## HOMOGENEITY OF NANOPHASE ELECTROCATALYSTS

#### SUPPORTED ON MESOPOROUS MATERIALS.



In the Department of Chemistry, University of the Western Cape

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"I declare that Characterization of nanoparticles and nanocomposites for reproducibility and homogeneity is my own work and that all the sources I have used or quoted have been indicated and acknowledged by means of complete references."



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ZIBONENI GOVERNOR GODONGWANA

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#### Abbreviations

BET	Brunauer Emmet Teller			
CA	Carbon Analogue			
CVD	Chemical Vapor Deposition			
CMK -1	mesoporous carbon molecular sieve synthesized from MCM-48			
	template.			
DSC	Differential Scanning Calorimetry			
EDS	Energy Dispersive Spectroscopy			
HER	Hydrogen Evolution Reaction			
HMS	Hexagonal Mesoporous Silica			
LSV	Linear Sweep Voltammetry			
LPG	Liquefied Petroleum Gas			
MCM	Mobil Composition of Matter			
PEM	Proton Exchange Membrane			
SEM	M Scanning Electron Microscopy			
SPE	Solid Polymer Electrolyte			
TEM	Transmission Electron Microscopy			
TGA	Thermo Gravimetric Analysis			
XRD	X-ray Diffraction UNIVERSITY of the			
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## HOMOGENEITY OF NANOPHASE ELECTROCATALYSTS SUPPORTED ON MESOPOROUS MATERIALS.

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The synthesis of porous graphitic carbon materials via a pyrolysis method using Hexagonal Mesoporous Silica (HMS) as a solid template as well as Pt catalysts supported on these mesoporous carbon materials is the subject of this study. All materials were characterized by X-ray diffraction (XRD), Selected Area Electron Diffraction (SAED), Nitrogen Sorption (BET), Transmission Electron Microscopy (TEM), Raman spectroscopy, Energy Dispersive Spectroscopy, Thermo Gravimetric Analysis (TGA), Differential Scanning Calorimetry and Linear Sweep Voltammetry.

A mesoporous carbon analogue was prepared by use of HMS as sacrificial template. In this study the XRD spectra as well as the TEM micrographs indicate a high degree of mesostructural ordering in the HMS silica prepared for use as a sacrificial template. The nitrogen sorption data confirmed that the HMS silica possessed high porosity and mesostructural ordering and was therefore suitable for use as a solid template for mesoporous carbon synthesis.

The application of Liquefied Petroleum Gas as a carbon precursor for preparation of graphitic mesoporous carbon was successfully achieved to prepare the carbon analogue that resulted in a mesoporous material exhibiting both well-ordered mesoporosity and high levels of graphitic character. The unique architecture of the HMS silica sacrificial template, which explains its large textural porosity, was achieved in the parent Si material and reproduced in the templated carbon.

The carbon analogue prepared by use of the HMS as sacrificial template was found to be highly porous and graphitic, with a large surface area exceeding that of the parent HMS silica sacrificial template and with mesopores in the exact size range of the Si template. The results obtained depict that a carbon mesoporous analogue of the SiO<sub>2</sub> based HMS was successfully achieved. The formation of graphitic structures in the pores takes place during the chemical vapor deposition step of HMS at high temperatures. The dissolution of the SiO<sub>2</sub> framework of the mesoporous HMS used as template was achieved by use of NaOH. Etching of the SiO<sub>2</sub> framework created the 3 nm pores in the carbon that were observed by N<sub>2</sub>BET. The regular mesostructure of the new carbon material is demonstrated by the appearance of the peaks at 7.39 and 12.64 <sup>0</sup> 2  $\theta$  in XRD spectra that indicated that there is a regular mesostructured carbon framework at 11.6 Å and 6.8 Å d spaced distances. This is a novel finding and has not been previously reported.

The results of this study show that a novel mesoporous carbon was obtained as an inverse replica of HMS silica, with a large pore diameter (3 nm), a BET surface area of 938 m<sup>2</sup>g <sup> $\Box$ 1</sup> and with a narrow pore size distribution (PSD) in the mesopore range. The results obtained show that mesoporous carbon with graphitic structures can be synthesized via the LPG route.

This new graphitic mesoporous material and the parent HMS silica mesoporous material were subsequently utilized as supports for the synthesis of Pt electrocatalysts. Three goals were achieved by the introduction of Pt nanoparticles upon the HMS silica support as well as on the mesoporous carbon material:

- 1) Retaining the mesoporous physical structure of the HMS and mesoporous carbon.
- 2) Achieving high Pt dispersion
- 3) And attaining a high Pt weight percent loading.

Preparation of the Pt based electrocatalysts involved techniques based on incipient wetness impregnation and chemical reduction of the metal. Three different procedures were used to deposit nanoparticulate Pt clusters on mesoporous silica or new carbon materials and these are as follows (1) preparation of Pt/carbon analogues whereby Pt is deposited before carbonization, (2) preparation of Pt/carbon analogues whereby Pt is deposited after carbonization but before etching of the silica template, and (3) preparation of Pt/carbon analogues whereby Pt is deposited after etching of the silica template.

XRD, TGA and SAED results confirmed the presence of graphitic carbon and Pt nano particulates. The mesoporous structure of the carbon support was maintained, high Pt dispersion was achieved and a high weight percent of Pt loading was demonstrated. Moreover the Pt based electrocatalyst showed similar hydrogen cathodic activity compared to the commercial Johnson Matthey Pt/C catalyst.

It was demonstrated in this study that a catalyst with hydrogen Evolution Reaction (HER) activity equivalent to that of the commercial Johnson Matthey catalyst (JM Pt/C) can be fabricated by a more facile synthetic route using pyrolytic liquefied petroleum gas as a carbon precursor. Moreover, it was demonstrated through TEM studies that for the carbon analogue sample the Pt particles were homogeneously and evenly distributed across the carbon support. Nitrogen sorption (BET) studies also confirmed homogeneity of the pore walls for the carbon analogue support.

A Pt particle size of about 3.7nm as well as some degree of graphitization of the conductive carbon support framework is postulated to have played a prominent role in catalytic activity towards hydrogen production.

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Keywords

#### **KEYWORDS**

HMS silica Template Mesoporous silica Pyrolysis

Etching

Mesoporous carbon

Graphitic carbon

Water electrolysis

Cathode

Fuel cell



#### **CHAPTER 1**

#### **1.1 GENERAL BACKGROUND AND INTRODUCTION**

Porous solids have extensive commercial applications as adsorbents, catalysts and catalyst supports due to their high surface areas. According to IUPAC definition [1] porous materials may be divided into three types based on their pore dimensions:

Туре	pe Pore Size (nm)		
Microporous	:	< 2	
Mesoporous	:	2-50	
Macroporous	:	-> 50	

Well known microporous materials are zeolites [2] and aluminophosphate molecular sieves [3] which are inorganic minerals having a crystalline three-dimensional framework comprised of tetrahedral atoms such as aluminium, silicon, phosphorous etc, bridged by oxygen atoms. These materials possess uniform channels, pores or cavities circumscribed by rings of a definite number of tetrahedral atoms. The exploitation of the architectural features of zeolites resulting in different acid sites and acid strengths, exchangeable ions, shape and size selective channels and pores has been well established by now.

Modification of the framework and extra- framework composition makes these materials useful for catalyzing heterogeneous reactions. Prior to 1990 [2] heterogeneous catalysis presented using zeolites was restricted to the use of materials with pore sizes less than 2 nm and consequently the reactant molecules trapped and transformed inside them were also small. The usefulness of the microporous

molecular sieves in processing high molecular weight reactants of increasing importance was limited by their pore size ( $\sim 0.7$  nm). Hence there has been an evergrowing interest in expanding the pore sizes of the zeotype materials from the micropore region to the mesopore region. The requirement of adsorbing larger molecules at the catalytic sites has led to the development of molecular sieves with pore diameters larger than those of the traditional zeolites. Moreover the inorganic framework of these mesoporous materials is not crystalline as in the case of zeolitic structures.

In order to preserve the remarkable catalytic properties of zeolite while expanding their use to process bulkier molecules, new synthesis routes have been undertaken to increase their pore diameters. This approach has led to the synthesis of ultra large pore molecular sieves. In 1982 Wilson and co-workers [4] synthesized a novel crystalline, microporous aluminophosphate (AlPO<sub>4</sub>) material with a pore diameter of about 0.8 nm. Later, in 1988, Davis *et al.* [5] reported the synthesis of VPI-5, an AlPO4 molecular sieve with 18 tetrahedral atoms that could sorb molecules about 1.2 nm in size. Since then, microporous materials with pore openings containing 20 tetrahedral atoms have been synthesized. These large pore openings overcome the configurational diffusion limitations of zeolitic systems.

However, these materials lack the required thermal stability and catalytic activity because their frameworks are electrically neutral. Researchers have made significant efforts to synthesize mesoporous materials such as silicas [6], transitional aluminas [7] or pillared clays and silicates [8, 9], which are electrically charged. However the pores in these materials are generally irregularly spaced and broadly distributed in size. Synthesis of amorphous silica-alumina with a narrow pore size distribution in the presence of tetraalkylammonium cations [10] has been reported, where the average pore diameter was related to the size of the tetraalkylammonium cations. Although these materials were found to be active for acid catalyzed organic reactions, they were not thermally stable at high temperatures.

In 1992 researchers at Mobil Research and Development Corporation reported the synthesis of a new family of silicate/aluminosilicate mesoporous molecular sieves (M41S) with exceptionally large uniform pore structures [11-17]. These materials possess well-defined mesopores whose diameters can be tailored in the range of 1.5-10 nm. The understanding about the synthesis of these materials and the corresponding mechanism has opened up a new era of molecular engineering. The most outstanding feature of the preparation of these materials is the role of the templating agents. The template molecules used are not single solvated organic cations as used in zeolite synthesis, but a self assembled surfactant molecular array around which the main structure is built up (Fig. 1.1). Surfactants are large organic molecules having а long hydrophobic tail of variable length (e.g. alkyltrimethylammonium cations with formula  $C_nH_{2n+1}(CH_3)_3N^+$ , where n > 8) and a hydrophilic head.



Fig. 1.1 The formation of mesoporous molecular sieves using long chain alkyl quaternary cations [18].

#### **1.2 SYNTHESIS OF MESOPOROUS MOLECULAR SIEVES**

Similar to zeolite and molecular sieves syntheses, mesoporous molecular sieves are hydrothermally synthesized by mixing organic molecules (surfactants), silica, and or a silica alumina source to form a gel, which is then crystallized at a temperature between 70-150°C for a selected period of time. Surfactant molecules function as templates forming an ordered organic-inorganic composite material [19]. The product

obtained after crystallization is filtered, washed with water and dried at ambient temperature. Surfactant molecules are removed by calcination leaving porous silicate/aluminosilicate network. The structure of mesoporous materials can be altered by varying the surfactant/SiO<sub>2</sub> ratio [20]. It has been found that as the surfactant/silica molar ratio increased [21], the siliceous products obtained could be classified into four groups as presented in Table 1.2.

Surfactant/silica	Phase
< 1.0	Hexagonal (MCM-41)
1.0-1.5	Hexagonal (MCM-48), HMS
1.2-2.0	Thermally unstable materials
2.0	Cubic octamer [(CTMA)SiO2.5]8

 Table 1.1 Classification of Mesoporous Molecular sieves [21].

One of the most unique and useful features of M41S family of materials is the ability to tailor the pore diameter (15–100Å). This can be achieved in three different ways; (i) by varying the chain length of alkyl groups (from 8 to 22 atoms) in surfactant molecules [11,16], (ii) by adding auxiliary chemicals such as 1,3,5 trimethylbenzene [11,16,19,22,23] which dissolve in the hydrophobic region of the micelles, thus increasing their size, or (iii) by aging a sample prepared at a lower temperature in its mother liquor at a higher temperature for different periods of time [24].

Besides, the pore diameter synthesis of mesoporous molecular sieves also depends on other factors such as temperature, pH and crystallization time [9,25]. Ever since the first report on the synthesis of mesoporous molecular sieves in alkaline medium appeared [11-17], a large number of publications on synthesis of mesoporous materials, mainly MCM-41 has been reported [26-30]. The synthesis of mesoporous materials has also been done in acidic and neutral medium. Huo *et al.* [27, 31]

reported the synthesis of mesoporous silica under acidic conditions, while Tanev and Pinnavaia [20] proposed a neutral templating synthesis mechanism based on hydrogen bonding between primary amines and neutral inorganic species (Table 1.3). Such mesoporous molecular sieves are named HMS (hexagonal mesoporous silica). These HMS molecular sieves were used as templates for supporting metals or as precursors for mesoporous carbons synthesis in this thesis.

Surfactant	Example	рН	Resulting Phase	Reference
S <sup>+</sup> I <sup>-</sup>	Cetyltrimethyl ammonium ions + silicate species	10-13 UNIVERSITY WESTERN C	Hexagonal, cubic and lamellar	[24]
S <sup>+</sup> X <sup>-</sup> T	Cetyltrimethyl ammonium ions + silicate species	< 2	Hexagonal	[31]
$\mathrm{S}^{0}\mathrm{I}^{0}$	C12H25NH2 + (C2H5O)4Si	< 7	Hexagonal	[32, 33]

Table 1.2 Routes for synthesis of mesoporous molecular sieves

S = surfactant species; I = inorganic species (Si); X = Cl<sup>-</sup>, Br<sup>-</sup> or OH<sup>-</sup>

#### **1.3 MODIFICATION OF MESOPOROUS SILICA**

Pure siliceous mesoporous molecular sieves possess a neutral framework, which limits their applications. In order to provide molecular sieves with potential catalytic applications, it is possible, as in the case of zeolites, to modify the nature of the framework by introduction of heteroatoms, by hydrothermal methods. Moreover, other elements can also be incorporated on the surface of the materials by grafting or impregnation.

