3.0 EXPERIMENTAL WORK

In this chapter, various experimental procedures adopted in the production and characterization of carbon nanoballs and the synthesis of PEM from polystyrene butadiene rubber will be presented. This chapter is divided into four major parts. The first part describes the various techniques employed in synthesizing carbon nanoballs by the Swirled Floating Chemical Catalytic Vapour Deposition (SFCCVD) method. The second part describes the synthesis of polymer exchange membrane by the sulphonation of polystyrene butadiene rubber and blending of the sulphonated polymer with carbon nanoballs, while the third part reports the procedure for the various analyses conducted on the sulphonated rubber. The last part of the chapter describes the fabrication and testing of Membrane Electrode Assembly (MEA) using the prepared electrodes and membrane. The flow diagram of various experiment conducted in this research is shown in Figure 3.1.
Proton Exchange Membrane (PEM) for Fuel Cell Application

Synthesis and characterization of carbon nanoballs by swirled floating catalyst chemical vapour deposition reactor

Sulphonation and casting of polystyrene butadiene rubber for proton exchange membrane synthesis for fuel cell application

Formulation of SPSBR/CNBs composite polymer exchange membrane for fuel cell application

- Viscosity measurement
- Effects of sulphonating agents
- Effects of sulphonation time
- Effects of sulphonation temperature
- IR and HNMR analysis to confirm sulphonation
- Elemental analysis
- Ion exchange capacity
- Proton conductivity
- Water uptake, solvent uptake and porosity to methanol
- Methanol cross over
- Thermal stability

Testing of the PEM in a single fuel cell stack.

Figure 3.1: Flow diagram of various analyses conducted on synthesis of polymer exchange membrane from PSBR and CNBs
3.1 Synthesis and Characterization of Carbon Nanoballs

The apparatus used for the carbon nanoballs production is the one developed by Iyuke (2005), presented schematically in Figure 3.2. It consists of a vertical silica plug flow reactor [1] immersed in a furnace [2] with a sensitive temperature regulator. A system of rotameters, pressure controllers and valves to control the flow of hydrogen, nitrogen, argon and acetylene gases into the reactor were also attached to the equipment. The upper end of the reactor is connected to a condenser [3] which leads to two delivery cyclones [4 &5] where the CNBs and other carbon nanoparticles (CNPs) produced are collected continuously. The ferrocene catalyst used was poured into a silica vaporiser [6] placed on a heater with a temperature regulator. This catalyst vaporiser is connected to the swirled mixer [7] which in turn leads into the reactor. Nitrogen was first turned on to purge the system of any impurity. The reactor and ferrocene heater were switched on while the nitrogen was running. At a reactor temperature of about 300°C, nitrogen was turned off to prevent it from reacting with oxygen. Argon was then turned on at the prescribed flow rate to continue purging and act as a carrier gas. At a reactor temperature of 900°C-1050°C and catalyst heater at 150°C, 5 grams of ferrocene was charged into the heater at intervals, while hydrogen and acetylene gases were turned on at specified flow rates (Iyuke et al, 2007; Abdulkareem et al, 2007). The smoky products or carbon vapour that evolved from the reactor were cooled at the condenser and collected in the cyclones. The turbulence created by the swirling reacting mixture in the reactor was able to reduce CNPs deposition on the reactor wall. The synthesised CNPs were analysed with the Transmission Electron Microscope (TEM) (JSM 840), High magnification transmission electron microscope (HMTEM) (Philips CM 200), Thermo gravimetric Analyser (TGA) (Perkin Elmer Pyris 1 TGA Anaylzer) and Raman spectroscopy (Jobin Yvon T 6400).
3.1.1 Non catalytic synthesis of carbon nanoballs

The synthesis of carbon nanospheres was carried out in a swirled floating catalytic chemical vapour deposition (SFCCVD) reactor (Figure 3.1). A similar procedure to that in Section 3.1 was followed except that in this case, the catalyst ferrocene was not used. The product from the cyclones was collected and analyzed. The soot was characterized using Transmission Electron Microscopy (TEM) (JEOL 100S Electron Microscope) and Thermo gravimetric Analysis (TGA) (Perkin Elmer Pyris 1 TGA Anaylzer), BET surface area analysis (Micromeritics TriStar Surface Area and Porosity Analyzer) and Powder X-ray difractometry (PXRD) (Bruker axs D8 Advance PXRD). No catalyst was required in the synthesis of the CNBs. The materials produced were very pure because they were not amorphous and did not require the removal of the catalyst post-synthesis process. The
reaction temperature (900-1000°C), acetylene and argon gas flow rates were varied in order to study their effect on the structure and yields of the CNBs obtained.

