1.0 Introduction

The concern for efficient use of clean energy all over the world has gathered rapid momentum and there is increasing awareness of the advantages of electro-chemical power as a source of clean energy production. Fuel cells, therefore, have been considered to be one of the future sources of clean energy for varieties of applications (Xing et al, 2004; Smitha et al, 2005; Millet and Mahadevan, 2005). When efficiency and environmental concern are the main issues, fuel cells can be considered as replacement for batteries. The fully fledged commercialisation of fuel cells by a few promising major suppliers has been greatly anticipated; but whether it will in fact be realised early in this millennium is uncertain because of the high cost of fuel cells compared to other energy sources (Gulzow et al, 2002; Gao et al, 2003). Out of the three components of fuel cells, namely electro catalyst, polymer electrolytes and bipolar graphite plates, the cost of polymer electrolyte is the highest. Reduction in the cost of the polymer electrolyte will help to improve the durability of the membrane in fuel cells. Apart from the cost of the components, long term reliability, distribution and supply strategy are some of other issues that need to be considered before fuel cells can be successfully introduced to the market in commercial quantities (Wang et al., 2005).

1.1 Background and Motivation

Most of the energy needed for domestic and industrial consumption comes from only one natural source, which is fossil fuel. This has led to the world fossil fuel demand outstripping fossil fuel production, resulting in a world energy crisis characterized by shortage in supply and price instability (Edward, 1987). A significant outcome from the energy crisis has been the realisation that the earth’s fossil fuels are limited resources that have been shrinking in recent years. There is also awareness that individuals and
countries have real responsibilities not only for future generations of energy but also to conserve the environment. This is because whatever is taken from the earth has an explicit cost to the geophysical state of the environment. Though there is no energy source that is completely environmentally safe, energy must be wisely used in order to minimise environmental hazard and optimize the efficiency with which it is produced (Kevin and Lewis, 1984). These concerns for the environment, as well as increasing dependence on imported fossil fuels have led to a call for alternative sources of energy, and better utilisation of existing energy sources (Yi and Nguyen, 1999; Lee et al, 2004).

Fuel cells, especially Proton Exchange Membrane Fuel Cells (PEMFC), are considered promising and an attractive replacement for existing sources of energy. This resource has a variety of applications in industry, transportation and small-scale power generation because of its low temperature of operation, allowing for easy start up, quick response to change in load and operating condition, as well as ease of assembling by the industrial process (Iyuke et al, 2003; Chedie and Munroe, 2003; Shibasaki et al, 2005).

Fuel cells are energy conversion devices that convert chemical energy into electrical and heat energy by electrochemical redox reaction at the electrodes of the cell, with water and heat as the only byproducts (Hays, 2005; Sopian and Wan Daud, 2006). The operation is set in motion by generating electrical potential when the fuel (usually humidified hydrogen or methanol) enters the anode and is transported through the porous electrode by convection and diffusion, and is subsequently split into proton ions (H⁺) and electrons (e⁻). The anodes conduct the electrons through an external circuit while the positive ions are conducted through the electrolyte (membrane) to the cathode. The oxidant, which is usually oxygen in air, enters the cathode and is also transported
through the porous electrode by convection and diffusion which later dissolves into the membrane phase of the catalyst layer, where it splits into individual atoms of oxygen (O\(^{-}\)). This exerts a strong negative attraction on the positive fuel ions through the membrane. When the hydrogen and oxygen ions combine, water is formed in the electrochemical reaction as shown in equations 1.1 – 1.3 (Guvelioglu and Stenger, 2005; Hays, 2005).

\[
\begin{align*}
\text{Anode:} & \quad 2H_2 \to 4H^+ + 4e^- \quad (1.1) \\
\text{Cathode:} & \quad O_2 + 4H^+ + 4e^- \to 2H_2O \quad (1.2) \\
\text{Over all electro chemical reaction:} & \quad 2H_2 + O_2 \to 2H_2O + \text{Energy} \quad (1.3)
\end{align*}
\]