1.3.1 Incorporation of heteroatoms.

Incorporation of heteroatoms by hydrothermal methods or by grafting or impregnation is described in the following subsections.

#### 1.3.1.1 Incorporation of heteroatoms by hydrothermal methods

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When trivalent cations like  $A1^{3+}$ ,  $B^{3+}$ ,  $Ga^{3+}$  and  $Fe^{3+}$  [34-40] substitute for silicon in the walls of the mesoporous silica, the framework possesses negative charges that can be compensated by protons providing acid sites. The number of acid sites and acid strength depend on the amount and nature of the incorporated metal. Such materials are used in acidic reactions and have potential applications in various petroleum refining processes [41, 42]. In this thesis the incorporation of Pt<sup>4+</sup> in the walls of the mesoporous silica or carbonaceous layer is described for application as catalysts.

#### 1.3.1.2 Grafting of Heteroatoms

In addition to variable pore diameters and large surface area, mesoporous molecular

sieves have a number of surface silanol (Si-OH) groups, which can be functionalized by introducing functional organic groups. This is normally achieved through attachment of silane-coupling agents to the mesoporous walls of previously synthesized and calcined materials [43]. In one of the methods, functionality is directly introduced through reaction of silanol groups [44-45]. In another method, a transition metal, metal oxide or a bimetal complex is grafted on the wall without the use of intermediate silane complex agent. Hence, surface hydroxyl groups are directly reacted with the metal species.

#### 1.3.1.3 Impregnation of Heteroatoms

The most frequently applied preparation method for heterogeneous catalysts is impregnation. The major advantage of this method is its simplicity. During impregnation a suitable support material is contacted with a solution containing a precursor of the active phase. Upon impregnation the pores of the support are filled with precursor solution. Upon drying of the support material after impregnation, the solvent (usually water) is evaporated and as a result the precursor of the active phase adheres to the surface of the support.

Generally, there are two different methods of impregnation [46-48]. In "wet" impregnation the amount of precursor solution added to the support material exceeds the pore volume. Although this is the simplest impregnation method it can result in the deposition of a vast amount of precursor material at the exterior parts of the support bodies during drying and the resulting heterogeneous catalysts display an egg-shell distribution of the active component. Nevertheless such a distribution might be beneficial from an application point of view, since it alleviates the need of reactant penetration deep inside the catalyst bodies, thus improving the catalytic process.

When the catalyst bodies are subject to a lot of friction during operation, causing

abrasion of the outer parts, other types of distribution of the active phase are necessary. For this purpose another type of impregnation is usually required, *viz.* incipient wetness impregnation. This method is also referred to as "dry" impregnation, since during the impregnation process the amount of precursor solution added to the support material equals the pore volume. As a result the support bodies appear to be dry, even after admission of the precursor solution. After the impregnation process, be it wet or dry, the impregnated support material needs to be dried in order to allow the precursor compound to be converted into a catalytically more suitable chemical phase.

Although drying of an impregnated support material appears to be very simple it should be noted that the conditions during drying can adversely influence the distribution of the precursor compound over the support material [46-48].

# 

This behavior is caused by solvent flows inside the pores of the support material during drying. As a result of these flows the precursor material is entrained through the pores, which can lead to inhomogeneous distributions after drying.

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#### **1.4 WATER ELECTROLYSIS.**

#### 1.4.1. Background

Low conductivity water electrolysis is fundamentally important for industrial scale renewable power generation applications and development of the "hydrogen economy" [49]. The use of water electrolysis addresses the intermittent nature and limitations of renewable energy whereby the user is connected to an electricity grid or some large and expensive battery or back up systems; by enabling the production and storage of hydrogen to occur during times of excess electricity generation thus allowing for the later regeneration of electricity.

Novel systems for power generation that require high efficiency, environmentally friendly processes are fuel cell technologies in which hydrogen is used as a primary fuel. In a fuel cell hydrogen may be formed by water electrolysis and this process may be used as the cleanest way of generating fuel in a fuel processor for the fuel cell utilization. The anode of the fuel cell must eventually be integrated with the catalyst in such a system [50].

Water electrolysis is the reverse process of a fuel cell as it converts electrical energy into chemical energy, i.e. hydrogen. Hydrogen can be stored in pressurized bottles or in materials such as metal hydrides. When energy is needed, hydrogen can then be converted back to electricity by use as fuel in a fuel cell according to Figure 1.2. The anode and cathode are separated by a physical barrier, in this case, a membrane. The electrodes can be composed of various materials, such as carbon and are normally doped with electrocatalytic materials so that energy consumption can be reduced.

In Figure 1.2 schematic presentations depicting differences between PEM Fuel cells and PEM electrolyzers are presented. Porous carbon materials are applied as catalyst support for electroactive metals such as Pt in the composite anodes or cathodes of these systems. The primary role of the carbon support used in both PEM eletrolyzers and fuel cells is to disperse metal nanoparticles and to provide the electrical connection between them.



Figure 1.2 Schematic representation of a Proton Exchange Membrane water



A solid polymer electrolyte membrane (PEM) is used as the electrolyte in the solid polymer electrolyzer, typically a proton conducting membrane such as Nafion, because corrosion problems are less and the proton conductivity of this material is high. In the process the energy necessary is provided by application of a suitable potential (V) promoting the reactions by exciting the valence electrons in semiconductor electrodes. This electronic energy is then transferred to the water molecule, helping to break the O-H bonds. Only the anode is exposed to the water in PEM electrolysis where oxidation of water gives oxygen and  $H^+$  (aq). Under the applied potential (V) the electrons move through the external circuit and the  $H^+$  (aq) are then driven through the proton conducting membrane to the cathode where gaseous hydrogen is evolved [52]. This process occurs according to the following reactions

#### Anodic reaction:

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- 1.23V$$
 (Equation 2.1)

**Cathodic reaction:** 

 $4H^+ + 4e^- \rightarrow 2H_2$  0.00V (Equation 2.2)

# 1.4.2 Development of cathodic materials with low overvoltage for hydrogen evolution in membrane electrolysis process.

For the principal chemical reaction for water electrolysis the electrodes should possess catalytic activity with high selectivity. Therefore, it is a highly topical goal to develop cathodes with low overvoltage (the difference between the electrode potential under polarization conditions and equilibrium potential) of hydrogen evolution [53-56].


One of the ways to reduce the power consumption needed to carry out electrochemical processes is to develop cathodic materials showing a low and stable overvoltage for hydrogen evolution. Moreover these materials should be inexpensive and mechanically stable, and cost effective to manufacture under industrial conditions and be suitable for application in membrane electrolyzers.

The cathodic evolution of hydrogen occurs at potentials that are more negative than that of the equilibrium hydrogen electrode. A shift in the potential under the action of an electric current,  $\varphi_i$ , from its equilibrium value,  $\varphi_\tau$ , which is necessary to initiate the reaction of cathodic evolution of hydrogen on a given electrode at a given rate of *j* is generally agreed to be termed as the overvoltage of hydrogen evolution,  $\eta_{H2}$ :

$$\eta_{\rm H2} = \varphi_{\rm j} - \varphi_{\rm r} \qquad (Equation \ 2.3)$$

The magnitude of the hydrogen overvoltage is a measure of the irreversibility of the cathodic evolution process of hydrogen, and it is dependent above all on the current density, *j*, as well as the nature of the electrode materials, temperature, and electrolyte composition. The voltage of hydrogen evolution is influenced by many factors with interdependence among the other properties of an electrode and the  $\eta_{H2}$  (overvoltage of hydrogen evolution) value. Depending on these factors,  $\eta_{H2}$  might vary from a few millivolts to 1.5 V and more.

Metals that can be used to prepare cathodes for hydrogen production are subdivided into two main groups [57], those showing a low overvoltage, viz. Pt, Pd, Au, Rh, Re, Ir, Ni, Co and Fe; and those showing a high overvoltage, viz. Sn, Bi, Zn, Pb, Ti, Ln, Hg etc. The first groups of metals as seen from this list, consists of precious metals an essential draw back of which is their high cost.

# CATALVSTS IN THE HV

### **1.5 NANOPHASE ELECTROCATALYSTS IN THE HYDROGEN**

EVOLUTION REACTION UNIVERSITY of the

Protons produced in the oxygen evolution reaction at the SPE-electrolyser anode are transported through the proton-conducting membrane towards the cathode where they are reduced in the hydrogen evolution reaction (HER) to evolve H<sub>2</sub> [58]. The HER can be applicable in either acidic or basic electrolytes. Also, nanophase nickel and platinum electrocatalysts exhibit high catalytic activities towards the HER in alkaline and acidic media, respectively. However, faster reaction rates were observed in acidic media due to easier evolution of H<sub>2</sub> from hydronium ions, H<sub>3</sub>O<sup>+</sup> because nafion is a solid acidic electrolyte [58, 59].

HER occurs via a Volmer-Heyrovsky-Ta fel reaction mechanism in which two pathways exist: the Volmer-Heyrovsky and Vo lmer-Tafel pathways. The Volmer step is an initial electrochemical discharge in which hydride species are formed on surface sites by simultaneous reduction and adsorption of protons. The Heyrovsky step is an electrochemical desorption process in which hydride reduction occurs at surface sites already occupied by hydride species. The Tafel<sup> $\uparrow$ </sup> step is a chemical recombination process in which H<sub>2</sub> is evolved via the interaction of adjacent hydride surface species.

2

The Volmer-Heyrovsky-Tafel mechanism can be written as follows [59, 60]: In alkaline media,  $2^{\uparrow}$ 

Volmer:	$H_2O + Ni + \bar{e} \rightarrow Ni-H_{ad} + OH_{-}(aq)$
Heyrovsky:	Ni-Had + H <sub>2</sub> O + $\bar{e} \rightarrow$ H + OH-( <i>aq</i> )
Tafel:	$Ni-H_{ad} + Ni-H_{ad} \rightarrow H + 2Ni$
Overall:	$H_2O + 2 \bar{e} \rightarrow H + OH(aq)$

In acidic media,

Volmer:	$H_3O^+(aq) + Pt + \bar{e} \rightarrow Pt-H_{ad} + H_2O^2\uparrow$
Heyrovsky:	$Pt-H_{ad} + H_3O^+(aq) + \bar{e} \rightarrow H^- + H_2O + Pt$
Tafel:	<b>Pt-H</b> ad + <b>Pt-H</b> ad $\rightarrow$ H <sub>2</sub> $\uparrow$ + 2Pt
Overall:	$2\mathrm{H}_{3}\mathrm{O}^{+}(aq) + 4 \ \bar{e} \rightarrow \mathrm{H} + 2\mathrm{H}_{2}\mathrm{O}$
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In both pathways the Volmer step is the rate-determining step and either pathway can occur depending on reaction conditions and applied potential. They may even occur simultaneously during the reaction. HER generally starts at low negative potentials, depending on electrolyte composition, and continues through large negative potentials. At low negative potential the Volmer-Tafel pathway is favoured, followed by the Volmer-Heyrovsky pathway at large negative potential. A surface-sensitivity effect is exhibited in the HER, in acidic media, on Pt single crystal facets. HER activities on Pt low-index single crystals have been observed to increase in the order:  $Pt(100) \le Pt(111) \le Pt(110)$  [59, 61].

To summarise, ideal electrocatalysts for the HER in acidic media should fulfill the following criteria:

Pt particle size should be reduced to nanoscale to increase surface-to-volume ratio and active surface area. A high Pt content is required for increased activity.

High dispersion of nanophase Pt on carbon for decreased loadings and increased active surface area.

High densities of low-index Pt (110) and Pt (111) crystal facets for increased reactivity.

To achieve these criteria active metals can be dispersed upon various suitable conductive supports as will be described in section 1.6.

#### 1.6 MESOPOROUS CARBON MOLECULAR SIEVES AND CARBON STRUCTURES.

Following the discovery of well-ordered silica based mesoporous materials; the supramolecular assembly approach to mesostructured material has rapidly expanded to include the synthesis of nonsiliceous materials. Among nonsiliceous mesoporous materials, mesoporous carbon material are of particular interest because of their extraordinary properties, such as high specific surface area, large pore volume, good mechanical stability and chemical inertness. Mesoporous carbon materials are potentially useful for a wide range of applications including gas storage, water and air purification, and catalytic supports in fuel cells or components of electrodes [62].

Mesoporous carbons with a large BET surface area, a high pore volume and a porosity made up of accessible pores with sizes > 2nm that facilitates mass transport of molecules or ions and a good electronic conductivity for rapid charge transfer can be obtained as inverse replicas of mesoporous silica materials which are used as templates [63]. These mesoporous carbons are of great interest for high performance applications such as electrocatalytic supports in fuel cells, water electrolysis, new type of hosts for quantum particles and wires in nanotechnology [63-64]. However, the framework of these mesoporous carbons is made up of amorphous material and so they have a poor electrical conductivity.

To improve the conductivity of mesoporous carbon supports the carbon framework must contain structures with some degree of graphitization. Till now, mesoporous carbon with completely graphitized structure remains an interesting topic for researchers and facile synthetic routes for these materials are still much the focus of research. Interest in these structures comes from the inherent structural strength due to the covalent in-plane carbon bonds in graphite, which is considered to be one of the strongest in nature. Graphite is extremely light (hence high strength/density ratio, 1–2 orders of magnitude greater than steel), highly electrically and thermally conducting and corrosion resistant. One example of these graphite carbon structures is the carbon nanotubes observed by Iijima (1991) while studying the surface of carbon electrodes used in an electric arc-discharge apparatus, which had been used to make fullerenes.

