

The Impact of Diffusion on Solid Oxide Fuel Cell Anode Performance

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ABSTRACT

The Impact of Diffusion on Solid Oxide Fuel Cell Anode Performance

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The impact of microstructure on gas phase diffusion in porous ceramic materials is not well understood. This information has particular relevance to the performance of Solid Oxide Fuel Cell designs in which the anode is supported on a porous ceramic, or is itself the support for the cell. This is especially so when the cell operates under conditions of high fuel utilisation and/or high current density. Under such conditions, the diffusion of reactants towards the fuel cell anode, and products away through the support, may well limit performance.

Data on the porosity, pore size characteristics and microstructure for two porous ceramic support materials are reported. Both experimental and theoretical work has been carried out on binary diffusion, using gases relevant to SOFC operation (H_2 , H_2O , CO , CO_2 , CH_4 , and N_2). After the study of diffusion process was conducted, the impact of gas phase diffusion within the porous ceramics on the performance of the SOFC was evaluated, particularly under conditions of high current density. Losses arising from the diffusion process were quantified by employing a one-dimensional model to describe the gas transport within the porous support and anode.

**To my parents
and to Marianthi**

With the drawing of this Love and the voice of this Calling

*We shall not cease from exploration
And the end of all our exploring*

T. S. Eliot "Little Gidding"

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Contents

<i>List of Figures</i>	<i>ix</i>
<i>List of Tables</i>	<i>xiii</i>
<i>Nomenclature</i>	<i>xv</i>
CHAPTER 1: INTRODUCTION	1
1.1 Introduction	1
1.2 What is a Fuel Cell	1
1.3 Different Types of Fuel Cells	3
1.3.1 Phosphoric Acid Fuel Cells (PAFC)	3
1.3.2 Proton Exchange Membrane Fuel Cells (PEMFC)	5
1.3.3 Molten Carbonate Fuel Cells (MCFC)	6
1.3.4 Solid Oxide Fuel Cells (SOFC)	8
1.3.5 Alkaline fuel cells (AFC)	9
1.3.6 Direct Methanol Fuel Cells (DMFC)	11
1.3.7 Conclusion	12
1.4 Objectives	13
1.5 Thesis Content	14
1.6 References	16
CHAPTER 2: THEORETICAL BACKGROUND AND LITERATURE REVIEW	17
2.1 Ceramic Solid Oxide Fuel Cells	17
2.1.1 Operating Principle and Thermodynamics of SOFCs	17
2.2 Solid Oxide Fuel Cell-Stack Designs	19
2.2.1 Tubular Design	20
2.2.2 Flat-Plate Design	21
2.3 Components of a Solid Oxide Fuel Cell	22
2.3.1 The Cathode	23
2.3.1.1 Type of Material	23

2.3.1.2	<i>Cathode Reaction</i>	23
2.3.2	The Anode	24
2.3.2.1	<i>Type of Material</i>	24
2.3.2.2	<i>Anode Reaction</i>	25
2.3.3	The Electrolyte	26
2.3.4	The Interconnect	27
2.4	Cell Design and Development	28
2.4.1	Electrode-supported Solid Oxide Fuel Cells-Design and Fabrication	28
2.4.2	Main Developers of Electrode-supported Designs of Solid Oxide Fuel Cell	30
2.4.3	Intermediate Temperature Solid Oxide Fuel Cells	33
2.4.4	The Issue of Concentration Polarisation	35
2.5	Diffusion of Gases in Porous media	37
2.5.1	An Initial Approach to Diffusion Process	37
2.5.2	Analysis of Gaseous Diffusion: systems with or without walls	38
2.5.2.1	<i>Systems without Walls</i>	38
2.5.2.2	<i>Systems with Walls</i>	39
2.5.3	Mechanisms of Flux	39
2.5.3.1	<i>Viscous Flux</i>	40
2.5.3.2	<i>Knudsen (free-molecule) Flux</i>	41
2.5.3.3	<i>Nonequimolar Flux</i>	41
2.5.3.4	<i>Surface Flux</i>	42
2.5.3.5	<i>Transition Regime</i>	42
2.5.4	Gas Diffusion in porous media-A more focused analysis	43
2.5.4.1	<i>Basic Considerations</i>	43
2.6	Methods of Measuring Diffusion Coefficients	44
2.6.1	Steady State Methods	45
2.6.1.1	<i>Wicke-Kallenbach Technique</i>	46
2.6.2	Unsteady State Methods	47
2.6.2.1	<i>Pulse Response Technique on Single Pellet Cell</i>	48

	Contents
2.6.2.2 <i>Chromatographic Pulse Response Technique</i>	49
2.6.3 Conclusion	50
2.7 References	52
 CHAPTER 3: EXPERIMENTAL PROCEDURE	 61
3.1 Introduction	61
3.2 Apparatus and Procedure	61
3.3 Parameters of the Experimental Design	65
3.3.1 Effect of the Pressure Drop	66
3.3.2 Time to Establish Steady State Diffusion	69
3.3.3 The Effect of the Concentration Boundary Layer	71
3.3.3.1 <i>Flow Regime</i>	73
3.3.3.2 <i>Estimation of the Convection</i>	
<i>Mass Transfer Coefficient</i>	74
3.3.3.3 <i>Boundary Layer Approximations</i>	78
3.4 Materials and Investigation Methods	79
3.4.1 Scanning Electron Microscopy	79
3.4.2 Mercury Porosimetry	79
3.4.3 Archimedes Measurements	81
3.5 Gas Chromatography	81
3.5.1 Gas Chromatograph Components	82
3.5.1.1 <i>GC Columns</i>	83
3.5.1.2 <i>GC Detectors: FID</i>	83
3.5.1.3 <i>GC Detectors: TCD</i>	84
3.5.2 Preparation of the GC	86
3.5.3 Creating the GC Methods	88
3.5.3.1 <i>H₂-N₂ GC Method</i>	88
3.5.3.2 <i>CH₄-N₂ GC Method</i>	92
3.5.3.3 <i>CO-N₂ GC Method</i>	94
3.5.3.4 <i>CO₂-N₂ GC Method</i>	94
3.5.4 Calibration of the GC	97
3.6 References	98

CHAPTER 4: INTERPRETATION OF BINARY DIFFUSION MEASUREMENTS	100
4.1 Introduction	100
4.2 Interpretation of Diffusion Measurements	101
4.2.1 General Equation of Diffusive Fluxes	101
4.2.2 Equimass and Equimolar Counterdiffusion	106
4.2.2.1 <i>Equimass Counterdiffusion</i>	107
4.2.2.2 <i>Equimolar Counterdiffusion</i>	108
4.3 Conclusions	111
4.4 References	111
 CHAPTER 5: RESULTS AND DISCUSSION	 113
5.1 Introduction	113
5.2 Microscopy	115
5.3 Mercury Porosimetry	119
5.3.1 Pore Volume Distribution and Penetration Curve of the CSZ Substrate	119
5.3.2 Surface Area Distribution of the CSZ Substrate	125
5.3.3 Pore Volume Distribution of the MMA Substrate	127
5.3.4 Surface Area Distribution of the MMA Substrate	129
5.3.5 Physical Properties of Porous Substrates	130
5.4 Water and Ethanol Uptake Tests	133
5.5 Image Analysis	134
5.6 Diffusion Measurements: Results	136
5.6.1 Precision of the Measurement Method	136
5.6.2 Diffusion Coefficients of Binary Mixtures of N ₂ with H ₂ , CH ₄ , CO and CO ₂ through CSZ and MMA Support Samples	137
5.6.2.1 <i>Interpretation of the Diffusion Results Employing the Kinetic Theory of Gases</i>	139
5.6.2.2 <i>Effect of Composition on the Effective Diffusion Coefficient</i>	142

5.6.2.3	<i>Effect of Flow rate on the Effective Diffusion Coefficient</i>	150
5.6.3	Diffusion Coefficients of the Binary Mixtures in CSZ1 and MMA1 Samples-Effect of the Support Material on the Effective Diffusion Coefficient	152
5.6.4	Diffusion Coefficients of CH ₄ -CO and CO ₂ -CO Gas Pairs through CSZ1 and MMA1 Support Samples	157
5.6.5	Prediction of Binary Diffusion Coefficients of Gases: Prediction from Theory and Empirical Correlations	161
5.6.5.1	<i>Estimation of Tortuosity</i>	163
5.6.5.2	<i>Comparison of Estimation Methods for Binary Gas Diffusion Coefficients</i>	167
5.7	Conclusions	169
5.8	References	170
 CHAPTER 6: ANODE SUPPORT PERFORMANCE MODELLING		174
6.1	Introduction	174
6.2	Models of Porous Media for Gas Diffusion	174
6.2.1	Parallel Path Pore Models	175
6.2.2	The Packed Spheres Model	177
6.3	The Dusty Gas Model	178
6.3.1	Modes of Gas Transport	179
6.3.1.1	<i>Knudsen Flow</i>	179
6.3.1.2	<i>Viscous or Convective Flow</i>	181
6.3.1.3	<i>Ordinary or Continuum Diffusion</i>	182
6.3.1.4	<i>Combined Transport Equations for Binary Mixture</i>	185
6.3.1.5	<i>Approximations for the Combined Transport Equations</i>	187
6.4	Model Development for the Concentration Polarisation	189
6.4.1	Steady State Diffusion Model	191
6.4.2	Unsteady State Diffusion Model	194
6.5	Results and Discussion	195
6.5.1	Results of the Steady State Model	195