Among the five main types of commercially available fuel cells, the Proton Exchange Membrane Electrode Fuel Cell (PEMFC) is the most promising choice for a clean energy source for automotive and portable applications (Cheddie and Munroe, 2003; Quan et al, 2005). This is because of its high energy density, rapid response to varying load, relatively quick start up, low operating temperature and virtually zero emission, all of which help in reducing air pollution and greenhouse effect (Quan et al, 2005; Shibasaki et al, 2005). The fundamental structure of the PEMFC comprises of an anode and a cathode electrode separated by a solid membrane that acts as an electrolyte (Iyuke et al, 2003; Maher and Sadiq, 2005; Hogarth et al, 2005). The membrane functions as an ionic conductor between the two electrodes, and a barrier for the passage of electron and gas cross leakage between electrodes (Xing et al, 2004). While the functions of the electrodes include provision of surface sites where ionization and de-ionization of fuel and oxidant take place, they act as a physical barrier between ions in the gaseous stream and liquid electrolyte. The membrane also provides a porous interface between ions in the gaseous stream and ions conducting the electrolyte (Song et al, 2003; Hays, 2005).
The heart of PEMFC is the Polymer Electrolyte Membrane (PEM). At present the most commercially available membrane is the Nafion® (Haubold et al., 2001; Cheddie and Munroe, 2003; Daniel, 2005). Nafion® is a co-polymer structure of perfluoro sulphonic acid polymer, consisting of a Teflon-like backbone with side chains ending with – SO$_3$H groups. Nafion has high hydrolytic and oxidative stability, and excellent proton conductivity. These properties are attributed to the three distinct regions that Nafion® is made up of, as shown in Figure1.1 (Xing et al, 2004). The first region is hydrophobic semi-crystal ionic (poly – tetrafluoroethylene), which primarily consists of the backbone chains. The backbone chains provide structural stability to the membrane and prevent it from dissolving in water. The second region is largely empty and amorphous, consisting of side chains (regularly spaced perfluoro vinyl ether) and some sulphonic acid groups. The final region consists of strongly clustered hydrophilic sulphonate ionic groups, which are responsible for conducting proton across the membrane (Haubold et al, 2001; Dhar, 2005). Ion conduction only takes place when the membrane is hydrated with water. Dehydration of the membrane results in lower ionic conduction with de-adhesion of the membrane. Excess water production occurs at high current densities, which results in reduced mass transport on the cathode side, leading to oxygen rate reduction at the cathode compared to hydrogen oxidation rate at the anode and thus reduces the performance of the cell (Cheddie and Munroe, 2003).

\[
\begin{align*}
[(\text{CF}_2 - \text{CF}_2)_{6.5} - \text{CF} - \text{CF}_2]_{230} \\
\text{O} - \text{CF}_2 - \text{CF} - \text{O} - \text{CF}_2 - \text{SO}_3 \text{H} \\
\text{CF}_3
\end{align*}
\]

Figure 1.1: Chemical structure of Nafion (Sopian and Wan Daud, 2006).
Despite the high potential of PEMFC as an environmental friendly alternative energy source, high cost and limited durability hinder its production for commercial application (Sopian and Wan Daud, 2006). Progress has been made over the past few years on ways to achieve the commercialization of this alternative energy source by reducing the cost of the cell contents consisting of the electrode, the flow field plate and membrane (Sopian and Wan Daud, 2006). But the monopoly of the membrane synthesis by a few nations and companies, and the lack of locally available material to provide alternatives to imported membrane, leads to heavy dependence on importation. To address this problem, this work is focused on the synthesis of proton electron membrane from polystyrene butadiene rubber, which is locally and readily available in South Africa. The research also intends to improve the proton conductivity and contact area of the synthesized membrane through blending with carbon nanoparticles (Tiyantah and Lemoen, 2004). Carbon nanoparticles include carbon nanoballs, carbon nanotubes, fullerenes etc; carbon nanotubes especially are bundles of layers of cylindrical graphite sheet with diameters ranging from 0.4 – 100nm and lengths ranging from several microns to millimeters (Hoenlein, et al., 2003; Teo et al, 2003; Kathayini et al, 2004). There are two kinds of nanotubes: single walled carbon nanotubes (SWNTs) and multi walled carbon nanotubes (MWNTs).