Carbon in its sp<sup>2</sup> hybridized bonding state, with two-dimensional layered graphite being the most stable form, has shown great promise for conversion into structures having one- and zero-dimensional topologies.



Figure 1.3 Structural diagram of porous graphitic carbon, a two dimensional graphite

[65].

According to Iijima et al [66] the discovery of fullerenes has added an important milestone in carbon research. More importantly, research in this field has proved that various possibilities exist for producing a whole new range of carbon structures of various sizes, shapes and dimensions. For example, carbon nanotubes are perfectly straight nanometre-sized tubules with properties close to that of the ideal graphite fiber.

Mesoporous silica materials (MSM) are used as templates for hosting metals or for the synthesis of mesoporous carbons, which are negative replicas of the MSM. There are different varieties of MSM that are applicable to the functions mentioned above, however, Mobil Composition of Matter MCM-41 and MCM-48 (number represents a batch number) and Hexagonal Mesoporous Silica (HMS) are mostly mentioned in literature [67]. On the other hand, HMS has several advantages compared to MCM-48 from a synthetic point of view :

- 1) The use of cheap alkyl amines as the structure directing agent
- 2) A higher silica recovery yield (>95 %) than MCM-48 (~50%)
- 3) A shorter synthetic time (18 h for HMS and 4 days for MCM-48) and
- 4) No hydrothermal reaction [68].

The pore connectivity of mesoporous materials is important in catalytic and electrochemical applications. However, the pore structure and the pore connectivity of HMS have not yet been elucidated.

Most existing mesoporous carbon structures are grown in the temperature range between 800 and 1500 <sup>0</sup> C and are made either by extruding polymer structures followed by heat treatment or by catalysing hydrocarbon gases using transition metal catalysts. The goal is to make porous carbons that are straight and stiff having the hexagons in the graphite honeycomb lattice perfectly oriented along the porous

carbon axis. The resulting structure will be nearly singly crystalline along the axial direction providing the theoretical strength of the covalent carbon bonds as in a single plane of graphite [69].

A number studies have appeared recently, which describe the preparation of porous carbon with a crystalline framework. Ryoo et al. [69] reported the synthesis of mesoporous carbon molecular sieves exhibiting a highly ordered X-ray powder diffraction (XRD) pattern.

These mesoporous carbon molecular sieves were synthesized using sucrose as the carbon precursor inside the cubic mesoporous silica molecular sieves MCM-48 [69] that were used as the template. The sulfuric acid was added as the carbonization catalyst. After the carbonization was complete the silica framework was removed

using NaOH or HF (Figure 1.3).





Figure 1.4 Schematic outline of the template synthesis procedure with silica molecular sieves: (a) mesoporous silica molecular sieve MCM-48, (b) MCM-48 after carbonization within pores, and (c) CMK –1 obtained after carbonization and then detemplating (removing Si framework) [69].

However, the carbon framework that resulted from the above procedure showed no Bragg lines in the region 2  $\theta$  greater than 10<sup>0</sup> on analysis by XRD, indicating that the carbon framework was atomically disordered and no degree of graphitization was produced. Nonetheless, the mesoporous carbon that was formed had a high specific surface area (BET area 1380 m<sup>2</sup> g<sup>-1</sup>).

#### **1.7 PHYSICO-CHEMICAL CHARACTERIZATION**

A number of techniques are used to characterize mesoporous molecular sieves. Among these, x-ray powder diffraction, transmission electron microscopy (TEM) and adsorption measurements are considered the essential techniques to identify the structure of the mesoporous molecular sieves. Thermal Gravimetric Analysis (TGA) and Raman spectroscopy have been applied to obtain additional structural information about molecular sieves. Braunauer-Emmett-Teller (BET) for surface area determination and pore size distribution. Selected-area electron diffraction (SAED) have been used in the qualitative measure of crystallinity and symmetry of materials. Scanning electron microscopy (SEM) has been used for producing images with great depth of field and high magnification. Energy dispersive spectrometer (EDS) has also been used for sample elemental composition or percentage weight. Linear Sweep Voltammetry (LSV) was also used for determining the catalytic activity of the materials, refer to chapter 2 for experimental work, sample preparations and set up conditions pertaining the use of these physico-chemical techniques.

# 1.7.1 X-ray diffraction (XRD). UNIVERSITY of the WESTERN CAPE

Powder x-ray diffraction can be used to identify the structure, phase purity, degree of crystallinity, unit cell parameters and crystallite size. It also helps in the study of the kinetics of crystallization of molecular sieves. As the powder pattern is the identifying spectrum of the molecular sieve structure, phase purity and percent crystallinity of the synthesized molecular sieve can be ascertained by comparison with the standard published pattern for the molecular sieve under investigation. XRD patterns of mesoporous phases exhibit peaks in the low angle region; the most intense peak being the (100) reflection. In the case of MCM-41 the wall thickness of hexagonal channels is usually calculated by subtraction of the inside pore diameters obtained by gas adsorption from the unit cell dimensions determined by XRD.
The process of X-ray diffraction by a crystal can be thought of as one of reflection of the X-rays off planes of atoms within the crystal. In a diffraction pattern from a crystal lattice, a number of reflections are generated, each one being associated with a lattice plane (identified by the Miller indices h, k,l) and occurring at an angular position (2 $\theta$ ) depending on the related interplanar spacing (d(hkl)) and on the X-ray wavelength ( $\lambda$ ), as defined by the well-known Bragg's law [70].

$$\lambda = 2d \sin \vartheta$$
 (Equation 2.3)

 $\lambda\text{-}$  the wavelength of the X rays

 ${\bf d}$  - the spacing of the planes in the crystal

 $2\theta$  - the angle of diffraction



Determination of crystal size from XRD may be calculated using the Scherrer equation.

The XRD line broadening versus crystallite size effect can be exploited to determine the average size of molecular sieves in a catalyst or of metal crystallites on various supports, e.g. Pt crystallite sizes in reforming catalysts. The Scherrer equation may be used to determine the average crystallite size of the Pt particles. The full-width at half maximum (FWHM), B, is related to the mean dimension of crystallites perpendicular to the hkl planes, t, by Scherrer's equation,

$$D = 0.9\lambda/\beta \cos \theta \qquad (Equation 2.4)$$

where D is the particle diameter (nm) measured at its half maximum intensity,  $\lambda$  is the wavelength of the X-ray radiation,  $\beta$  is the FWHM (radians) and  $\theta$  is the angle of reflection. The FWHM is strongly affected by crystal defects and distortions, which cause line broadening. Here, the variation in the FWHM ( $\beta$ ) is used as a rough indication of the changes in crystal size as a function of radiation dose [70]. The Scherrer's equation is mainly specific to perfectly spherical particles. As a result there may be discrepancies in particle size determination for non-spherical particles. In this study XRD is used to determine structure, degree of crystallinity, unit cell parameters and crystallite size of materials.

### 1.7.2 Determination of surface area and pore size distribution

Molecular sieves have the ability to adsorb probe molecules of different sizes. Sorption capacities for probe molecules such as n-hexane, water, benzene, nitrogen and so on, yield information about the hydrophilicity/hydrophobicity, pore dimensions and pore volume of the molecular sieves. The Braunauer-Emmett-Teller (BET) volumetric gas adsorption technique using gases such as nitrogen or argon is a standard method for the determination of the surface areas and pore size distribution of finely divided porous samples [71]. The relation between the mass of gas adsorbed and the equilibrium pressure of the gas at constant temperature is defined by the adsorption isotherm. This relation is represented by the BET equation i.e.

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$$\frac{1}{W[(P_0/P)-1]} = \frac{1}{W_mC} + \frac{(C-1)}{W_mC} \frac{P}{P_0}$$

(Equation 2.5)

Where, W = weight of N<sub>2</sub> adsorbed at a given relative pressure (P/P<sub>0</sub>)

 $W_m$  = weight of N<sub>2</sub> producing monolayer coverage ( $\theta$  =1.00 ml).

N<sub>2</sub>-adsorption-desorption isotherms of MCM-41, MCM-48 and HMS are of the type IV isotherm. This means increase in N<sub>2</sub> adsorption (within the P/P<sub>0</sub> range between 0.2 to 0.4) corresponds to capillary condensation within uniform pores. The sharpness and the height of this step reflects the uniformity of the pore size and the pore volume

respectively. In this study BET was used to determine pore size distribution and specific surface area of materials.

#### **1.7.3 Transmission electron microscopy**

Transmission electron microscopy (TEM) is used to elucidate the pore structure of mesoporous molecular sieves [23, 27, 62 - 67]. It provides topographic information of materials at near atomic resolution. However, the exact analysis of pore sizes and thickness of the pore walls is not possible without additional simulations because of the resolution problem. More than one model with a hexagonal array of large cylindrical pores with thin walls gives a similar XRD pattern, but TEM gives a direct, precise and simultaneous image of the pore. HRTEM can be successfully used to examine the microstructural feature of mesoporous molecular sieves [66, 67]. In addition to structural characterization, it can also be used to detect the location of metal clusters and heavy cations in the framework [59]. In this study TEM was used to determine the pore structure of materials.

# 1.7.4 Selected-area electron diffraction

Selected-area electron diffraction (SAED) can be used in the qualitative measure of crystallinity and symmetry of materials. In SAED, the electrons are scattered by electric fields associated with atoms in thin sample films. Diffraction patterns produced give single-crystal diffractive contributions from multitudes of crystallographic arrangements. In addition, highly polycrystalline materials may constitute concentric Debye-Scherrer rings in the pattern. The appearance of the diffraction pattern is dependent on the crystallinity of the sample material and may become more complex as the degree of polycrystallinity increases. Also, amorphous materials result in patterns that are diffused or blurry [68]. In this study, SAED is limited to a rapid qualitative measure of the crystallinity and symmetry of nanoparticles.

### 1.7.5 Scanning electron microscopy

Scanning electron microscopy (SEM) utilizes a focused beam of high-energy electrons that systematically scans across the surface of a specimen. The interaction of the beam with the specimen produces a large number of signals (radiations) at or near the specimen surface [69]. In this study SEM is used to produce images with great depth field and high magnification.

### **1.7.6 Energy Dispersive Spectroscopy**

Many SEMs are equipped with an energy dispersive spectrometer (EDS) detection system, which is able to detect and display most of the spectrum of elements making up the sample elemental composition or percentage weight . In the EDS, X-ray energy analysis may be accomplished by energy dispersion, which is the segregation of x-rays according to their energy. The method currently preferred for energy dispersion is with a semiconductor detector normally a Si(Li) crystal. A bias of – 500 to – 1500 volts is applied to the Si(Li) crystal (through positive and negative contacts) [69]. EDS is used to determine the elemental composition of particles. This composition is normally recorded as a percentage ratio, however there are qualitative problems associated with qualitative analysis in scanning electron microscopy. In this study EDS is used to determine sample elemental composition and percentage weight of materials.

### 1.7.7 Thermal Analysis

Data obtained from Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) analysis are useful in evaluating the thermal properties of molecular sieves [71]. Thermal analysis is widely used to study the structural stability of as-synthesized forms of molecular sieves such as zeolites and mesoporous materials. It provides information about the temperature required for the removal of adsorbed water, decomposition of the occluded organic cations in the pores and channels of molecular sieves and dehydroxylation at higher temperatures to produce Lewis acid sites and may give indications of temperature induced structural collapse.

After the loss of water molecules the shape and splitting of the endotherms (low temperature) helps to identify the location of water molecules and also helps in studying the kinetics of dehydration. The temperature at which an exotherm appears in the TGA, gives helpful information about the temperature required to remove the template molecules from the pores of the molecular sieves during calcination. Phase transformations (if any) can also be understood from the exotherms obtained at higher temperatures. In this study TGA is used to determine the to study the structural stability of as-synthesized forms of molecular sieves and electrocatalysts.

### 1.7.8 Raman Spectroscopy

Raman spectroscopy is an ideal tool for the investigation of carbon compounds, since Raman spectra can resolve changes in the microscopic structure of the crystals. Most Raman spectrometers are built in with a prism and an aperture to select the 514.6 nm nanometer line of a Coherent Ar ion laser, which is focused to a 100- $\mu$ m spot on the sample. The laser beam intersect the plane of the filter at a certain angle, normally 75 <sup>0</sup> on which the sample is suspended. The maximum laser power is normally limited to about 300 mW, although most spectra are taken at less than 100mW to prevent sample heating, and where possible lower powers down to 10 mW could be used [72].

Raman spectra can be used to characterize the extent of graphitization of prepared carbon samples; the well known D and G peaks of graphite are the main feature observed. The D and G peaks have varying degrees of intensity and width, in the 1350 and 1575 cm<sup>-1</sup> regions, respectively. The G peak corresponds to the only

allowed Raman transition in this region of the spectrum of large graphite crystals. The D peak is used as an indication of disordered, amorphous structure in the carbon framework [72]. In this study Raman spectroscopy is used to determine the extent of graphitization of already prepared mesoporous carbon materials.

### 1.7.9 Linear Sweep Voltammetry

In linear sweep voltammetry (LSV) a potential applied to a working electrode is swept from a lower limit to an upper limit over time (Figure 1.7) and the resultant current is measured as the output signal.



Figure. 1.7 Voltage versus time relation for Linear Sweep Voltammetry.



Figure.1.8 Typical linear sweep voltammogram for cathodic sweep.

In a typical linear sweep voltammogram, the scan begins from a potential corresponding to a point where no current flows through solution (Figure 1.8). As the voltage is swept further to the right (to more reductive values) a current begins to flow and eventually reaches a peak before dropping.

So as the voltage is swept from  $V_1$  to  $V_2$  (fig. 1.7) the equilibrium position shifts from no conversion at  $V_1$  to full conversion at  $V_2$  of the reactant at the electrode surface (Figure 1.8). The exact form of the voltammogram is a function of the voltage and mass transport effects. As the voltage is initially swept from  $V^1$  the equilibrium at the surface begins to alter and the current begins to flow.