	Contents
6.5.2 Results of the Unsteady State Model	200
6.6 Conclusions	205
6.7 References	207
CHAPTER 7: CONCLUSIONS AND FUTURE WORK	209
7.1 Conclusions	209
7.2 Future Work	210

List of Figures

Figure 1.1: Principle operation of a fuel	2
Figure 1.2: PAFC schematic	4
Figure 1.3: Polymer Exchange Membrane Fuel Cell	5
Figure 1.4: Molten Carbonate Fuel Cell	7
Figure 1.5: Solid Oxide Fuel Cell	8
Figure 1.6: Alkaline fuel Cell	10
Figure 2.1: Schematic representation of a SOFC operating on hydrogen and air	18
Figure 2.2: Tubular SOFC design	20
Figure 2.3: Flat-plate SOFC design	22
Figure 2.4: Wicke-Kallenbach diffusion cell	46
Figure 2.5: Transient operation of the diffusion cell	49
Figure 3.1: Schematic diagram of the apparatus	62
Figure 3.2: Cross section of the diffusion cell	63
Figure 3.3: Schematic of the porous sample	68
Figure 3.4: Diffusion in a semiinfinite medium	70
Figure 3.5: Concentration boundary layer development on a flat surface	72
Figure 3.6: Dimensions of the duct	73
Figure 3.7: Effect of a large Biot number on steady state concentration distribution	77
Figure 3.8: Schematic diagram of the Q94 gas chromatograph	83
Figure 3.9: Maximum filament current as a linear function of the TCD temperature	86
Figure 4.1: The diffusion problem of the two chambers connected with a tube	110

Figure 5.1: SEM micrograph of a polished surface of the CSZ substrate	116
Figure 5.2: SEM image of the CSZ unpolished surface	116
Figure 5.3: SEM micrograph of the unpolished fracture edge of the CSZ Substrate	116
Figure 5.4: SEM micrograph of a polished surface of the MMA sample	117
Figure 5.5: SEM micrograph of an unpolished surface of the MMA sample	117
Figure 5.6: SEM micrograph of the cross section of an unpolished fracture surface of the MMA sample	118
Figure 5.7: Pore volume distribution of the CSZ sample	120
Figure 5.8: Porogram of the intruded and the extruded volume of mercury against pressure for the CSZ substrate	121
Figure 5.9: A schematic representation of an “ink-bottle” pore	123
Figure 5.10: Three-dimensional pore-throat network	124
Figure 5.11: Surface area distribution for the CSZ sample	125
Figure 5.12: Volume pore size distribution of the MMA sample	128
Figure 5.13: Surface area distribution for the MMA sample	129
Figure 5.14: Micrograph of the cross section of the polished fracture surface of CSZ substrate	134
Figure 5.15: SEM image of the cross section of the polished fracture surface of the MMA sample	134
Figure 5.16: Effective diffusivities of H_2 in N_2 as a function of mole fraction of H_2	142
Figure 5.17: Concentration dependence of effective diffusion coefficient of CH_4 in N_2	147
Figure 5.18: Binary diffusivities of CO_2 in N_2 as a function of mole fraction of CO_2	147
Figure 5.19: Binary diffusivities of CO in N_2 as a function of mole fraction of CO	149
Figure 5.20: Effective diffusion coefficient of H_2 as a function of the flow rate	151

Figure 5.21: Comparison of H_2 effective diffusivities obtained using the initial samples CSZ and MMA with those obtained in CSZ1 and MMA1	153
Figure 5.22: Concentration dependence of diffusion coefficient of CH_4 in N_2 and comparison of the values in CSZ1 and MMA1 with those in CSZ and MMA samples	155
Figure 5.23: Binary diffusivities of CO in N_2 as a function of mole fraction of CO and comparison of the values for the two different support samples	156
Figure 5.24: Binary diffusivities of CO_2 in N_2 as a function of mole fraction of CO_2 and comparison of the values for the two different support samples	156
Figure 5.25: Effective diffusivities of CH_4 in CO as a function of methane mole fraction	159
Figure 5.26: Effective diffusivities of CO_2 in CO as a function of CO_2 mole fraction	159
Figure 6.1: Transport processes occurring in an anode-supported SOFC	190
Figure 6.2: Partial pressure variation across the CSZ and MMA supports	196
Figure 6.3: Anode concentration polarisation for the two supports of 2 mm thickness	197
Figure 6.4: Anode concentration polarisation for the two supports of 1 mm thickness	198
Figure 6.5: Anode concentration polarisation for the two supports of 0.5 mm thickness	198
Figure 6.6: H_2 and H_2O partial pressure profiles across the CSZ and MMA supports	199
Figure 6.7: Anode concentration polarisation for the two supports of 2 mm thickness	200
Figure 6.8: Hydrogen partial pressure profiles across the CSZ support, with increasing time	201
Figure 6.9: Hydrogen partial pressure profiles across the MMA support, with increasing time	202
Figure 6.10: Hydrogen partial pressures profiles in the CSZ support for a range of effective diffusivities	203

Figure 6.11: Hydrogen partial pressure profiles in the MMA support for a range of effective diffusivities	203
Figure 6.12: Water vapour partial pressure profiles across the CSZ support as time progresses	204
Figure 6.13: Water vapour partial pressure profiles across the MMA support, with increasing time	205

List of Tables

Table 3.1: Thermal conductivities of typical gases	89
Table 3.2: The set of the parameters of the method file for the mixture of H_2-N_2	91
Table 3.3: The set of the parameters of the method file for the mixture of CH_4-N_2	93
Table 3.4: The set of the parameters of the method file for the mixture of CO_2-N_2	95
Table 5.1: Structural properties of the porous substrates taken from the intrusion statistics	130
Table 5.2: Structural properties of the porous substrates calculated using data generated by mercury porosimetry	132
Table 5.3: Porosity values as obtained by water and ethanol uptake tests	133
Table 5.4: Porosities estimated by image analysis method	135
Table 5.5: Effective diffusion coefficient of H_2 in N_2 through CSZ	138
Table 5.6: Effective diffusion coefficient of H_2 in N_2 through MMA	138
Table 5.7: Values of binary diffusion coefficients of CH_4 , CO and CO_2 in N_2 through the CSZ support	138
Table 5.8: Values of binary diffusion coefficients for CH_4 , CO and CO_2 in N_2 , in MMA support	139
Table 5.9: Values of the function f_D	145
Table 5.10: Binary diffusion coefficients of H_2 in N_2 at different flow rates, through CSZ and MMA substrates	150
Table 5.11: Effective diffusion coefficient of H_2 in N_2 through CSZ1 sample	152
Table 5.12: The binary diffusion coefficients of CH_4 , CO and CO_2 in N_2 through the CSZ1 support	154
Table 5.13: Values of binary diffusion coefficients of CH_4 , CO and CO_2 in N_2 , in MMA1 support	154

Table 5.14: The effective diffusion coefficients of CH ₄ in CO through the CSZ1 and MMA1 supports	158
Table 5.15: The effective diffusion coefficient of CO ₂ in CO through the CSZ1 and MMA1 support	158
Table 5.16: Estimated tortuosity for a range of gas pairs	165
Table 5.17: The bulk density and the average tortuosity for the CSZ and MMA support	166
Table 5.18: Comparison of the results obtained from two estimation methods with the experimental data taken from this work	167
Table 5.19: Molecular diameters of the gases and the calculated values of the mean free path, at $T=25\text{ }^{\circ}\text{C}$, $P=1\text{ atm}$	168
Table 6.1: Effective diffusivities values for the binary mixture of H ₂ -H ₂ O along with parameters used for their calculation	192