Single walled carbon nanotubes are crystalline single graphite layers rolled up into a hollow graphite cylinder, with diameters ranging from 0.4 – 2 nm and a length of few microns (Szleifer and Yerushalmi-Rozen, 2005). The diameters and chiralities determine whether a single wall carbon nanotube is a conductor or semi conductor (Kaneto et al., 1999; Szleifer and Yerushalmi-Rozen, 2005; Katok et al, 2006). Multi-walled carbon nanotubes consist of several concentric graphitic layers with diameters ranging from 10 –
100nm and more than 10µm in length (Kaneto, et al, 1999). Teo, et al, 2003 described carbon nanotubes as electrical conductors with a complete covalent bond, a property that distinguishes them from metals and makes them not suffer from atomic diffusion or electronic migration. These unique properties make nanotubes suitable after modification for many industrial applications. Promising applications of carbon nanotubes include: reinforcement of components, hydrogen storage, catalysis, field emitter, electronic devices and fuel cell (Krinjin and John, 2000; Lozovik et al, 2003; Conteau et al, 2003; Philip et al, 2003; Kuwana et al, 2005). Other forms of carbon nanoparticles are; carbon nanofibres (CNFs), and carbon nanohorns (CNHs).

1.2 Research Problem

The urgent need for alternative sources of energy promotes the challenge to develop a new technology that will produce an efficient and environmentally friendly energy source other than fossil fuel. Fuel cell systems especially proton exchange membrane fuel cells are considered the most promising alternative method of converting and exploiting energy, and offers many benefits including low pollutant emission, sustainability, and reliability (Smitha et al, 2005; Li et al, 2005; Sopian and Wan Daud, 2006).

However, a number of issues need to be resolved before proton electron membrane fuel cell can be commercially and technologically viable. These include the availability, durability and monopolies of the membrane technology by few companies and nations. The most common polymer membrane is Nafion®, a poly perfluoro sulphonic hydrated acid produced by DuPont (Iyuke et al, 2003; Chen et al, 2005). Nafion® has been widely used due to its attractive properties, including high mechanical strength, high oxidative
and hydrolytic stability, and high ionic conductivity (Xing et al, 2004; Wang et al, 2005; Song et al, 2005). Loss of conductivity at high temperature, high permeability to the fuel and the monopoly of technology by a few nations and companies that supply the membrane, hinder the development of perfluoronated polymers for full commercial application (Bashir et al, 2001; Song et al, 2003; Chen et al, 2005).

In order to reduce the cost of polymer electrolyte membrane, the development of novel polymer electrolyte membrane has been actively carried out as an alternative to Nafion®. The problems with these alternative membranes are the excessive swelling, lower proton attraction, higher permeability to the fuel, low electrical conductivity and contact area (Chen et al, 2005). These problems are attributed to the process route used in introducing the sulphonated graft chain into high chemical stability fluorinated polymers, which results in poor bonding of the catalyst layer to the grafted membrane. They are therefore not suitable for the commercial realisation of proton electron membrane (Chen et al, 2004; Lee, 2004). Moreover, the biggest challenges in PEMFC commercialisation are thus to reduce the cost of membrane in the PEMFC and to transform laboratory findings into commercial benefit. The United States of America, Europe, Canada, and Japan are leaders in fuel cell research and fuel cell commercialization (Sopian and Wan Daud, 2006). A hydrogen future act was recently passed in the United States of America senate to prepare the nation for the future hydrogen economy and $1 billion from the USA government will be spent in the next five years to commercialise fuel cells and prepare the USA for the future hydrogen economy (Sopian and Wan Daud, 2006). With the rising awareness and interest in PEMFC as an alternative source of energy, there is a need to reduce the cost of membrane which is the heart of the cell. The purpose of this research, therefore, is to synthesize proton exchange membrane from locally sourced
materials. This could be achieved by using non-fluoronated membrane with a cheaper sulphonated polymer backbone. The sulphonation of polystyrene butadiene rubber and blending with carbon nanoparticles should produce high proton conductivity and good contact area membrane better in strength, performance and quality than the fluorinated membrane. This research is therefore set to answer the following questions on the design and development of Proton Exchange Membrane from synthetic rubber (polystyrene butadiene) that is readily available in carbon nanoparticles in South Africa:

1. Are the present membranes synthesised efficiently for commercial realisation and application?

2. What are the limiting factors in the currently available membrane that could be overcome in this research?

3. What are the advantages of the local synthesised membrane over the commercial existing membrane?

4. What are the effects of carbon nanoparticles on the quality and performance of the synthesized membrane?

1.3 Contribution to Knowledge

Formulation of membrane

The challenges in PEMFC research and development are to make the membrane which is the hearth of fuel cell available. This could be achieved through the development of an alternative membrane electrolyte from locally sourced material, which is the focus of this research. This work involves changing from the existing polyfluoro based membrane to non-polyfluoro membrane from locally available polystyrene butadiene rubber, easily
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sourced within South Africa environment. This should yield an effective membrane with better quality and commercial realization of membrane for technological development.

**Development of CNBs/PSBR composites polymer exchange membrane**

Based on the characteristic properties of carbon nanoparticles, blending of carbon nanoballs with the membrane should help to increase the contact area and strength of the synthesized membrane. This will improve the performance of the synthesized membrane by increasing the rate of proton attraction and provide a good barrier to the fuel and electron in the membrane electrode assembly (MEA). This hypothesis is supported by the billions of dollars being invested by South African Government and private sectors for the development of carbon nanoparticles and improved practical applications of PEMFC (Purvis, 2002). A consistent synthesis of nanoparticles is required for the production of quality membranes and other technological applications. This requires an effective process development for carbon nanoballs production, and thus constitutes a major contribution to the body of knowledge in the field.

**Fabrication of membrane electrode assembly**

This research work will be concluded with the fabrication and testing of membrane electrode assembly (MEA) in PEMFC stacks and the comparison of MEA performance with commercially available MEA.

**1.4 Aim and Objectives**

This research is focused on the formulation, casting, characterization and testing of a proton exchange membrane blended with carbon nanoparticles. The results of this work are intended to be technologically sound, environmentally friendly, and constitute a
commercially viable process route for the production of proton exchange membrane, benefiting the industries in South Africa and the world at large. The study will involve the assessment and determination of experimental data for the modelling and optimisation of the process. The aim would be achieved via the objectives outlined below:

1. To synthesize Proton Exchange Membrane (PEM) by sulphonation of the phenyl group in polystyrene butadiene at various concentrations of the sulphonating agent, weight of polymer, reaction time, speed of stirrer and temperature.

2. To synthesize carbon nanoparticles and blend them into the membrane films with carbon nanoparticles at various mass to optimize the resulting blends.

3. To cast thin films membrane from the blends of sulphonated polystyrene butadiene rubber and carbon nanoballs.

4. To characterize the membrane to determine the thermal stability, degree of sulphonation, ion exchange capacity, water intake, swelling ratio, porosity, solvent uptake, conductivity, solubility and chemical properties.

5. To compare the properties of the synthesized membrane with the existing membrane (Nafion®).

6. To fabricate and test compact membrane electrodes assemblies (MEA) in a single fuel cell stack.

7. To develop a predictive model to predict the performance of MEA in a single fuel cell stack.

1.5 Scope of Research

The scope of the research encompasses the preparation of fuel cell membrane from polystyrene butadiene rubber blend with carbon nanoparticles. It also includes the
characterization of the prepared membrane, fabrication and testing of membrane electrode assembly (MEA) in PEM fuel cell stack and the development of a deterministic model for the membrane design and synthesis.

1.6 Organization of Thesis

Chapter one gives the background/motivation, research problem, contribution to knowledge, aim and objectives and scope of the research. Chapter Two discusses the literature review of the previous work on fuel cell in general, membrane synthesis, and carbon nanoparticles synthesis and provides a rationale for focusing on Polymer Exchange Membrane Fuel Cells (PEMFC). Chapter Three describes the procedure for operating the various experiments conducted in this research. Chapter Four presents and discusses the results on this research into the production of carbon nanoparticles. Chapter Five includes the results and discussion of the investigation into the synthesis of membrane and membrane composite. Finally, Chapter Six presents the conclusions and recommendations for future work on the fabrication of MEA.