The current rises as the voltage is swept further from its initial value as the equilibrium position is shifted further to the right hand side, thus converting more reactant. The peak occurs, since at some point the diffusion layer has grown sufficiently above the electrode so that the flux of reactant to the electrode is not fast enough to satisfy that required by the Nernst equation and the current begins to drop. If the scan rate is altered the current response also changes.

In this study, LSV was used to determine the electrocatalytic activity of nanomaterials as well as Pt metals supported on mesoporous templates.

### **1.8 SUMARY OF THE LITERATURE REVIEW.**

- Pure siliceous mesoporous molecular sieves possess a neutral framework, which limits their applications. In order to provide molecular sieves with potential catalytic applications, it is possible, as in the case of zeolites, to modify the nature of the catalyst by supporting active metal centers on the high surface area of the support using post synthesis modification, however a silica based support is not useful for electrocatalysis due to its insulating nature.
- In this work, a novel and facile route to prepare porous carbon from SiO<sub>2</sub> based sacrificial templates is described by making use of hydrocarbon vapors. These porous carbons combine the structural properties typical of templated mesoporous carbon (i.e. high surface area, a high pore volume and porosity made up of accessible pores >2 nm) with a framework containing graphitic structures. The method developed is based on the use of mesoporous silica materials (HMS) as templates and Liquefied Petroleum Gas (LPG) gas, which is normally, composed of 90 % propane (C<sub>3</sub>H<sub>8</sub>), 2.5 % butane (C<sub>4</sub>H<sub>10</sub>) and higher hydrocarbons, and the balance ethane and propylene [73].
- To improve the conductivity of templated materials the carbon framework must contain structures with some degree of graphitization.

• Raman spectra can be used to characterize the extent of graphitization of prepared carbon samples; the well known D and G peaks of graphite are the main feature observed. The D and G peaks have varying degrees of intensity and width, in the 1350 and 1575 cm<sup>-1</sup> regions, respectively.

### **1.9. MOTIVATION OF THE STUDY**

- The world demand for primary energy keeps increasing and has little chance to decrease over the next decades, when considering the desirable and necessary development of less wealthy countries. Fossil fuels provide 90 % of primary energy, whereas hydrocarbons (crude oil and gas) are considered as closing energies to balance the level of demand. Crude oil and natural gas reserves are substantial, but limited. One half of the proven reserves of crude oil, and one third of gas reserves will be already used in 2020. Gas reserves will be sufficient to reach 2050, but proven reserves of crude oil will not last until that year. Hence there is a great demand to shift energy demands from fossil fuel combustion to sustainable energies that are safer, cleaner, and more efficient. These sustainable energies should provide an energy security due to their inexhaustible fuel stocks as well as their environmental compatibility.
- Hydrogen is well recognized as the clean fuel of the future. The most important industrial process for hydrogen production is catalytic steam reforming of hydrocarbons on nickel catalysts. However, a novel process consisting of a circulating fluidized-bed membrane reformer and catalyst regenerator (CFBMRR) has been suggested and demonstrated to produce pure hydrogen for fuel cell more efficiently and more flexibly.

- Water electrolysis is another method of producing hydrogen as clean fuel for the fuel cells. The advantage of water electrolysis compared to other methods of producing hydrogen is its low consumption of energy and simplicity, and lack of pollution.
- The SPE electrolyzer is the device that will make water electrolysis feasible
- Pt based nanophase catalysts are currently employed at the cathode of an SPE electrolyzer for hydrogen production.
- The problem associated with Pt is that it is expensive, however it has a potentially high performance. Embedding the Pt homogeneously and with high dispersion as nanoparticles on a support allows less particles to be used, reducing cost.
- The support increases the efficiency of the Pt by increasing the surface area upon which it is dispersed. With high dispersion of Pt an increase in surface area of the active metal, there is a simultaneous increase in the amount of active surface sites and concurrently decreasing cost.

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### 1.10. KEY CONCEPTS

- Catalysts facilitate the increase of reaction rates or otherwise slow reactions without being consumed in the reaction itself. This is achieved by lowering the activation energy threshold in the rate-determining step of the reaction.
- Heterogeneous catalysis is defined as the use of catalysts that are in a different physical state than the reactant. This type of catalysis involves the transport of reactant species to the catalyst surface where they are chemisorbed. Chemical interaction occurs between surface adsorbates followed by the breaking of chemisorptions bonds between adsorbates and catalyst surface and the liberation of products that are transported away from the catalyst surface [74].

- Electrocatalysis entails increasing the reaction rate and selectivity at electrodes, in electrochemical cells, using materials exhibiting high catalytic activity towards the electrode processes. Electrocatalysts act directly at interfaces by anchoring reagent species to their catalytic center or active sites. Suitable electrocatalysts have good corrosion stability over extended periods, good electrical conductivity to minimize resistance loss, and low cost [75].
- Pt group metal catalysts are typically used in electrocatalysis in the SPE electrolyzer and reducing the particle size to the nanometer domain can further enhance their catalytic activities.
- For the purpose of material cost reduction, suitable prepared nanophase electrocatalysts are usually dispersed on inert conductive support materials.

Liquefied petroleum gas (LPG) auto-reduces the Pt salt during chemical vapour deposition pyrolysis [76].

### **1.11 PROBLEM STATEMENT**

• The research problem is that, it is not possible to fit enough active sites on a two-dimensional support plane to achieve high catalytic activity. Therefore an increase of the active metal centers should be achieved by introducing a three dimensional plane to enhance surface area and to disperse the Pt in nanoparticulate form. The goal was to attain a larger active surface area using nanosized particles compared to an equivalent quantity of the bulk metal, which was the main focus of this study.

• Moreover a further goal was to prepare a three dimensional support that is electronically conducting and not insulating to disperse the active metal.

### **1.12 OBJECTIVES OF THE STUDY**

- The objective of this study is to develop a highly electronically conducting support materials with high surface area for the preparation of Pt-based electro-catalysts with the end application in the hydrogen evolution reaction and hydrogen production.
- The achievements of high surface area, high catalytic efficiency, high electron conductive catalysts based on Pt and mesoporous carbon material will contribute to the cost effective and energy efficient production of hydrogen. It is with this in mind that this study addresses the homogenous preparation of nanophase Pt electrocatalysts supported on mesoporous materials.

### 1.13 HYPOTHESIS



The preparation of Pt electrocatalysts is possible by supporting the active metal in nanoparticles on high surface area mesoporous graphite containing carbon materials.

### 1.14 **RESEARCH QUESTIONS**

- Is it possible to form mesoporous carbon using an HMS substrate as template?
- What is the optimum condition to achieve this? (Method development)
- Is this methodology reproducible? (Method validation)
- Is it possible to disperse Pt homogenously across a substrate in active form?
- What is the optimum condition to achieve this? (Method development)
- Does the metal catalyst posses high dispersion and exhibit high catalytic activity?

### 1.15 RESEARCH APPROACH

Highly-electroconductive porous carbonaceous supports that provide a high surface area for reaction will be prepared. These materials are of interest for high performance application as catalyst supports in solid polymer electrolyte (SPE) electrolyzers in water electrolysis and fuel cells. Their attributes will include:

- High-accessible porosity facilitating the mass transport of molecules or ions
- Good electronic conductivity for rapid charge transfer

Mesoporous carbons with accessible pore sizes > 2 nm can be obtained as inverse replicas of mesoporous silica materials used as templates. However, the framework of these carbons is usually made of amorphous material and hence they have a poor electrical conductivity. To improve the conductivity of templated materials the carbon framework must contain structures with some degree of graphitization.

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In this work a novel and convenient route for the preparation of highelectroconductive porous carbon, with graphitic framework structures, is presented. The HMS template was synthesized according to the procedure reported elsewhere [83]. The method was to prepare the carbon analogue based on the use of hexagonal mesoporous silica (HMS) material as a template and non-catalytic chemical vapour deposition pyrolysis (CVD) of liquid petroleum gas (LPG) as carbon precursor. This was followed by the dissolution of the HMS template framework by chemical etching. Finally, Pt nanoparticles were deposited onto the mesoporous carbon supports using an incipient wetness impregnation technique. EDS, XRD, BET, TEM, SAED, Raman spectra, TPR, TGA and DSC were employed to characterize the mesoporous carbon and the dispersion and homogeneity of the supported electrocatalyst.

### **1.16 DELIMITATIONS**

- The primary focus was to develop a mesoporous support with a high porosity and surface area and determine whether it could be used to disperse a catalytically active metal in a nanoparticulate form.
- The study will not address catalytic applications of catalysts in a working SPE electrolyzer. Also the mechanical workings of the catalyst in the SPE electrolyzer is beyond the scope of this study.
- The study will only encompass HMS material as a template in the preparation
  of mesoporous carbon supports. This is due to the high mechanical integrity
  of HMS compared to other silica molecular sieves (e.g. MCM-41 or MCM48). Also time constraints limit the use of other silica molecular sieves.
- The study is limited only to the cathode catalyst of the SPE electrolyzer due to the focus of the study. As a result of optimum performance of Pt in the cathodic reaction of the SPE electrolyzer, the study will be limited to the dispersion of pure Pt and no other metal or metal alloy.
- Due to the constraints of time and the availability of certain instrumentations, the characterization study was limited to the use of EDS, XRD, BET, TEM, SAED, Raman spectroscopy, TGA, DSC and Linear Sweep Voltammetry as characterization techniques.
- Characterization was limited by availability and operation constraints of instruments.
- The preparation and characterization of binary, ternary and quaternary catalysts was limited due to the constraints of time.

### **1.17 THESIS OUTLINE**

This thesis will be presented according to the following outline

Chapter 1: General background and introduction to Nanomaterials as well as physicochemical characterization.

Chapter 2: Experimental methods and chemical materials used in the study.

Chapter 3: Production of graphitic mesoporous material by hexagonal mesoporous silica template.

Chapter 4: Catalytic and structural analysis of Pt catalyst supported on a graphitic mesoporous carbon.

Chapter 5: Summary and conclusions NIVERSITY of the WESTERN CAPE

## **CHAPTER 2**

## **EXPERIMENTAL PROCEDURES**

### 2.1 CHEMICALS

The chemicals that were used in this study are presented in Table 4.1.

Chemical name	Specification	Supplier
1-Hexadecylamine, Tech,	90 %	Adrich
Tetraethoxysilane	99.9 %	Adrich
Sulphuric acid	98 %	KIMIX
Nafion Solution	5 wt% in the mixture of lower aliphatic alcohols and water	Ionomer (Dupont)
Hexachloro Platinic Acid (H <sub>2</sub> PtCl <sub>6</sub> .6H <sub>2</sub> O)	99.8 %	Next Chimica
Isopropanol	99.7 %	SAARCHEM
Ethanol	99.8 %	MERCK
Platinum (Pt/C)	40 wt%, 4.2 nm size	Johnson Matthey
Methanol	98%	SAARCHEM
Sodium Hydroxide Pellets	СР	KIMIX
Formaldehyde	40 %	KIMIX
Liquefied Petroleum Gas (LPG)	A mixture of propane $(C_3H_8)$ and butane $(C_4H_{10})$	AFROX

**Table 2.1**Summary of chemicals used in the study

### 2.2 PREPARATION OF HEXAGONAL MESOPOROUS SILICA (HMS)

In this study the parent mesoporous SiO<sub>2</sub> based HMS used as sacrificial template was synthesized in a similar method to that reported by Pinnavaia and coworkers [20] by adding a primary amine surfactant 1-hexadecylamine (Aldrich) as structure directing agent under stirring to an ethanol/water mixture (35/70, v/v). The mixture was subjected to stirring in an open vessel for 24 h. In a typical synthesis, 4.0 g of the silica source (Tetraethoxysilan, TEOS, Aldrich) was added dropwise under stirring to the solution containing the surfactant in an ethanol/water mixture (1/2.5, v/v) i.e.100ml ethanol and 250ml water. The mixture was once more subjected to stirring at 25  $^{0}$ C in an open vessel for 24 h.

The solid product was filtered and washed with distilled water. 150 ml of ethanol was added to the solid product and this mixture was heated at  $100 \, {}^{0}$ C under reflux with stirring for 2 h. The suspension was filtered and dried at  $100 \, {}^{0}$ C. The solid product was heated in a furnace to 550  ${}^{0}$ C at a heating rate of  $1 \, {}^{0}$ C/min and then calcined at 550  ${}^{0}$ C for 8 h . The high temperature calcinations step was necessary for detemplation and efficient removal of the (primary amine surfactant) template molecule, in order to access the pores in the following step. The yield of HMS product was approximately 2 g when using the specified amounts of starting materials.

### 2.3 PREPARATION OF MESOPOROUS CARBON MATERIAL

The calcined and thus detemplated mesoporous silica HMS was then used as a solid template for the preparation of mesoporous carbon material by a CVD method as conceptualized [76]. In a typical synthesis, two ceramic boats each with 1.0 g of HMS freshly prepared and detemplated were placed in a flow through quartz tube

furnace. The furnace was heated to the target temperature of 800 <sup>0</sup>C; from a starting temperature of 50 °C at a heating rate of 1.67 °C min<sup>-1</sup> under a LPG flow. When the target temperature of 800 °C was reached; the LPG was sustained at this target flow for 90 min of which for other synthesis pyrolysis time was varied 60min, 30min and 15min. Thereafter, the LPG flow was cut and the samples were taken out of the tube furnace to cool at ambient temperatures. The resulting mesoporous silica/carbon composite designated as (HMS/LPG 90) was refluxed with 50 ml of 1M NaOH at 75 <sup>0</sup>C under stirring to dissolve and remove the silica template. Finally the silica etched carbon analogue material designated as CA HMS/LPG 90, was washed with ultra pure water, rinsed and dried in the oven at 100  $^{\circ}$ C.