Nomenclature

Symbol	Physical Meaning	Units
c_i	Concentration of species i	mol m^{-3}
D_{AB}	Molecular diffusion coefficient of species A and B	$\text{m}^2 \text{s}^{-1}$
D_{AB}^{eff}	Effective diffusion coefficient of species A and B	$\text{m}^2 \text{s}^{-1}$
D_h	Hydraulic diameter	m
D_{KA}	Knudsen diffusion coefficient	$\text{m}^2 \text{s}^{-1}$
F	Faraday constant (charge on 1 mole of electrons = $N_A e$), 96485	C mol^{-1}
G	Mass flux	$\text{kg m}^{-2} \text{s}$
i	Current density	A m^{-2}
J	Molar flux	$\text{kmol m}^{-2} \text{s}^{-1}$
k	Permeability	m^2
k_B	Boltzmann constant, 1.381×10^{-23}	J K^{-1}
L	Thickness of porous support	m
M	Molar mass	g mol^{-1}
N_A	Avogadro's constant, 6.02205×10^{23}	mol^{-1}
p	Partial pressure of gas	Nm^{-2}
P	Absolute Pressure	Nm^{-2}
$\bar{r}$	Mean pore radius	m
R	Gas constant, 8.31441	$\text{J mol}^{-1} \text{K}^{-1}$
t	Time	s
T	Absolute temperature	K
V	Mean velocity	ms^{-1}
V_{cell}	Cell voltage	V
γ	Surface tension	erg cm^{-2}
ϵ	Porosity	-
η	Overpotential	V
μ	Dynamic viscosity	$\text{N m}^{-2} \text{s}$
ρ	Density	Kg m^{-3}
σ_{AB}	Collision diameter	$\text{\AA}$
τ	Tortuosity	-

Chapter 1

Introduction to Fuel Cells

1.1 Introduction

As environmental concerns receive increasing attention, the need for developing new technologies that address the conflicting issues of energy production and protection of environment becomes evident. The environmental quality and the high efficiency of fuels cells make them a potential alternative energy source for both stationary and transportation applications. Although fuel cells have been around for many years, it is only recently that technological advances have made them competitive with traditional power production methods.

While the fuel cell industry grows and further research advances are made, the challenge for the fuel cell industry will be to commercialise fuel cell systems by improving their performance and reducing cost. In this chapter a general introduction to fuel cells is given.

1.2 What is a Fuel Cell

Fuel cells are related to batteries. Both convert chemical energy directly into electricity. The difference is that batteries store a fixed amount of energy, while fuel cells operate and produce power as long as they are supplied with fuel. A fuel cell is therefore an energy conversion device that produces electricity and heat directly from a gaseous fuel through a constant temperature process, which involves electrochemical reactions. It is a highly efficient and environmentally friendly way to convert the chemical energy of the fuel into electrical energy without burning the fuel [1].

A fuel cell consists of two electrodes sandwiched around an electrolyte. Oxygen passes over one electrode (cathode) and hydrogen over the other (anode), generating electricity, water and heat.

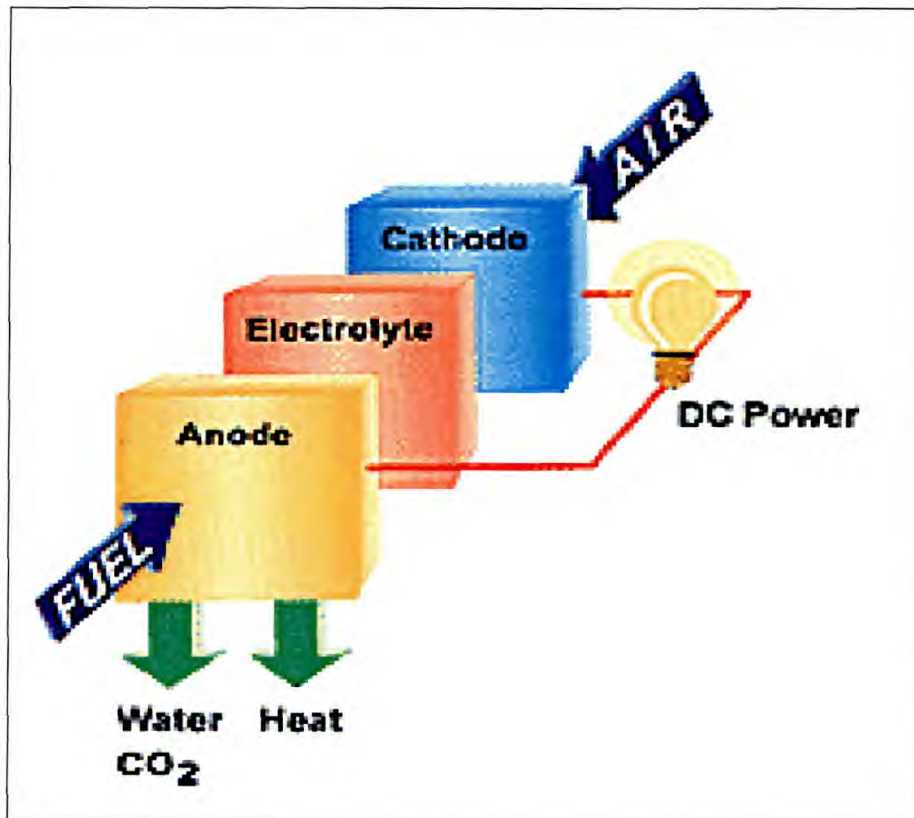


Figure 1.1: Principle operation of a fuel cell

Fuel cells use hydrogen, in its pure form or as obtained from hydrocarbons through reforming, as fuel and air as oxidant and produce water. This fact makes fuel cell applications very attractive from an emissions perspective, offering an alternative to the internal combustion engine.

In order for the fuel cell to operate it is necessary to use catalysts and special electrolyte materials resulting in a substantial increase in the manufacturing cost. The catalyst most commonly used is platinum and the electrolytes must be tolerant to acidic pH and be good conductors of protons. Furthermore, for fuel cell devices to be commercially viable it is necessary to match the performance of conventional technologies, preferably with the same cost. Therefore a lot of effort is being made to improve the performance of fuel cells, to find other, cheaper materials that can be used as catalysts or to find a more effective way to utilise the existing catalysts to get better performance with less material.

A fuel cell system, which includes a fuel reformer, can utilise the hydrogen from any hydrocarbon fuel, from natural gas to methanol, and even gasoline. Since the fuel

cell relies on chemistry and not combustion, emissions from this type of system would still be much smaller than emissions from the cleanest fuel combustion processes.

Attempts to develop fuel cells as power sources have been made over many years. Initially they were developed mainly for space and defence application. However, the recent drive for more efficient and less polluting power generation technologies resulted in substantial resources being directed into fuel cell developments. Fuel cells – because of their high efficiencies, low noise and pollutant output, and modular construction to suit load and excellent load following capability – promise to revolutionise the power generation industry [2].

At present several types of fuel cells are approaching the consumer market. The visions for the future use of fuel cells encompass the wide spectrum from power supply for small electronic equipment [3] with only few watts up to power stations in the megawatt range for centralised power production [4].

1.3 Different Types of Fuel Cells

Fuel cells are classified primarily by the kind of electrolyte they employ. This determines the kind of chemical reactions that take place in the cell, the kind of catalysts required, the temperature range in which the cell operates, the fuel required, and other factors. These characteristics, in turn, affect the applications for which these cells are most suitable. There are several types of fuel cells currently under development, each with its own advantages, limitations, and potential applications. A few of the most promising types are described in the following sections

1.3.1 Phosphoric Acid Fuel Cells (PAFC)

These fuel cells use liquid phosphoric acid as the electrolyte. The electrodes are made of carbon paper coated with a finely-dispersed platinum catalyst. The catalyst strips electrons off the hydrogen-rich fuel at the anode. Positively charged hydrogen ions then migrate through the electrolyte from the anode to the cathode. Electrons generated at the anode travel through an external circuit, providing direct current electric power, and return to the cathode. There the electrons, hydrogen ions and oxygen form water, which is discharged from the cell.

The reactions that take place in the cell and a schematic diagram of PAFC are shown below:

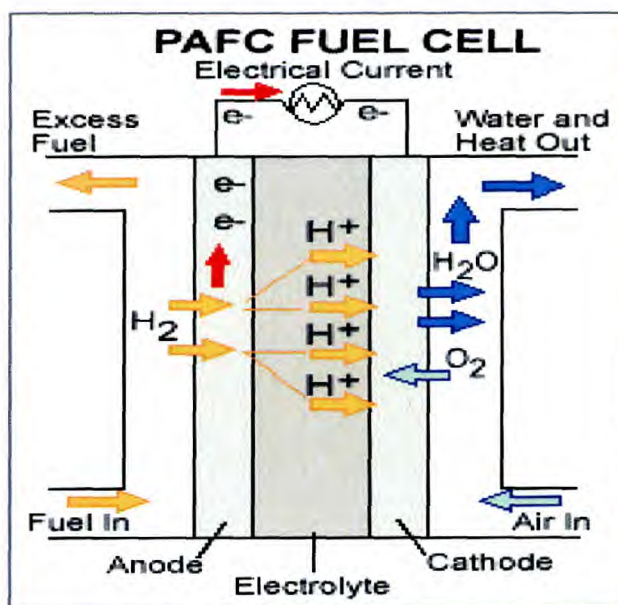
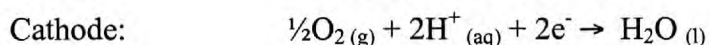


Figure 1.2: PAFC schematic.