3.1.2 X-ray diffraction (XRD) analysis
X-ray diffraction (XRD) (Philips X Pert) analyses were conducted for the qualitative and quantitative analysis (phase identification) of the carbon nanoparticles, using the powder method. Phase identification of the mineral constituents of the samples was done by X-ray diffractometry. The X-ray diffractometer was operated at a generator voltage of 40 kV and a current of 20 mA with the goniometry 2θ values varying from 0° to 80° at a scan rate of 1.0 s/step. After X-ray scanning of the samples, the background and peak-positions were identified and based on the peak-positions and intensities; a search-match routine was performed. High Score Plus software was used for the quantitative phase identification.

3.1.3 Surface morphology of carbon nanoballs
Both the High and Low Magnification Transmission Electron Microscope (TEM) were used to investigate the surface morphology of the carbon nanoparticles. To prepare the samples for TEM analysis, a trace amount of each sample (all of which were black in colour and in a powder form), was ultrasonically vibrated in methanol in small tubes for about 10 seconds until it was well dispersed and formed a suspension in the solvent. A drop of this suspension was spread on a 300 mesh copper grid with lacy carbon thin film and allowed to dry. After drying, the grid was loaded into the instrument for TEM operation and analysed by checking for the presence of long carbon chains. A clear picture was achieved by varying the magnification using a magnification knob. After photographed the desired picture, the carbon grid was discharged from the machine and
the next sample is analysed by following the same procedure, and again the microscopic image is printed.

3.1.4 Raman spectroscopy

This device was used to detect the presence of carbon nanoparticles by checked for the Raman Peaks corresponding to the carbon nanoparticles range. The operation can also be used to determine whether the nanoparticles produced are single-walled or multi-walled carbon nanotubes, nanofibres or nanoballs. The sample excitation was performed using 6mW of 514.5 nm light with a 1µm spot size. The integration time for the spectral collection was 120s per acquisition.

3.2 Proton Exchange Membrane Synthesis

Different weights (5, 10, 15, 20, 25 and 30 g) of polystyrene-butadiene rubber (PSBR) (Karbochem, South Africa) were dissolved in 250 ml of 1, 2 dichloroethane (Analytical grade ≥98%: Merck South Africa). This was followed by the gradual addition (drop wise) of different concentrations of chlorosulphonic acid (Analytical grade ≥98%: Merck South Africa) in 1, 2 dichloroethane solution (Analytical grade ≥98%: Merck South Africa) that were initially chilled in an iced bath to eliminate latent heat, into a vigorously stirred solution of PSBR in a four-neck round bottom flask reactor under argon atmosphere at room temperature. The sulphonation reaction was allowed to proceed for 2 to 48 hours. The reaction was terminated by adding ethanol (Assay ≥ 98%: Merck South Africa) and the precipitated sulphonated polymer was recovered, washed with deionized water until the pH of wash reached the values of 6 – 7. The product was then dried in an oven at 80°C for 2-3 hours. The Sulphonated Polystyrene Butadiene
Rubber (SPSBR) was characterized using Thermo Gravimetric Analysis, Differential Scanning Analysis, Elemental Analysis, Capillary Viscometer, FTIR and $^1$HNMR.

### 3.2.1 Fourier transform infrared (FT-IR) and nuclear magnetic resonance (HNMR) studies

The FT IR spectra of unsulphonated and sulphonated PSBR were scanned using a Vector O model FT-IR spectrometer and data was collected in the range of 400 – 4000 cm$^{-1}$. The $^1$H NMR spectra of unsulphonated and sulphonated PSBR were scanned using Brucker 400 Spectrometers to detect the occurrence of sulphonation. The solvent used to dissolve polymer samples was deuterated chloroform (CDCl$_3$) (Analytical grade ≥98%: Fluka, South Africa.)