Figure 1.4 presented in the literature review summarizes the above steps but instead of MCM-48, HMS is used as the mesoporous silica molecular sieve.

**ELECTROCATALYSTS** 



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This experimental section will serve to describe the Pt deposition/loading on mesoporous silica and mesoporous carbon on order to prepare the composite electrocatalyst; the order of deposition /loading on the template silicate or carbon support as well as the different techniques employed to characterize the synthesized catalysts. For one procedure, mesoporous silica HMS was impregnated with a Pt solution. Subsequently the pores of HMS were filled with pyrolytic carbon and the HMS was dissolved in alkaline medium (section 2.4.2). In the second procedure the HMS pores were first filled with pyrolytic carbon for various times, and the HMS/carbon material was subsequently impregnated with a Pt solution after which the HMS was dissolved (Section 2.4.3). For the third procedure HMS pores were filled with pyrolytic carbon, and the  $SiO_2$  framework subsequently dissolved in alkaline medium to prepare a mesoporous carbon analogue and then the carbon analogue was loaded with Pt ( section 2.4.4).

The characterization techniques applied were X-ray Diffractommetry (XRD), Linear Sweep Voltammetry (LSV), Transmission Electron Microscopy (TEM), Selective Area Electro Diffraction (SAED), Energy Dispersive Spectroscopy (EDS), Thermal Gravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), and Nitrogen Adsorption using Brunauer/Emmett/Teller (BET) technique. The preparation of the HMS sacrificial template was described in section 2.2

### 2.4.1 Deposition of Pt

A method reported by Smirniotis [77], which is fairly a standard zeolite incipient wetness impregnation procedure, used to deposit metals upon zeolites, was used to prepare Pt based composite electrocatalysts by deposition of Pt upon HMS or the carbon analogue developed in this study. This method i nvolved preparation of a 0.1545 M solution of  $H_2PtCl_6$  and impregnating about 1g of the support (HMS, mesoporous silica- carbon composite or carbon analogue) with 1ml of this solution and then drying the slurry formed at 100  $^{\circ}C$  for 1 hour .

The resulting samples were thoroughly rinsed and dried at 100  $^{0}$ C. Following the above steps, the Pt <sup>4+</sup> salt in the solution is reduced to Pt<sup>0</sup> by a methanol/ formaldehyde technique [86]. Reduction takes place. according to the following reaction:

 $PtCl_{6}^{-2} + 2HCHO + 2H_{2}O \rightarrow$   $Pt^{0} + 2HCOOH + 6Cl^{-} + 4H^{+}$ [4.1]

Note that in the first set of samples described in the experimental procedures, Pt was deposited upon HMS before carbon deposition (section 2.4. 2). In the following set of experiments Pt was deposited upon HMS after carbon deposition (sections 2.4.3 and

2.4.4) and in the set of experiments Pt was deposited on the carbon analogue after dissolution of HMS.

#### 2.4.2 Preparation of carbon analogues whereby Pt is deposited before carbon

1g of the HMS support was impregnated with 2ml of 0.1545M H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O solution. The slurry formed was dried in the hot air oven at 80  $^{0}$ C until visibly dry. The Pt/HMS or HMS/Pt sample was then transferred to a ceramic crucible and was inserted in a flow through quartz tube furnace. (The above procedure was repeated to prepare each of the following samples i.e. HMS/Pt/LPG\_15, HMS/Pt/LPG\_30, HMS/Pt/LPG 60 and HMS/Pt/LPG 90).

The sample was then exposed to a flow of LPG under controlled conditions. This was performed to deposit the pyrolytic carbon in the pores of the metal activated HMS mesoporous Si support. The starting temperature was 50 °C and this temperature was ramped up at a heating rate of 1.67 °C·min<sup>-1</sup> until a maximum temperature of 800 °C was attained. At 800 °C the LPG began to flow through the quartz tube furnace and this flow was sustained for 15, 30, 60 and 90 minutes for HMS/Pt/LPG\_15, HMS/Pt/LPG\_30, HMS/Pt/LPG\_60 and HMS/Pt/LPG\_90 respectively.

The LPG flow was then stopped; thereafter the samples were cooled and taken out of the furnace to cool at ambient temperature. The samples were not subjected to metal reduction; due to the fact that LPG served as an auto reduction agent, to reduce the Pt salt (Pt<sup>4+</sup>) to the metal (Pt<sup>0</sup>). On observation the samples were black; this signified that the samples were carbonized fairly uniformly. The samples were each divided in half and one half was then subjected to washing with 50 ml of 1M NaOH solution at 75  $^{\circ}$ C under stirring to remove the silica template. The resulted silica etched Pt containing carbon material was washed with ultra pure water and dried in an oven at

100  $^{0}$ C. The other portion of each sample, still containing Si was reserved for further analysis.

### 2.4.3 Preparation of carbon analogues whereby Pt is deposited after carbon but before etching of silica template.

2.00g of HMS silica template was placed in ceramic crucible boats and inserted in a flow through quartz tube furnace. The furnace was heated to a target temperature of 800 °C from a starting temperature of 50 °C at a heating rate of 1.67 °C min<sup>-1</sup>. At 800 °C the LPG began to flow through the quartz tube furnace. This flow was sustained for 15, 30, 60 and 90 minutes for HMS/LPG\_15, HMS/LPG\_30, HMS/LPG\_60 and HMS/LPG\_90 respectively.



The LPG flow was then stopped; thereafter the sample was taken out of the furnace to cool at ambient temperature. 1g of each sample of HMS/LPG subjected to LPG for various times (composite) were each impregnated with 2ml of 0.1545M H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O Hexachloro Platinic acid solution. The slurry formed was dried in a hot air oven at 80 °C until dry. The metal salt formed (Pt<sup>4+</sup>) was chemically reduced (see section 2.4.1) to Pt<sup>0</sup> using Methanol Formaldehyde plating solution (see equation 4.1). These sample were labeled HMS/LPG 15/Pt, HMS/LPG 30/Pt, HMS/LPG 60/Pt and HMS/LPG 90/Pt respectively. The samples were each divided in half, and one half was then subjected to refluxing with 50 ml of 1M NaOH solution at 75 <sup>0</sup>C under stirring to remove the silica template. The resulted silica etched Pt carbon material was washed with ultra pure water and dried in the oven at 100 °C. The other portion of each sample, still containing Si was reserved for further analysis.

### 2.4.4 Preparation of carbon analogues whereby Pt is deposited after carbon and after etching of silica template

2.00g of HMS silica template was placed in ceramic crucible boats and inserted in a flow through quartz tube furnace. The furnace was heated to a target temperature of 800  $^{0}$ C from a starting temperature of 50  $^{0}$ C at a heating rate of 1.67  $^{0}$ C min<sup>-1</sup>. At 800  $^{0}$ C the LPG was flowed at this target temperature for 90 minutes to form the HMS/LPG\_90 composite sample.

The sample was then subjected to washing with 50 ml of 1M NaOH solution at 75  $^{0}$ C under stirring to remove the silica template. The resulting silica etched carbon analogue material was washed with ultra pure water and dried in an oven at 100  $^{0}$ C, 1g of this carbon analogue was impregnated with 2ml of 0.1545M H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O Hexachloro Platinic acid solution. The slurry formed was dried in a hot air oven at 80  $^{0}$ C until visibly dry. The metal salt formed (Pt<sup>4+</sup>) was chemically reduced (to Pt<sup>0</sup>) using Methanol Formaldehyde plating solution (see equation 4.1). The resulted silica etched Pt carbon material was washed with ultra pure water and dried in the oven at 100  $^{0}$ C and labeled MC\_90/Pt.

### 2.5 INK PREPARATIONS FOR LINEAR SWEEP VOLTAMMETRY EXPERIMENTS

The quantities of materials used during ink preparation for linear sweep voltammetry experiments are presented in Table 2.1. It is important to note that during mixing ethanol was firstly added to the catalyst powder to avoid an exothermic reaction between the catalyst and the Nafion solution. The mixture was then stirred for 24 hrs in order to disperse the particles throughout the solution. The same ink formulation

was used to prepare an ink solution of the standard Pt/C (40%) electrocatalyst supplied by Johnson Matthey (JMPt/C) as comparison.

Table 2.2 Summary of ink formulation

Component	Quantity
Catalyst	0.02 g
Ethanol	4 ml
Nafion solution (5%, Dupont)	200 µl



#### 2.6 SAMPLE CHARACTERIZATION UNIVERSITY of the

Samples were characterized by various techniques and the experimental conditions are specified in this section.

Table 2.2 lists characterization techniques used during catalystic development.

Table 2.3	<b>Characterization</b>	techniques	used during	catalyst	development.
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Туре	Purpose	
Scanning electron microscope (SEM) & Energy dispersive X-ray (EDX)	Morphology & elemental composition	
X-ray diffraction (XRD)	Crystallinity, particle size, phase analysis	

Transmission electron microscope (TEM)	Crystallinity, particle size	
Selective area electron diffraction (SAED)	Crystallinity and crystal symmetry	
Raman spectra	Structural ordering	
Thermo-gravimetric analysis (TGA)	Thermal stability	
Brunnauer-Emmet-Teller (N <sub>2</sub> BET)	Surface area and pore diameter	
Linear sweep voltammetry (LSV)	Electrochemical activity	

### 2.6.1 Scanning electron microscope (SEM)

Chemical composition was obtained by EDS analysis which was coupled to a SEM Hitachi X650. EDS samples were mounted using a conductive double-sided tape. A thin (ca. 10 nm) coating of carbon sputter was deposited onto the HMS sample to reduce the effect of charging. The silica etched carbon analogue material was not coated with carbon.

### 2.6.1.1 Sample preparation

A carbon tape was placed on top of a specimen holder and then the sample was mounted on top of the carbon tape, finally the specimen was introduced in the SEM instrument. The SEM was hyphenated with an EDS instrument coupled to a computer using GENESIS software for elemental analysis.

2.6.2.1 Experimental details

Name of the instrument : Hitachi X 650 Scanning electron microscope

Applied voltage : 25 kV

Current	: 1µA
Illumination angle	: 0.1 mrad
Magnification range	: 0.35X to 1KX
Resolution	: 50 µm
Working distance	: 15 mm

### 2.6.2 X-ray diffraction (XRD)

### 2.6.2.1 Sample preparation

The catalyst powder was mounted in a sample holder, leveled using a spatula and finally introduced in the x-ray diffractometer.

Voltage	: 40 kV
Current	: 40 mA
Scanning range	: 2.5°-90° (2θ angle)
Time per step	: 29 seconds
Wavelength	: 1.54 Å (CuK <sub>α</sub> )
Stepsize	: 0.4 °
Detector	: NaI

### 2.6.3 Transmission electron microscope (TEM)

### 2.6.3.1 Sample preparation

Two or three droplets of methanol were poured into the sample holder, and a small amount of less than 5 mg of a sample was added and then the mixture was shaken for some time until all the nanoparticles were dispersed in the solution. One droplet of the solution was deposited on a carbon film supported on a copper grid and allowed to dry.

### 2.6.3.2 Experimental details



### 2.6.4 Selected-area electron diffraction (SAED)

Sample grids from the transmission electron microscopy (TEM) study were retained for SAED analysis. The SAED pattern was obtained using a spot analysis with a TEM (Hitachi H-800 EM), and patterns were recorded on a photographic film.

### 2.6.5 Raman spectra

### 2.6.5.1 Experimental details.

The triple subtractive configuration of a Jobin-Yvon T64000 Raman spectrometer with a micro-Raman attachment and the 514.5nm line of an argon ion laser were used to measure the Raman spectra of the carbon analogue (CA-HMS/LPG\_90) sample. The laser diameter at the sample was approximately 1.5 micron, and the power at the sample was 1.22mW. Spectra were accumulated using a liquid nitrogen cooled CCD detector and the acquisiton time was 240 seconds.

On sample carbon analogue (CA-HMS/LPG\_90) three different spots were measured, and the laser spot was defocused by 35 micron vertically to minimize local heating.

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### 2.6.6 Thermo-gravimetric analysis (TGA)

2.6.6.1 Sample preparation

A small	amount of the	sample powder	was int	roduced to th	e thermo-gravimat	tric
furnace.	The experiment	t was performed	l in an aiı	r atmosphere,	whilst subjecting	the
sample t	o heating at a co	ntrolled rate.				

### 2.6.6.2 Experimental details

Name of the instrument	: Rheometric scientific thermal analyzer
Heating range	: 25 °C – 900 °C
Heating rate : 5	°C/min
O <sub>2</sub> supply rate	: 50 ml/min

#### 2.6.7 **Brunnauer-Emmett-Teller (N 2BET)**

Changes in the surface area, pore volume and pore size distribution of samples were determined by means of the Brunnauer-Emmet-Teller (N<sub>2</sub>BET) technique using a Micromeritics Accelerated SA and Porosimetry (ASAP) 2010 system.

### 2.6.7.1 Sample preparation

Approximately 20 mg of the sample was transferred and sealed in a sample tube. Samples were degassed and dried at 165 °C under vacuum. The experiment was conducted isothermally at -196 <sup>0</sup>C with a constant N<sub>2</sub> flow applied during analysis.



2.6.8.1 Experimental details

2.6.8

Linear sweep experiments for the HER on electrocatalyst films using inks as prepared in section 2.5 and table 2.1 were conducted at  $25 \, {}^{\circ}C$ .