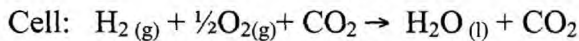
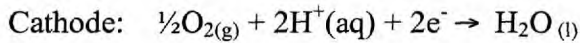
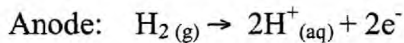
The phosphoric acid fuel cell (PAFC) is considered the "first generation" of modern fuel cells. It is one of the most mature cell types and the first to be used commercially. This type of fuel cell is typically used for stationary power generation, but some PAFCs have been used to power large vehicles such as city buses.

PAFCs are more tolerant of impurities in the reformat than PEM cells, which are easily "poisoned" by carbon monoxide. PAFCs can tolerate a CO concentration of about 1.5%, which broadens the choice of fuels they can use. If gasoline is used, the sulphur must be removed. They are 85% efficient when used for the co-generation of electricity and heat, but less efficient at generating electricity alone (37 to 42%). This is only slightly more efficient than combustion-based power plants, which typically operate at 33 to 35% efficiency. PAFCs are also less powerful than other fuel cells, given the same weight and volume. As a result, these fuel cells are typically large

and heavy. PAFCs are also expensive. Like PEM fuel cells, PAFCs require an expensive platinum catalyst, which raises the cost of the fuel cell. A typical phosphoric acid fuel cell costs between \$4,000 and \$4,500 per kilowatt.

1.3.2 Proton Exchange Membrane Fuel Cells (PEMFC)

The reactions in a PEMC are the following:



These cells operate at relatively low temperatures (about 80°C), have high power density, can vary their output quickly to meet shifts in power demand, and are suited for applications such as automobiles where quick start-up is required.

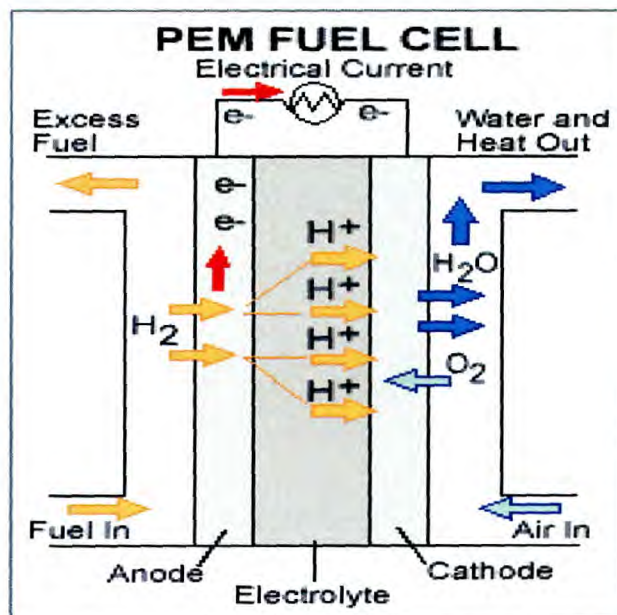


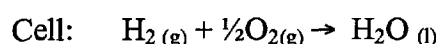
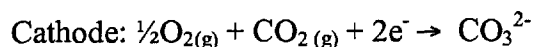
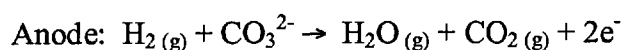
Figure 1.3: Polymer Exchange Membrane Fuel Cell

The proton exchange membrane is a thin plastic sheet that allows hydrogen ions to pass through it. The membrane is coated on both sides with highly dispersed metal alloy particles (mainly Pt and Pt/Ru) that are active catalysts. The electrolyte used is a solid organic polymer based on a polyperfluorosulfonic acid monomer. The solid electrolyte is an advantage because it reduces corrosion and management problems. Hydrogen is fed to the anode side of the fuel cell where the catalyst splits the

hydrogen molecules and releases electrons and hydrogen ions (protons). The electrons travel in the form of an electric current that can be utilised before it returns to the cathode side of the fuel cell where oxygen has been fed. At the same time, the protons diffuse through the membrane (electrolyte) to the cathode, where the hydrogen atom is recombined and reacted with oxygen to produce water, thus completing the overall process. This type of fuel cell is, however, sensitive to fuel impurities such as carbon monoxide (CO).

1.3.3 Molten Carbonate Fuel Cells (MCFC)

Molten carbonate fuel cells (MCFCs) are currently being developed for natural gas and coal-based power plants for electrical utility, industrial, and military applications. MCFCs are high-temperature fuel cells that use an electrolyte composed of a molten carbonate salt mixture suspended in a porous, chemically inert ceramic lithium aluminium oxide (LiAlO_2) matrix. Since they operate at extremely high temperatures of 650°C and above, non-precious metals can be used as catalysts at the anode and cathode, reducing costs. The electrochemical reactions in a MCFC are:



Improved efficiency is another reason MCFCs offer significant cost reductions over phosphoric acid fuel cells (PAFCs). Molten carbonate fuel cells can reach efficiencies approaching 60%, considerably higher than the 37-42% efficiencies of a phosphoric acid fuel cell plant. When the waste heat is captured and used, overall fuel efficiencies can be as high as 85%.

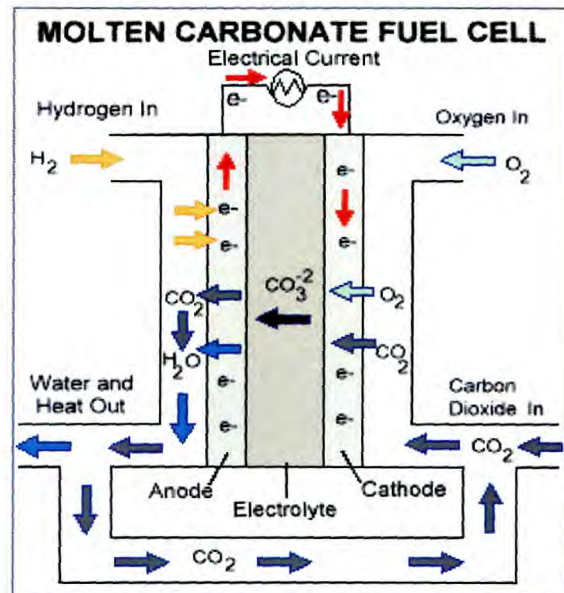


Figure 1.4: Molten Carbonate Fuel Cell

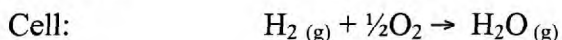
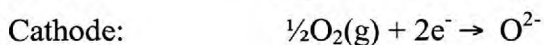
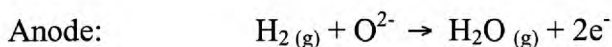
Unlike alkaline, phosphoric acid, and polymer electrolyte membrane fuel cells, MCFCs do not require an external reformer to convert more energy-dense fuels to hydrogen. Due to the high temperatures at which they operate, these fuels are converted to hydrogen within the fuel cell itself by a process called internal reforming, which also reduces cost.

Molten carbonate fuel cells are not prone to carbon monoxide or carbon dioxide "poisoning" – they can even use carbon oxides as fuel – making them more attractive for fuelling with gases made from coal. Although they are more resistant to impurities than other fuel cell types, scientists are looking for ways to make MCFCs resistant enough to impurities from coal, such as sulphur and particulates.

The primary disadvantage of current MCFC technology is durability. The high temperatures at which these cells operate and the corrosive electrolyte used accelerate component breakdown and corrosion, decreasing cell life. Currently corrosion-resistant materials are explored for components as well as fuel cell designs that increase cell life without decreasing performance.

1.3.4 Solid Oxide Fuel Cells (SOFC)

The reactions taking place in a solid oxide fuel cell are,



Solid oxide fuel cells (SOFCs) use a non-porous ceramic as the electrolyte. Since the electrolyte is a solid, the cells do not have to be constructed in the plate-like configuration typical of other fuel cell types. SOFCs are expected to be around 50-60% efficient at converting fuel to electricity. In applications designed to capture and utilize the system's waste heat (co-generation), overall fuel use efficiencies could top 80-85%. The basic components and a schematic diagram of a SOFC are shown in Figure 1.5.

