimum production process for CNT/platinum electrocatalytic electrode production for a PEM fuel cell.

1.6 Structure of the Thesis

This thesis is divided into six chapters. The first chapter reports on the general introduction of the thesis. The aim and objectives of the research are also fully illustrated in this chapter. This chapter also reports on the areas to be covered on this research. Chapter two is the chronicle of the previous works that have been carried out on fuel cell, carbon nanotubes and the use of these carbon materials in the fuel cells. Chapter three reports all the experimental procedures adopted in this work. This chapter is divided into three parts. The first part reports on the synthesis of carbon nanotubes using a swirled floating chemical catalytic vapour deposition (SFCCVD) and horizontal chemical vapour deposition (CVD) reactors. The description and the procedures for using these reactors for the synthesis of these carbon materials are reported. This part also contains the purification and characterization of the synthesized CNTs. The second part of this chapter describes the preparation of the various loadings of Pt–CNT catalyst using the purified CNTs and platinum salt. The characterizations of this catalyst are also reported in this part. The third section of this chapter reports the preparation of the catalyst electrodes.
using the prepared Pt–CNT catalyst and carbon paper. The coupling of the catalyst electrodes and the sulphonated membrane using a hot pressing method to make a membrane electrode assembly (MEA) is also reported in this part. Finally, the testing of the fabricated MEA in a single proton exchange membrane fuel cell is also discussed. The materials, equipment and facilities used to carry out all the experimentations and characterizations in this work are extensively reported in this chapter. Chapter four reports the results obtained on the synthesis of carbon nanotubes using swirled floating catalyst chemical vapour deposition and horizontal chemical vapour deposition reactors. The results of all the characterizations and purification of these materials are also contained in this chapter. The results obtained in the preparation of various loadings of Pt–CNT catalyst, the parametric effect of Pt adsorption on CNT and the characterizations of results on these catalysts are discussed in the first section of chapter five. The other section discusses the analysis of catalyst electrodes and performance of MEAs in a single PEM fuel cell with regards to the loadings on the electrodes. Chapter six writes out the conclusions emanated from the analyses of the results of the research and recommendations for further studies.