Electrolyte	: 0.5 M H <sub>2</sub> SO <sub>4</sub>
Working electrode	: Glassy (vitreous) carbon
Glassy carbon area	: Geometric surface area = $0.07 \text{ cm}^2$
Reference electrode	: Standard Calomel Electrode (SCE) in 3M KCl
Counter electrode	: Platinum wire
Scanning range	: 0.0V to -1.5 V (versus SCE)
Scanning rate	: 20 mV/s
Step potential	: 15 mV

### CHAPTER 3

### PRODUCTION OF MESOPOROUS CARBON MATERIAL USING HMS MESOPOROUS SILICA TEMPLATE.

### **3.1 INTRODUCTION**

Among the various methods used to prepare mesoporous carbons, the solid template approach is attractive because it allows control of the pore structure and morphology of the resulting carbon materials. Solid templating of mesoporous carbons is based on the pyrolysis of carbon precursors within the pore channels of mesoporous silica templates. There are two strategies by which carbon precursors may be introduced into the pore channels of mesoporous silica i.e. liquid impregnation or chemical vapor deposition (CVD). Liquid impregnation, which is usually followed by polymerization and pyrolysis (carbonization) steps or cycles, has been extensively studied [77]. On the other hand, there are fewer reports on the synthesis of mesoporous carbon materials by gas-phase chemical vapor deposition (CVD).

CVD is a well-established method for preparing porous carbon, carbon nanofibres, and carbon nanotubes [78]. It has a number of advantages over the liquid phase impregnation method, such as high degree of pore filling and easy control over the amount of pyrolytic carbon deposited in the template pores, enabling the formation of graphitic pore walls and avoiding the formation of additional microporosity. In chemical vapor deposition, a carrier gas is used to deliver the carbon precursors into

#### Chapter 3

the pore channels of the mesoporous silica template followed by thermal treatment at a target temperature to form the carbon framework. Thermal treatment allows the polymerization and carbonization of the carbon precursor to occur simultaneously in the pore channels of mesoporous silica template [79].

Well-ordered mesoporous carbon materials have been obtained via CVD using mesoporous silica materials as solid templates. Various particle morphologies, including nanotube-like carbon and hollowsphere carbon, have been fabricated via chemical vapor deposition [79]. Despite their excellent structural ordering and well-defined pore size distribution, mesoporous carbon materials obtained via sacrificial solid template approaches generally possess amorphous pore walls. It is therefore highly desirable to prepare mesoporous carbon materials, which have crystallinity (i.e., graphitic character) in their pore walls.

Recently, Ryoo and co-workers [80] reported the fabrication of graphitic mesoporous carbon materials via an in-situ conversion of aromatic compounds into mesophase pitch within the pore channels of aluminosilicate mesoporous materials. Several heating and cooling cycles were required to obtain the graphitic mesoporous carbon materials. Pinnavaia and co-workers [81] employed a similar method to synthesize graphitic mesoporous carbon from aromatic hydrocarbon precursors at ambient pressures by the replication of mesostructured silica template in the presence of a catalyst. The methods reported by Ryoo and Pinnavaia required catalysts to convert the carbon precursor to mesoporous carbon. Fuertes and Alvarez [82] used liquid impregnation followed by carbonization of poly-vinyl chloride within the pore channels of mesoporous silica to prepare graphitic mesoporous carbons.

### **3.2 ELEMENTAL COMPOSITION**

The elemental composition of hexagonal mesoporous silica (HMS), silica carbon composite (HMS/LPG\_90) and carbon analogue (CA\_HMS/LPG\_90) was

determined. HMS and the carbon analogue were successfully prepared according to the synthesis routes described in sections 2.2 and 2.3 respectively.

Figure 3.1 presents the EDS analysis of the parent HMS compared to the sample after CVD treatment (HMS/LPG\_90) and the NaOH etched carbon analogue (CA HMS/LPG 90).



Figure 3.1 EDS of HMS, HMS/LPG\_90, CA\_HMS/LPG\_90

The elemental composition of the hexagonal mesoporous silica (HMS), silica carbon composite (HMS/LPG\_90) and carbon analogue (CA\_HMS/LPG\_90) as obtained by EDS analysis of spectra using GENESIS software is presented in Table 3.1.

Sample	Wt% Si	Wt% O	Wt% C
HMS	59.15	40.85	0.00
HMS/LPG_90	59.15	28.33	46.66
CA_HMS/LPG_90	4.16	13.22	82.62

Table 3.1 Elemental composition of HMS, HMS/LPG\_90 and CA\_HMS/LPG\_90

The EDS intensities for the HMS reveal that HMS is composed of Si and O elements. No carbon peak was detected in the parent Si based HMS used as sacrificial template. Whereas on observation of the silica carbon composite (HMS/LPG\_90) formed after pore filling of the parent HMS material, peak intensities for Si, O and C were detected. The carbon analogue (CA\_HMS/LPG\_90) formed after removal of Si based HMS by etching with NaOH, showed peak intensities for Si, O and C.

The SiO<sub>2</sub> weight percentage of 59.15 % and zero percentage of carbon shows the absence of the carbon in the HMS. Whereas, after dissolution of the silica wall in the silica carbon composite (HMS/LPG\_90) when the carbon analogue (CA\_HMS/LPG\_90) is formed; there is a significant drop in the silica weight percentage down to 4.16 % and a significant increase in the weight percentage of carbon to 82.63 %.

Therefore, elemental composition by EDS analysis revealed that the dissolution of the silica template was mostly complete, and that a carbon material had been successfully prepared by CVD route followed by etching with NaOH.

#### 3.3 STRUCTURAL CHARACTERIZATION BY XRD.

In Figure 3.2 the XRD pattern of mesoporous silica (HMS), silica carbon composite (HMS/LPG\_90) and carbon analogue (CA\_HMS/LPG\_90) are shown.



Figure 3.2 Powder XRD patterns of mesoporous silica — HMS, mesoporous silica/carbon composite — HMS/LPG\_90 and silica etched Mesoporous carbon material — CA\_ HMS/LPG\_90.

The XRD of the parent SiO<sub>2</sub> based HMS material shows the typical spectrum for these materials. It should be noted that due to lack of access to low angle XRD the main and identifying peak partly visible at the origin of the spectrum could not be fully resolved. It was not possible to scan XRD at low angles to determine the pore mesostructure of the hexagonal mesoporous silica (HMS), silica carbon composite (HMS/LPG 90) and carbon analogue (CA HMS/LPG 90). The HMS/LPG 90 material that had been subjected to CVD with LPG as described in section 2.3 shows very little evidence of crystalline ordering in the XRD in the range scanned. However, the XRD pattern of the carbon analogue exhibits two peaks that were noted in the following angle region at 7.39 and 12.64  $^{0}$  2  $\theta$  and a further two peaks in the high angle region 25.3  $^{0}$  2  $\theta$  and 43.5  $^{0}$  2  $\theta$ . The high angle peaks are due to the (002) and (101) diffractions ascribed to graphitic carbon [84]. The d<sub>002</sub> spacing obtained from the (002) peak is 3.38 close to the d spacing of ideal graphite s at the high angle region 25.3  $^{0}$  and 43.5  $^{0}$ (with  $d_{002} = 3.35$ 

 $2 \Theta$  imply that the mesoporous carbon is mesostructurally well ordered and possesses a carbon framework with a significant amount of crystalline-graphitic character.

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The existence of the peaks at 7.39  $^{0}$  and 12.64  $^{0}$  2  $\theta$  is evidence of the existence of some carbon as part of the pore wall or framework of the carbon analogue that is mesostructurally well ordered. Hence the carbon analogue formed not only contains some degree of graphitic carbon. It also is well ordered on the mesoscale and thus may also contain some form of repeating carbon framework that is structurally ordered albeit not necessarily a graphitic carbon framework. This has not been observed before in the pore wall at d spaces of 11.6 and 6.8  $\Box$  corresponding to the 2  $\theta$  values of 7.39 and 12.64  $^{0}$ . The low angle peaks observed in the XRD spectra for this carbon analogue can thus be indicative according to Ryoo et al, of regular longer range framework d-spacings that correspond to a regular structure in the mesopore array.

Moreover, the inflection of the scan at its origin indicates the typical peak characteristic of mesoporous materials with pores in the region of 2 nm both for HMS and the carbon analogue as was confirmed by  $N_2BET$  and further detailed in section 3.7.

#### **3.4 SELECTED AREA ELECTRON DIFFRACTION**

The structural ordering of the carbon framework was also evidenced in Figure 3.3 a-c which depicts the selected area electron diffraction (SAED) pattern of the three samples. HMS (mesoporous Si template) and HMS/LPG\_90 patterns show only diffuse rings indicating a lack of crystalline of pore walls ordering, whereas CA\_HMS/LPG\_90 shows structural ordering consistent with the XRD in Figure 3.2. The SAED pattern of the mesoporous carbon depicts several diffraction rings characteristic of graphitic ordering



Figure 3.3 Selective Area diffraction of (a) HMS; (b) HMS/LPG\_90 and (c) CA HMS/LPG 90

The SAED patterns may possibly be due to crystallinity apparent in the XRD patterns (figure 3.2) and provide further evidence of the existence of some degree of graphitization in the pore walls of the carbon analogue (CA\_HMS/LPG\_90).

### 3.5 STRUCTURAL CHARACTERIZATION BY RAMAN SPECTROSCOPY.

The Raman spectra shown in Figure 3.4 is also consistent with the presence of graphene sheets within the pore walls of the carbon analogue (CA\_HMS/LPG\_90).



Figure 3.4 (a) Raman spectra of the carbon analogue (CA\_HMS/LPG\_90)




Figure 3.4 (b) Raman spectra of graphite carbon [85].

The Raman spectrum (Figure 3.4 (a)) of carbon analogue (CA\_HMS/LPG\_90) shows two bands at 1350 cm<sup>-1</sup> (D band) and ca. 1580 cm<sup>-1</sup> (G band). Band G is due to the carbon-carbon stretching ( $E_{2g}$ ) mode for graphene sheets [85]. The presence of this band therefore provides further evidence for the presence of graphite in pore walls in the carbon analogue. The D band might be due to the presence of (amorphous carbon) in a new mesostructural ordering of the pore walls as is shown by the low angle peaks visible in the XRD spectrum sections 3.3, figure 3.2.

Figure 3.4(b) is an example of a Raman spectrum of a structure of template carbons obtained after the dissolution of the silica framework for the disordered and graphitic regions [85].

# 3.6 STRUCTURAL CHARACTERIZATION BY THERMOGRAVIMETRIC ANALYSIS.

The presence of a degree of graphitic carbon within the pore walls is further supported by thermogravimetric analysis, when the sample was slowly heated in air. The weight loss curves thus obtained are represented in Figure 3.5 (a) and in (b) are shown



Figures 3.5 (a) TGA of CA\_HMS/LPG\_90





Figures 3.5 (c) DSC of CA\_HMS/LPG

The weight loss curves at 550-650  $^{\circ}$  C (Figure 3.5 (a)) can be assigned to the presence of graphitised carbon in the carbon analogue sample (section 3.6). The heat flow curve at 550  $^{\circ}$ C (Figure 3.5c) further supports this proposition, showing a distinct exortherm centered at just above 500  $^{\circ}$ C. Indicating that most of the sample was indeed graphitic in nature. This is further support by the DSC curve (figure 3.5c) of sample CA\_HMS/LPG\_90 which shows a single clear exotherm centered at 550  $^{\circ}$ C.

#### 3.7 PORE SIZE DISTRIBUTION AND SURFACE AREA.

In Figures 3.6 (a) and (b) the pore size distribution and in Table 3.2 the surface area obtained by  $N_2$  BET of HMS and the carbon analogue (CA\_HMS/LPG\_90) is depicted respectively.





Figure 3. 6 (a) Pore size distribution by N<sub>2</sub>BET of HMS



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Table 3.2 Textural properties of HMS, HMS/LPG\_90, and CA\_HMS/LPG\_90 materials

Sample	Surface area	Pore diameter	
Ĩ	$(m^2/g)$	(nm)	
HMS	756	3	
HMS/LPG_90	151	2.4	
CA_HMS/LPG_90	938	3	

 $N_2BET$  analysis shows that HMS and the carbon analogue (CA\_HMS/LPG\_90) have considerable nanoporosity in the size range 3nm.

Table 3.2 compares the surface area of the parent HMS, the HMS silica carbon composite and the carbon analogue (CA\_HMS/LPG\_90) after etching and removal of the SiO<sub>2</sub> framework. These results show that HMS surface area was relatively high but after infilling with carbon, the surface area was reduced to  $151m^2/g$ . The results also show that the carbon analogue obtained after etching away HMS template was indeed highly porous, with a large surface area of  $938m^2/g$  that exceeded that of the parent HMS silica sacrificial template that had a surface area of  $756m^2/g$ , the (CA\_HMS/LPG\_90) carbon analogue had mesopores in the exact size range of the HMS SiO<sub>2</sub> template. The data shows that a negative carbon mesoporous replicate or analogue of the Si based HMS was successfully achieved.

These results signified that a highly porous carbon analogue of the HMS silica template was successfully synthesized with a high surface area by a new carbonization route.



#### 3.8 CONCLUSIONS:

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The XRD pattern as well as the BET adsorption indicates a high degree of mesostructural ordering in the parent HMS silica synthesized hydrothermally. The nitrogen sorption data confirm that the HMS silica possessed good mesostructural ordering and was therefore suitable for use as a solid template for mesoporous carbon synthesis. The characteristics of the mesoporous carbon analogue determined by XRD, SAED, BET, TGA, DSC and Raman spectroscopy show that the carbon analogue was indeed graphite and highly porous, with a large surface area exceeding that of the parent HMS silica sacrificial template and with mesopores in the exact size range of the Si template. Hence, a negative carbon mesoporous replicate or analogue of the Si based HMS was successfully achieved.