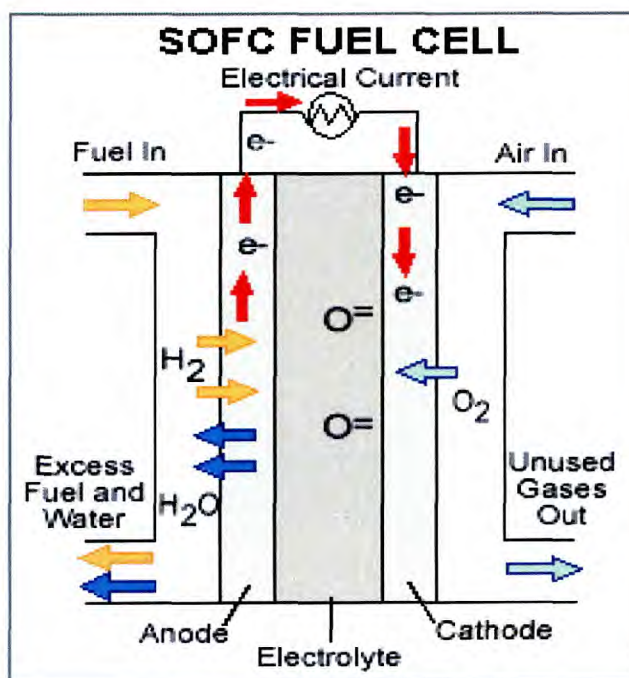


Figure 1.5: Solid Oxide Fuel Cell

Solid oxide fuel cells operate at very high temperatures, around 1,000°C. High temperature operation removes the need for precious-metal catalyst, therefore reducing cost. It also allows SOFCs to reform fuels internally, which enables the use

of a variety of fuels and reduces the cost associated with adding a reformer to the system.

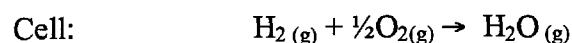
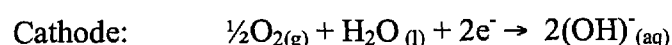
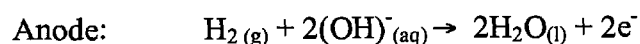
SOFCs are also the most sulphur-resistant fuel cell type; they can tolerate several orders of magnitude more sulphur than other cell types. In addition, they are not poisoned by carbon monoxide (CO), which can even be used as fuel. This allows SOFCs to use gases made from coal.

High-temperature operation has disadvantages. It results in a slow start-up and requires significant thermal shielding to retain heat and protect personnel, which may be acceptable for utility applications but not for transportation and small portable applications. The high operating temperatures also place stringent durability requirements on materials. The development of low-cost materials with high durability at cell operating temperatures is the key technical challenge facing this technology.

Lower-temperature SOFCs are presently being developed for operation at or below 700°C. This type of SOFCs has fewer durability problems and cost less. Lower-temperature SOFCs produce less electrical power, however, and stack materials that will function in this lower temperature range are under progress.

1.3.5 Alkaline fuel cells (AFC)

The reactions in an AFC are:



Alkaline fuel cells (AFCs) were one of the first fuel cell technologies developed, and they were the first type widely used in the U.S. space program to produce electrical energy and water onboard spacecraft. These fuel cells use a solution of potassium hydroxide in water as the electrolyte and can use a variety of non-precious metals as a catalyst at the anode and cathode. High-temperature AFCs operate at temperatures

between 100°C and 250°C. (However, more-recent AFC designs operate at lower temperatures of roughly 23°C to 70°C.)

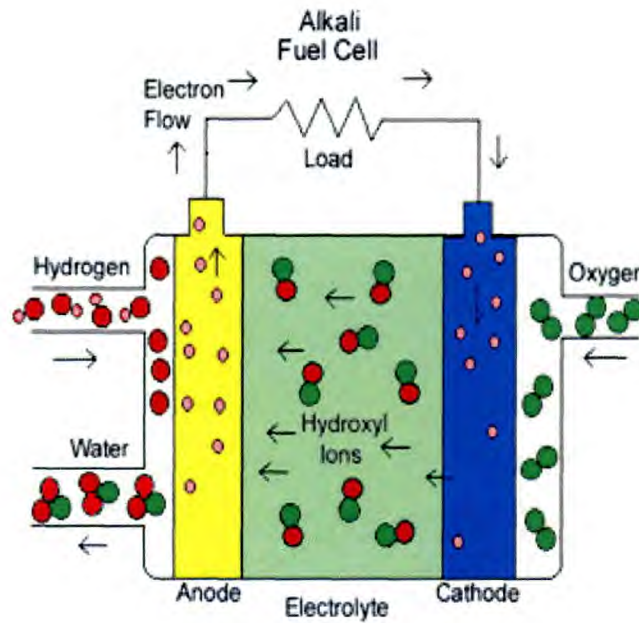


Figure 1.6: Alkaline fuel Cell

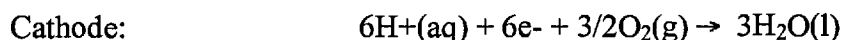
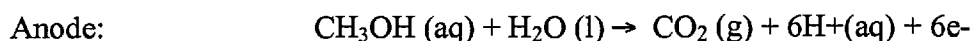
AFCs are high-performance fuel cells due to the rate at which chemical reactions take place in the cell. They are also very efficient, reaching efficiencies of 60% in space applications.

The disadvantage of this fuel cell type is that it is easily poisoned by carbon dioxide (CO_2). In fact, even the small amount of CO_2 in the air can affect the cell's operation, making it necessary to purify both the hydrogen and oxygen used in the cell. This purification process is costly. Susceptibility to poisoning also affects the cell's lifetime, further adding to cost.

Cost is less of a factor for remote locations such as space or under the sea. However, to effectively compete in most mainstream commercial markets, these fuel cells will have to become more cost effective. AFC stacks have been shown to maintain sufficiently stable operation for more than 8,000 operating hours. To be economically viable in large-scale utility applications, these fuel cells need to reach operating times exceeding 40,000 hours. This is possibly the most significant obstacle in commercialising this fuel cell technology.

1.3.6 Direct Methanol Fuel Cells (DMFC)

Most fuel cells are powered by hydrogen, which can be fed to the fuel cell system directly or can be generated within the fuel cell system by reforming hydrogen-rich fuels such as methanol, ethanol, and hydrocarbon fuels. Direct methanol fuel cells (DMFCs), however, are powered by pure methanol, which is mixed with steam and fed directly to the fuel cell anode, eliminating the need for a fuel reformer. The electrochemical reactions for a DMFC are given here:



Efficiencies of about 40% are expected with this type of fuel cell, which would typically operate at a temperature between 50-100°C. This is a relatively low range, making this fuel cell attractive for tiny to mid-sized applications, to power cellular phones and laptops. A major problem, however, is fuel crossing over from the anode to the cathode without producing electricity. Many companies claim to have solved this, and are working primarily on DMFC prototypes for use by the military in powering electronic equipment in the field.

1.3.7 Conclusion

A summary of the most known fuel cells is given below:

	FUEL CELL TYPE				
	<u>AFC</u>	<u>PEMFC</u>	<u>PAFC</u>	<u>MCFC</u>	<u>SOFC</u>
Electrolyte	Concentrated KOH	Nafion	Concentrated H_3PO_4	$\text{LiCO}_3/\text{K}_2\text{CO}_3$	Yttria stabilised zirconia
Operating Temperature	80°C	80°C	200°C	650°C	650-1000 °C
Charge carrier	OH^-	H_3O^+	H_3O^+	CO_3^{2-}	O^{2-}
Electrolyte state	Mobile or immobilised liquid	Solid	Immobilised liquid	Im/seed liquid	Solid
Electrode	Doped carbon electrode, Pt, Ag	Doped electrodes Pt	Doped electrodes Pt	Nickel electrodes	Nickel and solid oxide ceramic electrodes
Catalyst	Platinum	Platinum	Platinum	Nickel	Perovskites
Cogeneration heat	None	None	Low quality	High	High
Fuel Cell Efficiency %HHV	~30%	40-50%	40-50%	50-60%	45-55%, 70% with cogeneration
Fuel and oxidant	Pure H_2 Air or pure O_2	Pure H_2 Air or pure O_2	H_2 , CH_4 , CH_3OH	H_2 , CH_4 , Air	H_2 , CH_4 , CH_3OH Air
Anode reaction	$\text{H}_2 + 2(\text{OH}^-) \rightarrow 2\text{H}_2\text{O} + 2\text{e}^-$	$\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$	$\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$	$\text{H}_2 + \text{CO}_3^{2-} \rightarrow \text{H}_2\text{O} + \text{CO}_2 + 2\text{e}^-$	$\text{H}_2 + \text{O}^{2-} \rightarrow \text{H}_2\text{O} + 2\text{e}^-$
Cathode reaction	$\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2(\text{OH}^-)$	$\frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$	$\frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$	$\frac{1}{2}\text{O}_2 + 2\text{e}^- + \text{CO}_2 \rightarrow \text{CO}_3^{2-}$	$\frac{1}{2}\text{O}_2 + 2\text{e}^- \rightarrow \text{O}^{2-}$

1.4 Objectives

The main objective of this project is to examine the effect of diffusion on supported solid oxide fuel cell performance and in particular on the performance of the support-anode compartment.