### 3.2.2 Thermal analysis

The Differential Scanning Calorimetric (DSC) analysis of sulphonated and unsulphonated PSBR was carried out using the 822E DSC analyzer. Measurements were performed over the range of 30$^\circ$C to 400$^\circ$C at the heating rate of 5$^\circ$C/minute under nitrogen atmosphere flushed at 75 ml/minute. The thermal stability of sulphonated and unsulphonated PSBR was tested using the Perker Elmer Pyris 1 TGA/DTA analyzer. The sample was heated to 800$^\circ$C at 10$^\circ$C/minute in nitrogen gas flushed at 150 ml/minute to determine the decomposition temperature of both the sulphonated and unsulphonated PSBR.

### 3.2.3 Viscosity measurement

Samples of both sulphonated and unsulphonated PSBR of 0.5 g were dissolved overnight in 100 ml of 1, 2 dichloroethane. Inherent viscosities were determined using the Cannon
– Fense Capillary viscometer with a 0.5 gdl\(^{-1}\) solution of rubber at 30°C. Prior to viscosity measurement, the solubility of the sulphonated and unsulphonated rubber was analysed to determine the best solvent to be used for the dissolution of the rubber.

### 3.2.4 Ion exchange capacity (IEC) and degree of sulphonation (DS)

The ion exchange capacity (IEC) and degree of sulphonation (DS) of sulphonated polystyrene butadiene rubber (SPSBR) were determined by measuring the percentage of sulphur in the dry sample of SPSBR, using the elemental analysis method. The IEC was then calculated using equation 3.1 (Bebin et al., 2006):

\[
IEC = \frac{1000S_c}{MW_S}
\]

(3.1)

where; \(S_c\) is the sulphur content (percentage weight rate), \(MW_S\) is the molecular weight of sulphur and 1000 is the multiplying factor to obtain IEC value in mmol/g. The value of IEC calculated from equation 1 was used to determine the DS of SPSBR, using the relationship shown in equation 3.2 (Paturzo et al., 2005):

\[
DS = \frac{IEC \times M_{PSBR}}{1 - \left(\frac{IEC \times M_{SO3H}}{MW_{SO3H}}\right)}
\]

(3.2)

Where IEC is the ion exchange capacity (mol/g), \(M_{PSBR}\) is the molecular weight of the polystyrene butadiene rubber (g/mol) and \(MW_{SO3H}\) is the molecular weight of SO\(_3\)H (g/mol)

### 3.3 Casting of SPSBR Membrane

10g of Sulphonated Polystyrene Butadiene (SPSBR) was dissolved in 200ml of 1, 2, dichloro ethane at an elevated temperature to form a casting solution. This casting solution was then cast using a laboratory doctor blade casting machine, as shown in Figure 3.3. Prior to the casting, the doctor blade of the casting tape was set to a known
thickness with the aid of feeler gauges of appropriate thickness. The casting was done by pulling the casting head of the blade along the length of the paper, and it was then cured for 4 days by exposing it to the air and subsequently peeling it off the support. The cast membrane was then dried further in an oven at 75°C for 4-5 hours and finally vacuum dried for 4 hours to remove the residual solvent. The membrane was then analysed to determine the proton conductivity, water uptake, water desorption and swelling ratio.

![Laboratory scale tape caster](image)

Figure 3.3: Laboratory scale tape caster (Lavisage, 2004)

### 3.3.1 Proton conductivity of SPSBR membrane

The proton conductivity of the membrane was measured by alternating current impedance over a frequency range of 1-10⁶Hz, using 1M H₂SO₄ as the electrolyte. The value at the intersection of the high frequency impedance curve with the real axis was taken as the membrane resistance and the proton conductivity was calculated using:

\[
\sigma = \frac{T}{RS}
\]  

(3.3)
where: $\sigma$ is proton conductivity (S/cm), $T$ (cm) and $S$ (cm$^2$) are the thickness and surface area of the membrane sample respectively, and $R$ is the resistance determined from the impedance plane.