The formation of graphitic structures in the pore walls of the mesoporous carbon analogue takes place during the chemical vapor deposition step of HMS at high temperatures. The dissolution of the  $SiO_2$  framework of the mesoporous  $SiO_2$  used as template creates the 3 nm pores in the carbon that were detected in the N<sub>2</sub>BET.

The apparently regular mesostructure of the carbon could be further supported by the appearance of the new XRD peaks at 7.39 and 12.64  $^{0}$  2  $\theta$  that may indicates that there is a regular carbon framework at 11.6 and 6.8 W. d spaced distances. This is a novel finding and has not been previously reported.

Moreover the large mass loss obtained by TGA at  $550^{\circ}$ C may indicate that most of the carbon analogue comprise of the graphitic carbon. This is further supported by clear graphite XRD peaks in the region  $26.11^{\circ} 2 \theta$  and  $43.54^{\circ} 2 \theta$  and also by Raman spectroscopy. This degree of graphitization in a mesoporous analogue has also not previously been reported.



#### CHAPTER 4

### CATALYTIC AND STRUCTURA LANALYSIS OF Pt CATALYSTS SUPPORTED ON GRAPHITIC MESOPOROUS CARBON.

#### 4.1 AIMS AND OBJECTIVES

This chapter describes three different procedures to deposit nanoparticulate Pt clusters on mesoporous material. The mesoporous material included HMS, HMS/LPG and the carbon analogue of HMS. Thereafter, the electrochemical activity of these Pt (supported) electrocatalysts is compared to the commercial carbon supported Pt/C Johnson Matthey catalyst as benchmark.

#### **4.1.1 Introduction**

Pt-based electrocatalysts are usually employed at relatively low temperatures in proton exchange membrane fuel cells (PEMFC), Solid Polymer Electrolyzers (SPE) and direct methanol fuel cells (DMFC) as cathode electrocatalysts. It is well known that the catalytic activity of the metal is strongly dependent on the particle shape and size distribution. Conventionally, preparation of the Pt based electrocatalysts involves techniques based on incipient wetness impregnation (IWI) and chemical reduction of the metal [84]. Incipient wetness impregnation has the advantage of technical simplicity and reproducible Pt loading [86, 87].

The preparation of ordered mesoporous carbon with graphitic framework using ordered mesoporous materials (HMS) as a silica template has been described in chapter 3. These carbon materials can be used as catalyst supports, electrode materials, adsorbents, and templating matrixes for fabricating nanostructures because of their prominent characteristics, such as high surface area, relatively uniform pore

size, and ordered pore structure. Such materials are further to have an interconnected pore network, tailorable surface properties, and thermal and mechanical properties [88].

The electrochemical properties of a porous carbon can be used as an electrode in direct-methanol fuel cells (DMFCs), electrochemical double-layer capacitors, and lithium ion batteries, have been found to be closely related to its graphitic nature . The utilization of carbon supported noble metal particles as electrocatalysts for fuel cells has increased interest towards understanding of their towards the electrochemical reactivity of nanoparticles [88].

#### 4.2 **RESULTS AND DISCUSSION**

The materials prepared in sections were characterized by various techniques as described in section 2.2, 2.3, 2.4.1, 2.4.2, and 2.4.3 and the results of characterization are presented in the following subsections accompanied by a discussion of the results.

## 4.2.1 X-ray Powder Diffractommetry ERSITY of the

In Figures 4.1 and 4.2 the crystalline phase identification and phase purity of the parent mesoporous silica HMS as prepared in section 2.2, mesoporous silica Pt catalyst as prepared in section 2.4.1 as well as HMS/Pt/LPG series as prepared in section 2.4.2 together with their carbon analogues (CA\_HMS/Pt/LPG) series as prepared in section 2.4.3 are shown.

These samples were prepared by first depositing Pt upon  $SiO_2$  HMS template prior to pore filling with carbon and prior to dissolution of the sacrificial Pt template.



Figure 4.1 XRD crystallinity of HMS, HMS/Pt/LPG series prepared at different carbonization times.

The XRD spectra in Figure 4.1 are for the aliquots of samples that did not have the  $SiO_2$  removed by NaOH etching whereas the XRD spectra in Figure 4.2 show the same samples after  $SiO_2$  etching with NaOH.



Figure 4.2 XRD crystallinity of CA HMS/Pt/LPG series prepared at different carbonization times.

The HMS/Pt/LPG series as prepared in section 2.4.2 and still containing  $SiO_2$  i.e. HMS/Pt/LPG 15, HMS/Pt/LPG 30, HMS/Pt/LPG 60 and HMS/Pt/LPG 90 together with their carbon analogue (CA HMS/Pt/LPG) produced after NaOH etching series as prepared in section 2.4.4 i.e. CA HMS/Pt/LPG 15, CA HMS/Pt/LPG 30, CA HMS/Pt/LPG 60 and CA HMS/Pt/LPG 90 as well as HMS/Pt exhibit several peaks that may be indexed to Pt miller indices of (111), (200), (220), (311) and (222) corresponding with 2 theta degrees of 39.69°, 46.22°, 67.68°, 81.47° and 86.30° respectively in XRD patterns.

All the XRD patterns clearly show the characteristic peaks of a face centered cubic crystalline Pt. The d spacing for the higher 2 theta angles 39.69<sup>0</sup>, 46.22<sup>0</sup>, 67.68<sup>0</sup>, 81.47° and 86.30° was found to be 2.3° Å, 1.96 Å, 1.38Å and 2.22 Å and 1.13 Å respectively. Moreover, graphitic carbon peaks at 2 theta values at 25.6 and 43.7  $^{0}$ 

with miller indices (002) and (101) respectively, were obtained; however for the latter carbon 2 theta value, there was a significant Carbon peak overlap with the Pt (200) peak. To note, from the XRD spectra shown in Figure 4.2. it can be observed that the carbon analogue HMS/Pt/LPG 90 and carbon analogue HMS/Pt/LPG 60 showed broad but prominent peaks at 25.6  $^{0}$  2  $\theta$ , whereas other carbon analogues did not show this prominent peak. This could be due to the fact that the SiO<sub>2</sub> content of the HMS template was not fully removed or that the carbon graphitic content was higher giving the (002) peak of graphite, which is more likely, since this peak is also present in the carbon analogue (Figure 3.2). The broad XRD peaks at lower 2 thetha degrees (below  $20^{\circ}$ ) are due to the amorphous support from the sample holder for the carbon analogue HMS/Pt/LPG 15 and carbon analogue HMS/Pt/LPG 30 sample (see also figure 4.1). Whereas for the carbon analogue HMS/Pt/LPG 60 and carbon analogue HMS/Pt/LPG 90, it is possible that the peaks are due to some degree of mesostructural ordering arising from the mesoporous carbon framework, since longer pyrolysis times were applied during synthesis of these samples than of the former analogue HMS/Pt/LPG 15 samples (i.e. carbon and carbon analogue HMS/Pt/LPG 30). The d spacing for the lower 2 theta angles 2.5<sup>o</sup> 8,06<sup>o</sup>, 8.25<sup>o</sup>, and  $12.45^{\circ}$ , was found to be 35.311 10.96  $\Box$ , 10.7  $\Box$ , and 7.09  $\Box$  respectively. The lowest peak  $2.5^{\circ}$  at 35.31because of instrumental

limitations but is due main structural feature of mesopores of 3nm of the HMS template and the porous carbon (Figures 3.6 a, b)

In Figure 4.3 the XRD crystallinity of CA\_ HMS/LPG\_90/Pt as prepared in section 2.4.4 and Pt supported on mesoporous carbon as prepared in section 2.3 catalysts is shown. This is the only sample of the series where Pt was deposited after CVD of LPG and pore filling by carbon that was characterized by XRD because the other samples prepared in this series were not highly active towards the hydrogen evolution reaction (HER), (see Table 4.3).



Figure 4.3 XRD crystallinity of CA\_HMS/LPG\_90/Pt and Pt supported on mesoporous carbon catalysts.

Both spectra in figure 4.3 show a high crystalline habit for Pt, which is similar to those depicted in figure 4.1 and 4.2. The XRD patterns of the CA\_HMS/LPG\_90/Pt as well as the Pt supported mesoporous carbon catalyst both exhibit several peaks that may be indexed to (111), (200), (220), (311) and (222) diffractions with 2 theta degrees of 39.69<sup>0</sup>, 46.22<sup>0</sup>, 67.68<sup>0</sup>, 81.47<sup>0</sup> and 86.30<sup>0</sup> respectively. All the patterns clearly show the characteristic peaks of a face centered cubic crystalline Pt. Graphitic carbon peaks at 2 theta values at 25.6 and 43.7<sup>0</sup> with miller indices (002) and (101) respectively, were obtained showing that the carbon analogue pore wall retained its graphitic structure after Pt deposition. The main structural difference between these samples and prepared by depositing Pt prior to infilling of pore is the relative intensity of the Pt peaks of the samples MC\_90/Pt and CA\_HMS/LPG/Pt, which were significantly stronger that all other samples. This corresponds with the larger Pt particle size of these samples compared to the samples whereby Pt was deposited

before carbon (Table 4.2) as shown in tables 4.1. XRD particle sizes were determined by the Scherrer's equation (see section 1.7.1) and were recorded in Tables 4.1 and 4.2 as follows:

Catalyst	Deposition times (min)	XRD size (nm)
HMS/LPG_/Pt	15 / 30 / 60 / 90	5.2 / 16 / 9.8 / 8.32
Carbon Analogue HMS/LPG_/Pt	15 / 30 / 60 / 90	2.5 / 4.7 / 2.8 / 3.7
MC_90/Pt	UNIVERSITY	of the APE

Table 4.1 XRD particle size as function of LPG deposition time whereby Pt is deposited after carbon.

Catalyst	Deposition times (min)	XRD size (nm)
HMS/Pt	0	8.37
HMS/ Pt/LPG_/	15 / 30 / 60 / 90	2.3 / 5.2 / 2.7 / 3.2
Carbon Analogue CA_HMS/ Pt/LPG_/	15 / 30 / 60 / 90	2.0 / 4.5 / 2.5 / 3.3

Table 4.2 XRD particle size as function of LPG deposition time whereby Pt is deposited before carbon.

Table 4.2 shows that the particle size for CA\_HMS/LPG\_90/Pt determined from the Scherrer equation is exactly the same as that determined by the TEM particle size (see section 4.2.3).

Table 4.1 and 4.2 also show that most samples had Pt nanoparticles sized between 2-16  $\rm nm$ 

The data in Table 4.3 (section 4.2.2) gives a summary of catalytic activities towards the hydrogen evolution reaction on mesoporous silica supported Pt and mesoporous silica templated Pt/carbon analogue materials and shows that not all catalysts were equally active but that a Pt particle size of 3.7 nm or below as well as some degree of graphization within the carbon framework played a prominent role in catalytic activity towards hydrogen production as evidenced in Figure 4.3. The effect of the particle size upon the activity did not correlate directly as shown in the electrochemical studies detailed in Table 4.3. Moreover, the catalyst (CA\_ HMS/LPG\_90/Pt) with a particle size of 3.7nm was found to be the most active catalyst towards hydrogen production by electrochemical linear sweep Voltammetry (see section 4.2.6). Even though other catalysts had similar Pt particle sizes.

#### 4.2.2 Linear Sweep Voltammetry

Linear sweep Voltammetry experiments described in section 2.6.8 for the hydrogen evolution reaction (HER) at the cathode were conducted for the Pt mesoporous silica composites, HMS/Pt/LPG catalyst series, CA\_HMS/Pt/LPG catalyst series, HMS/LPG/Pt catalyst series, CA\_HMS/LPG/Pt catalyst series, and the mesoporous carbon supported Pt (MC/Pt) catalysts. The linear sweep voltammetry results of the sample are presented in table 4.3 and reveal that the CA\_HMS/LPG\_90/Pt catalyst has the highest activity towards hydrogen production and this activity is in the same activity range towards hydrogen production as that of the commercial Johnson Matthey Pt/C catalyst. Again it must be emphasized that electrocatalytic activity did not correlate with Pt particle size.

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Table 4.3	Summary	of	particle	size	and	catalytic	activities	towards	the	hydrogen
evolution	reaction (H	ER	).							

Material	Deposition times	Current Density (j/mA.cm <sup>-2</sup> )	XRD particle size (nm)	
HMS	0	0.7		
HMS/LPG	15/30/60/90	0.6 / 0.5 / 0.6/ 0.6		
HMS/LPG_Pt	15/30/60/90	7.8 / 6.8 / 8.4 / 7.2	5.2 / 16 / 9.8 / 8.32	
HMS/Pt	0	5.0	8.37	
HMS/Pt/LPG_	15/30/60/90	1.4 / 2.1 / 3.9 / 3.4	2.3 / 5.2 / 2.7 / 3.2	
CA_HMS/LPG_90	90UNIVE WEST	RSIT <sub>5:0</sub> the		
CA_HMS/Pt/LPG_	15/30/60/90	8.6/ 8.9 / 8.2 / 6.0	2.0 / 4.5 / 4.9 / 2.5 / 3.3	
CA_HMS/LPG_/Pt	15/30/60/90	6.9 / 6.4 / 5.8 / 10	2.5 / 4.7 /2.8 / 3.7	
MC_90/Pt	90	6.0	8.2	
JM Pt/C	0	9.70	4.2	

HMS and mesoporous carbon are generally non-catalytic and no specific trend could be observed upon increased carbonization times for materials without Pt. In table 4.3, only a very little change in HER activity is observed upon increased carbonization

#### Chapter 4

periods in the case of HMS/Pt/LPG series or in the HMS/LPG/Pt series, indicating that degree of carbonization did not significantly affect activity.