The impact of the microstructure of a porous ceramic on gas phase diffusion within the material is not well understood. This project aims to contribute to a better understanding of this interaction, working with porous ceramic materials relevant to the construction of supported solid oxide fuel cell, namely the porous support and the porous electrode materials.

Both experimental and theoretical work will be carried out on binary diffusion, using gases relevant to SOFC operation (H_2 , H_2O , CO , CO_2 , CH_4 , and N_2). Once the diffusion process has been studied, the impact of gas phase diffusion within the porous ceramics on the performance of the SOFC will be evaluated, particularly under conditions of high current density. Losses arising from the diffusion process will be quantified and new, improved microstructures may be recommended.

The measurement of binary gas diffusion coefficients in porous ceramic materials constitutes the main part of this work. Such materials were supplied by Rolls- Royce and have been used by the Rolls-Royce Strategic Research Centre as the porous substrates for the construction and development of a novel stack configuration, the 'multi-cell membrane assembly' (multi-cell MEA). The novelty of this work is demonstrated in its main objectives:

1. the fabrication of the appropriate test rig that will enable accurate, steady state measurements of gas phase diffusion coefficients;
2. the method of interpreting the obtained diffusion data;
3. the study of the microstructure of the porous ceramics. This is a significant issue since the structure of the porous medium is considered to play an important role in the gas transport. For this study a number of techniques will be used to characterise the structure and determine the physical properties of the materials;

4. the review of existing theoretical models of diffusion in porous media and the use of appropriate one;
5. based on the experimental data, a cell anode performance model will be derived which will allow for diffusional losses.

1.5 Thesis Content

This thesis presents a detailed investigation of the binary gaseous diffusion through porous materials, which are used for the fabrication of supported anode solid oxide fuel cells.

In this chapter, a brief introduction has provided the scene associated with the field of fuel cells.

Chapter 2 first presents a theoretical background, describing the principles of operation, the main components and the development of solid oxide fuel cells. It also discusses the problems arising from electrode-supported cell designs. In this way it provides the proper link for introducing the issue of gas transport and diffusion in porous structures. In this part the diffusion process in porous media is carefully analysed. A literature survey reviews the existing techniques for measuring binary gas diffusivities and it also aims to retrieve information that is useful in setting up the experimental procedure for carrying out the diffusion measurements.

In Chapter 3 the experimental procedure is presented. Important parameters of the experimental design, which are rarely taken into consideration in such measurements, are investigated. The gas chromatography instrumentation specifically configured for this type of measurements is explained and the gas chromatograph analytical methods are documented.

The theory and the transport equations used for interpreting the diffusion data and calculating the diffusion coefficients, are presented in Chapter 4. A new method for analysing data obtained from binary diffusion measurements, not used before, is introduced and explained.

Chapter 5 is divided into two parts. In the first part the results of the microstructural investigation are shown and structural properties of the porous ceramic substrates are tabulated. The second part constitutes the matrix of the diffusion results and includes also the discussion and the interpretation of the effective diffusion coefficients measurements.

Chapter 6 contains the anode-support performance modelling. Since the dusty gas model approach constitutes the basis of the performance modelling, a thorough review of the model is presented and the transport equations are derived. The equations for ordinary diffusion are used to model the transport of gas species through the porous supports. The species concentration variations are calculated and the losses resulting from the diffusion process are quantified by estimating the concentration polarisation.

Chapter 7 concludes this study and gives recommendations for future work.

1.6 References

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Chapter 2

Theoretical Background and Literature Review

2.1 Ceramic Solid Oxide Fuel Cells

A ceramic solid oxide fuel cell consists of two porous electrodes: an anode and a cathode separated by an electrolyte. Fuel is fed to the anode, undergoes an oxidation reaction and releases electrons to the external circuit. Oxidant is fed to the cathode, accepts electrons from the external circuit and it is reduced. The electron flow, from the anode to the cathode, produces direct-current electricity (and heat) [1]. The electrolyte conducts ions between the two electrodes.

This process is not subjected to the limitations of the Carnot cycle of a heat engine, as the solid oxide fuel cell converts the chemical energy of a fuel directly into electrical energy without going through the intermediate combustion step. Thus the usual losses involved in the conversion of fuel to heat, to mechanical energy and then to electrical energy are avoided. As a result, not only total efficiencies but also the electrical efficiency can be high. Also the pollutant output from fuel cells is magnitudes lower than that from conventional technologies.

Apart from the general advantages of fuel cells such as environmentally friendly operation, solid oxide fuel cells are fuel flexible and can operate on multiple fuels, including carbon-based fuels. This results in potentially higher overall fuel to electric conversion efficiency of around 60% for single cycles and up to 85% efficiency for total systems [2-4]. Due to their high exhaust gas temperature they have the ability to provide high-grade heat that can be used for generating power with a steam turbine (in a cogeneration cycle) to air-conditioning using absorption-type chillers [7].

2.1.1 Operating Principle and Thermodynamics of SOFCs

The working principle of a solid oxide fuel cell (SOFC) is shown in Figure 2.1. Oxygen from air is reduced at the cathode to O^{2-} anions, which are transported through the gas tight ceramic membrane (the solid oxide electrolyte), to the anode where they react with the fuel molecules (H_2 , CO or CH_4) to give the combustion products (H_2O and CO_2) and release the electrons. The electrons are then transported

back to the cathode through the external circuit, thereby delivering electrical power [8,9].

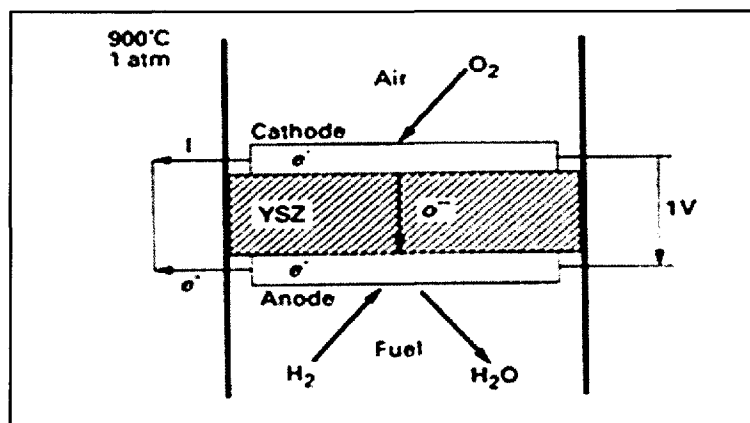


Figure 2.1: Schematic representation of a SOFC operating on hydrogen and air [8].

Since the solid electrolyte conducts the O^{2-} ions only at high temperature, the cell is operated at 650-1000°C. The required high temperature drives the rapid reaction kinetics and allows reforming of hydrocarbon fuel in the cells, for example methane can be readily reformed to hydrogen and carbon monoxide. The latter does not poison the anode reaction at these elevated temperatures.

The electrochemical reactions occur in the electrodes within a very small distance of the electrolyte surface. This zone is referred to as the functional layer. The electrode is primarily a current collector structure, which must be porous to allow gas access to the functional layer. The electrolyte has to be gas impermeable to avoid direct mixing and combustion of the gases.

The fuel cells are generally characterised by a reversible voltage (E_r) also called open-circuit voltage (E_{ocv}), which is the maximum voltage that a SOFC can produce under given conditions of temperature and gas composition. This voltage is related to thermodynamic potentials, which are given by the Nernst equation at equilibrium [1]. At the standard state the reversible voltage of the cell is given by the free energy (ΔG) of the fuel oxidation reaction, according to the equation,

$$E_r = -\Delta G/nF \quad [1,10] \quad (2.1)$$

n = number of electrons transferred,

F = Faraday constant

This voltage is typically 1.1-1.2 V for a single cell operating on hydrogen and air, and if it is not loaded. Under load conditions the voltage of a single cell decreases to about 0.6-0.9 volts [2].

Moreover, the fuel to electric efficiency of a fuel cell is defined as the product of the electric and fuel efficiencies (ϕ_F, ϕ_E) . The remaining chemical energy is available as high quality heat, allowing the operation of combined cycles with gas and/or steam turbines, thus further boosting fuel/electric efficiency [2].

The fuel efficiency (ϕ_F) is defined by the ratio of ΔG to ΔH of the fuel oxidation reaction. Internal losses (resistive, ohmic (iR), within the electrolyte and overpotential (η) at both electrode/electrolyte interfaces) lead to a further decline in cell voltage and hence the efficiency. Thus the voltage, E , available from the operating cell is given by the equation,

$$E = E_r - iR - \eta_a(i) - \eta_c(i) \quad (2.2)$$

and the ratio E/E_r is defined as the electric efficiency (ϕ_E) . In the above equation iR represents the internal resistance or ohmic loss (i is the current density and R the internal resistance of the cell) and η_a, η_c are the anode and cathode overpotentials at current density i respectively. Both η_a and η_c are the voltage drops required to drive the electrode reactions at finite rates. They arise due to activation and mass transport phenomena in both the anode and cathode electrodes. These voltage drops vary with cell current density (and temperature) in a non-linear manner. The result is that both fuel cell output and efficiency fall as load current increases. Fuel cells are more efficient at part load than full load, a potential advantage in low-load applications [10].