### 3.3.2 Water uptake, water desorption and swelling of SPSBR membrane

The water uptake capacity of the membrane was determined by immersing the known weight and dimensions of the membrane in distilled water for a number of days until the membrane was saturated with water. The weight of water was measured daily after the liquid water on the surface of the membrane was cleaned. The water uptake was determined from the weight difference between the wet and dry membrane as shown in equation 3.4 (Gao et al., 2003):

$$\text{Water uptake (absorption)} \,(\%) = \frac{w_{\text{wet}} - w_{\text{dry}}}{w_{\text{dry}}} \times 100 \quad (3.4)$$

Where $w_{\text{dry}} \,(g)$ and $w_{\text{wet}} \,(g)$ are the masses of dried and wet samples, respectively.

To measure the water desorption rate of the membrane, the sample membrane was immersed in distilled water for 24 hours, it was then removed from the water and exposed to air at different temperature and the weight of the membrane was measured at intervals of one hour. The water desorption of the membrane was determined as:

$$\text{Water desorption} \,(\%) = \frac{w_{\text{wet}} - w_{\text{dry}(t)}}{w_{\text{wet}} - w_{\text{dry}}} \times 100 \quad (3.5)$$

Where; $w_{\text{wet}}$ is the weight of wet membrane $(g)$, $w_{\text{dry}(t)}$ is the weight of dry membrane at time $(t) \,(g)$, $w_{\text{dry}}$ is the weight of dry membrane $(g)$. While the membrane swelling ratio was evaluated using equation 3.6:

$$\frac{T_{\text{wet}} - T_{\text{dry}}}{T_{\text{dry}}} \times 100 \quad (3.6)$$
Where $T_{\text{wet}}$ is the thickness of the wet membrane and $T_{\text{dry}}$ is the thickness of the dry membrane.

### 3.3.3 Total solvent uptake and membrane porosity to methanol

The solvent uptake of the synthesized membranes was carried out gravimetrically. Prior to the analysis, membranes of different degrees of sulphonation and thickness were dried at 80°C overnight to expel the residual solvent and weighed for their dry weight ($W_{\text{dry}}$).

The dried membranes were then immersed in methanol of various concentrations in M/dm$^3$ (0, 0.5, 1, 2, 4, 6, 8, 10, 12 and 24.63) until equilibrium was reached. The saturated membranes were blotted to absorb all the surface solvent and weighed ($W_{\text{wet}}$).

The wet membrane porosity ($\epsilon$) to methanol and water/methanol uptake was calculated using equations 3.7 and 3.8 respectively (Sangeetha et al., 2005):

$$\epsilon = \frac{\text{Fluid uptake volume}}{\text{Total volume}} = \frac{(W_{\text{wet}} - W_{\text{dry}}) \rho_{\text{dry}}}{(W_{\text{wet}} - W_{\text{dry}}) \rho_{\text{dry}} + (W_{\text{wet}} \rho_{\text{sol}})}$$  \hspace{1cm} (3.7)

where: $\rho_{\text{dry}}$ is the density of dry membrane = 0.93g/cm$^3$

$\rho_{\text{sol}}$ is the density of the methanol solution (g/cm$^3$)

$W_{\text{wet}}$ is the weight of the wet membrane (g)

$W_{\text{dry}}$ is the weight of dried membrane (g)

$\epsilon$= porosity of the wet membrane

The overall uptake of solvent molecules per sulphonic acid group in the membrane ($\lambda_{\text{total}}$) was calculated using equation 3.8 (Sangeetha et al., 2005)
\[ \lambda_{\text{total}} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \cdot \frac{EW}{18x_{\text{water}} + 32.04(1 - x_{\text{water}})} \]  \hspace{1cm} (3.8)

\( x_{\text{water}} \) is the molar fraction of water in the solution

\( \text{EW} \) (mol/g) is the equivalent weight of the membranes, which can be calculated from equation 3.9 (Shang et al., 2005)

\[ \text{EW} = \frac{1}{\text{IEC}} \]  \hspace{1cm} (3.9)

The uptake of water molecules per sulphonic acid group \( (\lambda_{\text{water}}) \) and uptake of methanol molecules per sulphonic acid group \( (\lambda_{\text{methanol}}) \) were calculated using equations 3.10 and 3.11 respectively.