A significant increase in the electroactivity is observed upon platinisation of the mesoporous template (HMS/Pt) versus HMS from 0.7 to 5.0V/MA.cm<sup>-2</sup> showing that Pt by itself even on a non-conducting support enhances catalytic activity. In general samples that contained SiO<sub>2</sub> (HMS/Pt/LPG) but where the Pt was deposited before LPG were less electroactive than SiO<sub>2</sub> containing samples where Pt was deposited after LPG. HMS/LPG/Pt series was considerably more active than the HMS/Pt/LPG series. This may indicate that it is mainly the Pt particles on the surface of the electrocatalyst that are participating in the reaction, in the SiO<sub>2</sub> containing materials. If the activity of HMS/Pt is compared to the HMS/LPG/Pt series it is possible that the carbonization of the SiO<sub>2</sub> support enhanced catalytic activity. Full removal of the SiO<sub>2</sub> sacrificial framework did not enhance the activity greatly as can be seen by comparing HMS/LPG/Pt series activity to that of CA\_HMS/LPG/Pt, except in the case of CA\_LPG\_90/Pt which was the most active sample prepared.

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In the carbon analogue series the samples where Pt was deposited before carbonization (CA\_HMS/Pt/LPG) were generally more active than those prepared by first carbonizing and then depositing Pt except in the case of CA\_HMS/LPG\_90. CA\_HMS/LPG\_90/Pt and JM Pt/C share generally similar HER activities ( $\pm$  9.7 - 10 mA.cm<sup>-2</sup>) [58]. CA\_HMS/LPG\_90/Pt therefore shows the greatest promise as a new electrocatalyst in the hydrogen evolution reaction.

#### 4.2.3 TEM analysis

On further analysis of the most active electrocatalysts by TEM (Figure 4.4) it was observed that the Pt particles were evenly distributed across the mesoporous carbon network in the case of CA\_HMS/LPG\_90/Pt, and that the particles were generally 3.7nm in size or smaller.



Figure 4.4 TEM of CA\_ HMS/LPG\_90/Pt

Homogeneous distribution could contribute to the activity of this CA\_HMS/LPG\_90/Pt electrocatalyst because of the presence of the numerous Pt active sites available for the hydrogen evolution reaction (HER).



Figure 4.5 TEM of MC\_90/Pt

For the Pt supported on mesoporous carbon catalyst XRD and TEM indicated that no even Pt particle distribution was achieved probably due to agglomeration sintering of the Pt particles hence a larger average Pt size (Figure 4.5) of 8.32nm was confirmed from the TEM results and from XRD.

Further characterization was mainly performed on the most active catalyst, CA\_HMS/LPG\_90/Pt.

#### 4.2.4 Selective Area Electron Diffraction.

In Figure 4.4 the SAED pattern for CA\_HMS/LPG\_90/Pt is shown.



Figure 4.6 SAED of CA\_ HMS/LPG\_90/Pt

The SAED pattern in figure 4.6 for CA\_HMS/LPG\_90/Pt exhibit several diffraction rings [002]; [101] and [200] characteristic of graphitic ordering. The SAED patterns are in accordance with the XRD patterns in figure 4.3. The XRD miller indices of [200] due to Pt is superimposed on [101] due to carbon, hence the SAED diffraction

ring (101) has bright spots due reflections from to Pt (002) particles. The bright spots also are indicative of the highly crystalline nature of the Pt as shown in the XRD spectrum in Figure 4.3.

#### 4.2.5 Pore size distribution and surface area.

In Figure 4.7 the pore size distribution of CA-HMS\_90/Pt is depicted and shows mesoporosity with a pore size centered at 3nm similar to the HMS SiO<sub>2</sub> template.



Figure 4.7 N<sub>2</sub>BET of CA\_HMS/LPG\_90/Pt

In table 4.3 the surface area and pore diameter of CA\_HMS/LPG\_90/Pt is compared with the industry standard commercial JM Pt/C electrocatalyst.

Sample	Surface Area (m <sup>2</sup> /g)	Pore diameter (nm)		
CA_HMS/LPG_90/Pt	155	3		
JM Pt/C	132.09	15.59		

 Table 4.4 BET textural properties

The surface area obtained by N<sub>2</sub>BET of CA\_ HMS/LPG\_90/Pt is lower than the parent HMS SiO<sub>2</sub> template or the carbon analogue; however this catalyst has a nanapore size in the size range 3 nm. Furthermore, the pore structure of the original HMS silica template was retained (see section 3.7, table 3.2). The low surface area may be linked to the high Pt loading (see also table 4.5) that occurred during incipient wetness impregnation, as a result the Pt may have blocked many of the mesopores hence decreasing the surface area of the carbon template support. The surface area for the CA\_ HMS/LPG\_90/Pt is higher than the commercial Johnson Matthey Pt/C catalyst but the pores are smaller. The electrochemical catalytic activity towards hydrogen production for the CA\_ HMS/LPG\_90/Pt is slightly higher than that of the commercial Johnson Matthey Pt/C catalyst. Since catalytic activity is a function of Pt metal porosity, size and morphology, surface area as well as electrconductivity it is most probable that a combination of these variables contributed to the activity of the new electrocatalysts prepared in this study.

#### 4.2.6 Thermal analysis.

In Figure 4.8 the TGA and DSC of CA\_HMS/LPG\_90/Pt is shown. A weight change of 52.9% was observed at 500 <sup>o</sup>C which was accompanied by a sharp exothermal peak at the same temperature.



Figure 4.8 TGA and DSC of CA\_HMS/LPG\_90/Pt. The color of the axis refer to spectra.

The presence of the graphitic carbon network within the pore walls of the carbon support of sample CA\_HMS/LPG\_90/Pt is further confirmed by thermogravimetric analysis when the sample was slowly heated in air. The weight loss curves at 480-500 ° C can be assigned to the combustion of the graphitised carbon in the carbon

analogue sample. The sharp heat flow curve at 500 °C further supports this suggestion and the mass remaining after the exotherm at 500  $^{0}$ C is an indication of high Pt loading as is further confirmed by EDS (section 4.2.7, table 4.5).

#### 4.2.7 Elemental composition.

The approximate elemental composition of the sample CA\_HMS/LPG\_90/Pt was determined by EDS and results averaged from three spot analysis are presented in Figure 4.9 and Table 4.5.



Figure 4.9 EDS of CA\_HMS/LPG\_90/Pt

Table 4.5 Elemental composition of CA	_HMS/LPG_90/Pt and MC_90/Pt
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Sample	Wt C %	Wt Pt %		
CA_HMS/LPG_90/Pt	21.40	78.60		
MC_90/Pt	84.74	15.24		

Since such a low sample size is analyzed in this technique, it is difficult to quantitavely determine the exact mass % of Pt. However, it is clear that a far lower Pt loading achieved MC 90/Pt than the was on on carbon analogue CA HMS/LPG 90/Pt and this would explain the lower HER activity observed for MC 90/Pt. In future it would be useful to try and increase the Pt loading for this sample. In table 4.5, the high weight percent of Pt is an indication that the Pt is so small as a result it is invisible by TEM.

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For the introduction of Pt nanoparticles upon the HMS silica support as well as on the mesoporous carbon material three goals were taken into consideration:

- 1) Retaining the mesoporous physical structure of the HMS and mesoporous carbon.
- 2) Achieving high Pt dispersion

4.3 CONCLUSIONS:

3) And attaining a significantly high Pt weight percent loading.

In this chapter, it is demonstrated that a catalyst (CA\_HMS/LPG\_90/Pt) with HER activity equivalent to that of the commercial Johnson Matthey catalyst (JM Pt/C) can be fabricated by a synthetic route by using HMS template and pore filling with

pyrolytic LPG gas as the carbon precursor, followed by Pt impregnation of the composite HMS/LPG and reduction of Pt after which the SiO<sub>2</sub> template is removed.

A new mesoporous carbon which ultimately contains some graphitic character is successfully utilized as a Pt support for the synthesis of a catalyst CA\_HMS/LPG\_90/Pt. XRD and TGA results confirmed the presence of graphitic carbon and Pt nano particulates when all three procedures were implemented.

Since no clear activity trend was observed for varying orders of LPG and Pt deposition from LSV results, it has been shown that activity is a complex function of particle size, conductivity and mesoporosity. However, a Pt particle size of 3.7 and lower as well as some degree of graphitization of the carbon support plays a prominent role in catalytic activity towards hydrogen production for the catalyst.

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The surface area for the CA\_ HMS/LPG\_90/Pt is higher than the commercial Johnson Matthey Pt/C catalyst but the pores are smaller. The electrochemical catalytic activity towards hydrogen production in the HER reaction for the CA\_ HMS/LPG\_90/Pt is slightly higher than that of the commercial Johnson Matthey Pt/C catalyst. Since catalytic activity is a function of surface area as well as electroconductivity it is most probable that a combination of these variables contributed to the activity of the new electrocatalysts prepared in this study.

#### **CHAPTER 5**

#### SUMMARY AND CONCLUSION

The synthesis and characterization of porous graphitic carbon materials via a pyrolysis method using HMS as a solid template as well as Pt catalysts supported on these mesoporous carbon materials is developed in this study.

A mesoporous carbon analogue was prepared by use of HMS as sacrificial template. The use of LPG as a carbon precursor for preparation of graphitic mesoporous carbon was successfully applied to prepare the carbon analogue resulted in a mesoporous material that exhibited both well-ordered mesoporosity and high levels of graphitic character. The unique architecture of the HMS silica sacrificial template, which explains its large textural porosity, was achieved in the parent SiO<sub>2</sub> material and reproduced in the templated carbon.

The samples were characterized by XRD, SAED nitrogen sorption (BET), TEM, Raman, EDS, TGA, DSC and linear sweep voltammetry. The XRD spectra as well as the TEM micrographs indicate a high degree of mesostructural ordering in the HMS silica prepared for use as a sacrificial template. The nitrogen sorption data confirmed that the HMS silica possessed good mesostructural ordering and was therefore suitable for use as a solid template for mesoporous carbon synthesis.

The carbon analogue prepared by use of the HMS as sacrificial template was found to be highly porous and graphitic, with a large surface area exceeding that of the parent HMS silica sacrificial template and with mesopores in the exact size range of the  $SiO_2$  template. The results demostrated that a carbon negative mesoporous replicate or analogue of the  $SiO_2$  based HMS was successfully achieved. The formation of graphitic structures takes place during the chemical vapor deposition step of HMS at high temperatures. The dissolution of the SiO<sub>2</sub> framework of the mesoporous SiO<sub>2</sub> used as template by use of NaOH for etching purposes created the 3 nm pores in the carbon that were observed in the N<sub>2</sub>BET. The regular mesostructure of the new carbon material is evidenced by the appearance of the new peaks at 7.39 and 12.64  $^{0}$  2  $\Theta$  in XRD spectra that indicated that there is a regular mesostructured carbon lattice framework at 11.6 and 6.8  $\Box$ . d spaced distances. This is a novel finding and has not been previously reported.

The results in this study showed that a novel mesoporous carbon was obtained as an inverse replica of HMS silica, has a large pore diameter (3 nm), large BET surface area 938 m<sup>2</sup>g  $^{\Box 1}$ , narrow pore size distribution (PSD) in the mesopore range. The results obtained show that mesoporous carbon with graphitic structures can be synthesized and moreover a Pt based electrocatalyst with the same hydrogen cathodic activity for hydrogen production as the commercial Johnson Matthey Pt/C catalyst can be synthesized.

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This new graphitic mesoporous material and the parent HMS silica mesoporous material was subsequently utilized as a support for the synthesis of Pt electrocatalysts. For the introduction of Pt nanoparticles upon the HMS silica support as well as on the mesoporous carbon material three goals were taken into consideration:

- 4) Retaining the mesoporous physical structure of the HMS and mesoporous carbon.
- 5) Achieving high Pt dispersion
- 6) And attaining a significantly high Pt weight percent loading.

Preparation of the Pt based electrocatalysts involved techniques based on wet impregnation and chemical reduction of the metal. Three different procedures were used to deposited nanoparticulate Pt clusters on mesoporous carbon materials and these are as follows (1) preparation of Pt/carbon analogues whereby Pt is deposited

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before carbon, (2) preparation of Pt/carbon analogues whereby Pt is deposited after carbon but before etching of the silica template, and (3) preparation of Pt/carbon analogues whereby Pt is deposited after carbon and after etching of the silica template XRD and TGA results confirmed the presence of graphitic carbon and Pt nano particulates The mesoporous structure was maintained, high Pt dispersion was achieved and a high weight percent of Pt loading was demonstrated. Moreover a Pt based electrocatalyst with the same hydrogen cathodic activity for hydrogen production as the commercial Johnson Matthey Pt/C catalyst can be synthesized.

Since no clear activity trend was observed for varying orders of LPG and Pt deposition from linear sweep voltammetry results, it has been shown that activity is a complex function of particle size, conductivity and mesoporosity. However, a Pt particle size of about 3.7nm as well as some degree of graphitization of the carbon framework plays a prominent role in catalytic activity towards hydrogen production for the catalyst.

It was demonstrated in this study that a catalyst (CA\_HMS/LPG\_90/Pt) with HER activity equivalent to that of the commercial Johnson Matthey catalyst (JM Pt/C) can be fabricated by a cheap synthetic route by making use of pyrolytic LPG gas as the carbon precursor. The surface area for the CA\_ HMS/LPG\_90/Pt which was the most active catalyst prepared in this study is higher than the commercial Johnson Matthey Pt/C catalyst but the pores are smaller. The electrochemical catalytic activity towards hydrogen production for the CA\_ HMS/LPG\_90/Pt is slightly higher than that of the commercial Johnson Matthey Pt/C catalyst. Since catalytic activity is a function of surface area as well as electrconductivity it is most probable that a combination of these variables contributed to the activity of the new electrocatalysts prepared in this study.

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