2.2 Solid Oxide Fuel Cell-Stack Designs

A SOFC single cell, under typical operating conditions, produces less than 1 V; values of power density in the range of 0.4-1.2 W/cm^2 per cell, at 0.7 V, at temperature of 750°C have been recently reported [28]. Therefore the cells must be connected in electrical series/parallel in a stack to achieve workable power outputs and higher voltages that are necessary for most practical purposes.

At present, two main SOFC stack configurations are under development:

- tubular design with two main types, the sealless and the segmented-cell-in-series type
- flat plate design

2.2.1 Tubular Design

The tubular designs belong to the class of supported concepts. In the Westinghouse design one tube represents a single cell, Figure 2.2. This design is by far the most advanced SOFC concept (100 *kW* units). Stacks are constructed by bundling a number of tubes together and connecting them with Ni felt pads. Support tubes of Ca-stabilised zirconia (or in the latest design air electrode material, itself) sealed at one end form structural parts on to which active components of the fuel cell are deposited.

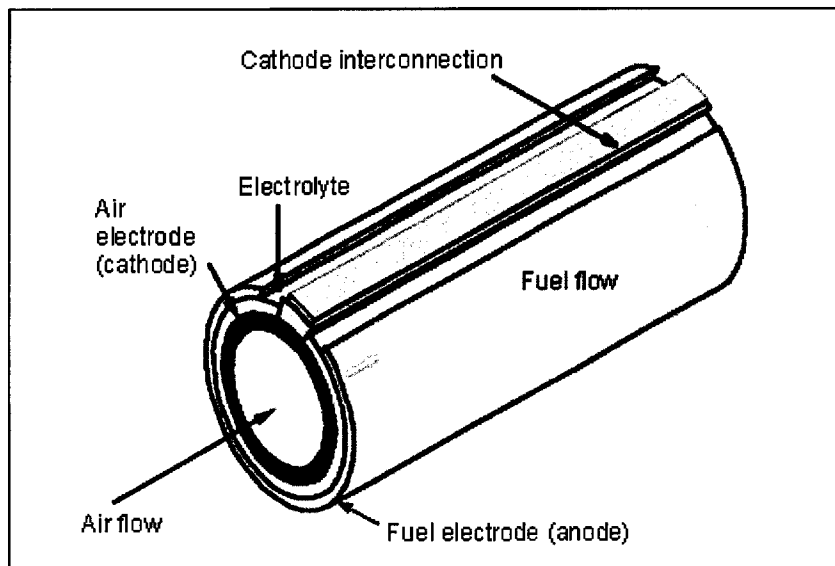


Figure 2.2: Tubular SOFC design [1].

In this design, the cathode electrode plays the role of the support. A dense electrolyte layer covers the cathode except in a strip along the active cell length. This strip of exposed cathode is covered with a gastight interconnect layer and the anode covers the electrolyte surface but not the interconnect region. Typical dimensions of the tubes are: 15-20 *mm* diameter, 1.5 *mm* wall thickness, 0.66-1.00 *m* in length (2 *m* long tubes are planned for MW systems).

The design does not require a seal, and the oxidant is injected through a co-axial ceramic injector tube near to the closed end of the cell and flows through the space between the cell and the injector tube to the open end of the cell. Fuel flows concurrent to the oxidant on the outside of the tube and the exhaust gas containing some unused fuel after passing through a diffuser plate combines with the partially oxygen depleted-air where it combusts [2].

The major advantages of the tubular concepts are: no high temperature seals between cathode and anode compartments are required, and staged injection of fuel and oxidant is possible. In addition, the tubular design has the advantage of providing a more robust ceramic structure for the cell, since each thin cell is formed on a thick support.

On the other hand, the design has a relatively long current path through the cell. During operation, the current travels through the plane of the interconnect and electrolyte and in the plane of the anode and cathode. The current paths are short in the interconnect and electrolyte but long in the anode and cathode. The long current path in the electrodes results in higher internal cell resistances and greater resistive losses. In addition the support tube adds weight and volume to the cell thus reducing the power density [1].

2.2.2 Flat-Plate Design

Currently, the most widely investigated type of SOFC stack is the planar or flat plate design, which is viewed to have the potential of delivering the cheapest SOFC unit. The design also offers simple geometry and multiple fabrication options.

The flat-plate design consists of cell components configured as thin, planar plates. Common plate shapes are rectangular (square) or circular. Typical flat-plate SOFCs use the single cell and interconnect as structural components. The electrolyte layer was often used as the thickest component of the single cell, thus acting as the cell structural support. However, in modern designs, such as the intermediate temperature solid oxide fuel cells (IT-SOFCs), it is one of the electrodes that acts as the structural support of the cell. The interconnect serves as a bipolar gas separator, contacting the anode and cathode of adjoining cells. The interconnect frequently has

ribs on both sides to form gas channels, Figure 2.3. External and internal co-flow, counter flow and cross-flow manifolding options are possible [1].

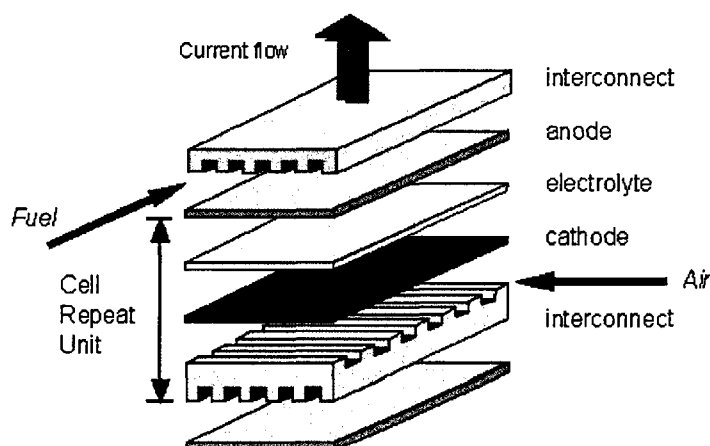


Figure 2.3: Flat-plate SOFC design [2,11].

The planar concept offers power densities of around 1 MW m^{-3} , cheaper fabrication methods (conventional ceramic green processing techniques) and simplified quality control as each component is fabricated separately and can be inspected before stack construction. The major challenges are the development of suitable seals and interconnect materials.

2.3 Components of a Solid Oxide Fuel Cell

The high operating temperatures of SOFC are mainly dictated by the slow oxygen transfer rate through the electrolyte at lower temperatures. This combined with the multi-component nature of the fuel cell and the required life expectancy of several years restricts the choice of materials for cell and manifold components. Each material used not only has to function optimally in its own right but has to be viewed in conjunction with the other cell components. Common requirements of the cell components are [2]:

- a) chemical stability in the fuel cell environment ($p(\text{O}_2) > 20 \text{ kPa}$ on the cathode side and $< 10^{-17}$ on the anode side) and compatibility with other cell components;
- b) phase and microstructure stability;

- c) minimum thermal expansion mismatch between various cell components (laminated structure) to avoid cracking during fabrication and operation;
- d) for structural components, reasonable strength and toughness at the cell operating temperature, as well as reasonable thermal shock resistance;
- e) low vapour pressure to avoid loss of the material;
- f) must allow cost competitive component fabrication.

2.3.1 The Cathode

The cathode provides the reaction sites for the electrochemical reduction of oxygen. It has to be compatible with the other components not only at the operating temperature, but also at the temperature at which the ceramic is manufactured. Also, it must be porous enough to allow gas transport to the sites of reactions and have sufficient catalytic activity for the reduction of oxygen.

2.3.1.1 Type of Material

Noble metals such as platinum are unsuitable for practical reasons because of the cost. At present the most common cathode material used in SOFC systems is doped lanthanum manganite LaMnO_3 (LSM). The latter has a high electrical conductivity in oxidising atmospheres, compatibility with Y_2O_3 – stabilised ZrO_2 (YSZ) electrolyte and acceptable thermal expansion match with other cell components.

A number of other materials have been considered, such as strontium doped lanthanum cobaltite (LSCo), a material with much higher electronic conductivity than LSM [13]. However it presents the disadvantages (compared to LSM) of a high thermal expansion coefficient and lower stability due to interface reactions with the electrolyte.

2.3.1.2 Cathode Reaction

The cathode reaction in a SOFC involves the reduction of oxygen,



where (c) and (e) are the states at the cathode and the electrolyte respectively.