\[ \lambda_{\text{water}} = \lambda_{\text{total}} x_{\text{water}} \]  \hspace{1cm} (3.10)

\[ \lambda_{\text{methanol}} = \lambda_{\text{total}} (1 - x_{\text{water}}) \]  \hspace{1cm} (3.11)

### 3.3.4 Methanol permeability in SPSBR membrane

Methanol crossover through the synthesized membranes at different degrees of sulphonation and membrane thickness was measured in two identical chamber containers. A membrane of a known degree of sulphonation and thickness with a surface area of 7.069 cm\(^2\) was placed between identical chambers of volume 70 cm\(^3\) as shown in Figure 3.4. One of the chambers contained concentrated methanol while the second chamber contained water. The liquids in the two chambers were well stirred with a magnetic stirrer to obtain a homogenous solution. A small amount of liquid was drawn from the second chamber at different times to determine the concentration of methanol that crossed over. The methanol concentration in the water was measured with UV spectroscopy of A SQ – 4802 UV/VIS model.
3.3.5 Morphology of the rubber

The morphological structure of both the sulphonated and unsulphonated polystyrene butadiene rubber was discovered using the Scanning Electron Microscope (SEM) (JEOL 100S). The Scanning Electron Microscopy analysis of representative samples was conducted in two stages using SEM model JEOL 840. About 1g of samples was mounted on aluminum stubs using colloidal graphite as a mounting media. Thereafter samples were carbon coated, then treated with a deposition of gold palladium to make the rubber surface conductive. The coated samples were finally examined under the microscope for morphological determination.

![Diagram](image)

**Figure 3.4:** Schematic of methanol determination crossover setup.

3.4 Formulation of Sulphonated Polystyrene Butadiene Rubber and Carbon Nanoballs

Sulphonated polystyrene butadiene rubber synthesized at optimum operation conditions were blended with the carbon nanoballs. The optimal condition was arrived at, based on
the route that gives the optimal degree of sulphonation, ion exchange capacity, thermal stability, water intake and swelling ratio with the least time, temperature and quantity of reagent used. 10 grams of sulphonated polystyrene butadiene rubber was dissolved in 1, 2 dichloro ethane. This was then followed by the dispersion of various masses of carbon nanoballs (0.1, 0.2, 0.3, 0.4 and 0.5 g) in 1, 2 dichloro ethane. The mixture was stirred for a period of 1-3 hours until it became homogenous. The blended polymer was then cast and analysed to determine the proton conductivity, thermal stability, water uptake, and morphology and methanol crossover.

3.5 Membrane Electrode Assembly

Prior to the Membrane Electrode Assembly (MEA), the synthesized membrane, both blended and unblended, was treated to ensure that it was entirely in its protonic form, and so as to remove any metal impurity in the membrane. The pre-treatment procedure included boiling of the membrane in 3wt% of hydrogen peroxide (H₂O₂) for one hour, followed by boiling in deionized water for one hour. The membrane was then boiled in 0.1M H₂SO₄ for 1 hour and finally boiled in deionized water for 1 hour to remove the excess acid deposited at the membrane surface. The MEA was prepared by sandwiching the synthesized membrane between two electrodes and then hot pressed (Figure 3.5) at 100°C for 3 minutes at a pressure of 173.53Psi.
3.6 MEA Testing in a Single Fuel Cell Stack

The schematic of the operation of the single cell in a fuel cell test apparatus has been presented in Figure 2.1. The fuel gases (hydrogen and oxygen) were allowed to diffuse through the porous backing layer and also to the electrolyte/electrode interface where electro catalytic reaction takes place. While $H^+$ transport occurs through the electrolyte membrane, the electrons are transported through the external circuit. The single cell was installed in a fuel cell testing apparatus shown in Figure 2.1, equipped with gas sources, temperature control, and gas flow-rate control rotameters, back pressure regulators for both hydrogen and oxygen, and a load of resistant box. Hydrogen and oxygen (Afrox, South Africa) were used in the fuel operations. Hydrogen was passed through a humidifier to wet the gas and fed into the anode at a flow rate of 712 ml/min and 20 kPa. Oxygen entered the fuel cell through the cathode at a flow rate of 433 ml/min and 15 kPa. The electrons generated from the anode were connected to a digital multimeter.
(1906 Competing Multimeter), with an external variable resistance to measure the current and voltage produced by the cell.