At the anode the reverse reaction occurs,



where (a) is the state at the anode. The overall cell reaction is therefore,

$$O_2(c) = O_2(a) \quad (2.5)$$

The reaction is made up of a series of bulk and surface processes. One or several of these processes can be rate-determining steps. In order to understand the cathode polarisation, identifying the various reaction steps and determining the rate-controlling step are necessary. Some possible controlling steps may be: gas diffusion external to the electrode or within the pores of the electrode; adsorption and dissociation of oxygen on the electrode surface or the electrolyte; diffusion of adsorbed oxygen on the electrode or into the electrode/electrolyte interface; diffusion of dissolved oxygen in the electrode or electrolyte; diffusion of electron holes in the electrolyte; and charge transfer across the electrode/electrolyte phase boundary [12].

As it can be seen, definite reaction mechanisms have not yet been established due to simultaneous parallel reactions and therefore discussion upon the proposed kinetic schemes has been the subject of many relevant studies.

2.3.2 The Anode

The main function for the SOFC anode is to provide reaction sites for the electrochemical oxidation of the fuel. Thus, the anode material has to be stable in the fuel-reducing environment and have sufficient electronic conductivity and catalytic activity for the fuel gas reaction at the operating conditions. The key requirements remain the same as those discussed above for the cathode. Compatibility, thermal expansion match, porosity, strength, fabricability and low cost are again important.

2.3.2.1 Type of Material

A number of ceramic and metallic materials can potentially meet these requirements. Due to the reducing conditions of the fuel gas, metals can be used as SOFC anode materials. At the high operating temperature of the SOFC, suitable metals are restricted mainly to nickel, cobalt and noble metals. Electronic conducting ceramics and mixed conducting oxides can also be appropriate. The conventional material for the anode is nickel metal, dispersed on a Y_2O_3 -stabilised ZrO_2 (YSZ) support.

Nickel is preferred mostly because of its low cost (when compared with other metals such as cobalt, platinum and palladium) and YSZ is incorporated as a support to

maintain the porous structure of nickel over long periods at high temperatures, and to provide other desired properties for the anode. The role of the YSZ in cermets is multiple: to act as a supporting matrix for nickel-metal particles, ensure their uniform dispersion and prevent coarsening of the metallic particles at the fuel cell operating temperature. The YSZ also provides an anode thermal expansion coefficient acceptably close to those of the other cell parts. The YSZ support is considered as “inactive” although the support may play an important role in determining the catalytic activity of the anode.

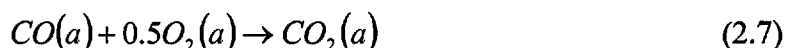
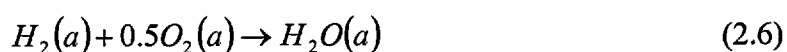
In most cases the anode is fabricated as a mixture of nickel oxide with zirconia. The nickel oxide is then reduced *in situ* to nickel metal when exposed to the fuel in the SOFC. The reduction of NiO to nickel increases the porosity of the anode. The porosity increase is caused by volume change as a result of oxygen loss due to the conversion of the oxide to its metallic form. As the characteristics and the stability of the anode microstructure are considered to significantly affect electrode performance, the control of electrode morphology is one of the most important factors in the preparation of nickel/YSZ anodes. A number of fabrication techniques along with the conventional powder mixing processes have been devised to prepare the anode structure and obtain the desired morphological stability [1,14].

2.3.2.2 Anode Reaction

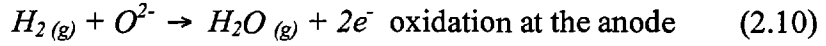
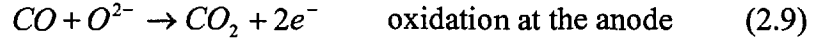
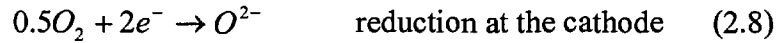
At the anode the main reaction is the electrochemical oxidation of hydrogen and carbon monoxide. Sulphur impurities, which are present in the fuel, can react at the anode. It is also where the reforming of hydrocarbons can occur.

When the carbon monoxide and the hydrogen are fed at the anode the oxidation of hydrogen produces water, and the carbon monoxide could react with water to give carbon dioxide and hydrogen, or be chemically oxidised to CO₂. The formation of water would occur at the interface of nickel metal and YSZ.

The overall equations at the anodes are,



So considering the oxygen reduction at the cathode, the carbon monoxide and hydrogen react at the anode with oxygen ions giving,



It seems that hydrogen oxidation, Equation (2.6), is influenced by two important factors: gas composition and electrode microstructure. For example, the presence of H_2O and CO in the gas, and the morphology of the nickel and YSZ, has been shown to have a dominant effect on the polarisation behaviour of the anode. Other factors such as electrode thickness may also influence the hydrogen oxidation reaction [14].

2.3.3 The Electrolyte

The main function of the SOFC electrolyte is to conduct ions between the anode and the cathode. The electrolyte carries the ions produced at one electrode to the other electrode to balance the charge from the electron flow and complete the electrical circuit in the fuel cell. The electrolyte also separates the fuel from the oxidant in the fuel cell. Thus the electrolyte material must be stable in both the reducing and oxidising environments, impermeable to the reacting gases and sufficiently conductive (ionically) at the operating conditions. Additionally, chemical and thermal compatibility with the other components at operating and fabrication temperatures are necessary [1].

The most common electrolyte in a SOFC is stabilised ZrO_2 . This material possesses an adequate level of oxygen-ion conductivity and exhibits desirable stability in both oxidising and reducing atmospheres.

Zirconia on its own does not have the appropriate properties for fuel cells and for that reason it has to be stabilised by metal oxides such as CaO , Y_2O_3 , MgO , Sc_2O_3 and some rare-earth oxides. They have a high solubility in ZrO_2 and can form cubic fluorite solid solutions, which are stable at high temperature and with a high conductivity. Among the various stabilised zirconias, the Y_2O_3 -stabilised material is the most common.

Doping, namely the addition of the oxides, stabilises the cubic fluorite phase of ZrO_2 (which results from the stabilisation with oxides) from room temperature to its melting point. It also increases its oxygen vacancy concentration, which in turn gives rise to high oxygen-ion mobility [2]. The dopants are divalent or trivalent oxides.

Doped CeO_2 is a possible candidate to replace zirconia as a SOFC electrolyte. CeO_2 doped with a divalent or trivalent oxide develops high oxygen-ion conductivity at elevated temperatures. However, the ionic conductivity regime is rather narrow and in reducing environments, ceria based systems lose oxygen and develop electronic conductivity (e.g. $p(\text{O}_2)$ limit at 800°C of about 10^{-8} - 10^{-10} kPa) [2]. The best oxygen ion conducting electrolyte is doped bismuth oxide with about an order of magnitude higher conductivity at 700 - 800°C than zirconia, but with the disadvantages of easy reduction, high reactivity and very low strength and toughness.

2.3.4 The Interconnect

The interconnect connects the anode of a fuel cell to the cathode of another fuel cell in electrical series. The interconnect also separates the fuel from the oxidant in adjoining cells of a stack. Thus the interconnect must be stable in oxidising and reducing conditions, impermeable to gases and sufficiently conductive to support electron flow at the operating conditions.

Its electronic conductivity needs to be high, whereas the ionic conductivity must be negligible. Since the SOFC operates at high temperatures, the interconnect must be chemically and thermally compatible with the other cell components at operating and fabrication temperatures. Matching of the thermal expansion coefficient with those of the other components is needed to avoid cracking and the separation of the laminated sheets on the electrolyte. No connected porosity is needed to avoid gas leakage. Additionally, low volatility, mechanical strength, good adherence to the electrode materials and moderate cost are required [12].

The most common ceramic interconnect material is LaCrO_3 but high-temperature alloys can also be used. The chemical composition of LaCrO_3 is modified by non-

stoichiometry and by introducing appropriate dopants such as alkaline earth cations (Mg^{2+} , Sr^{2+}) and cations such as Al^{3+} and Mn^{3+} . In this way it obtains the appropriate properties.

In the tubular design, interconnections are made with $\text{La}_{1-x}(\text{Sr}, \text{Mg})_x\text{CrO}_3$ and cells are connected with nickel felt pads. In the planar stacks, three interconnect options—ceramic, metallic (high temperature alloys) and cermet—are possible. Metals have the advantages of high electric and thermal conductivities, which minimise temperature gradients in stacks and ease fabrication, but require corrosion resistant layers, and the thermal expansion mismatch is generally large.

Other materials that are used to a smaller extent are CoCr_2O_4 or YCrO_3 . Early SOFCs used doped CoCr_2O_4 as the interconnect material [15].

2.4 Cell Design and Development

In addition to the main classification of solid oxide fuel cells into tubular and planar designs, they can be also grouped depending on which cell component is to perform the supporting function in the cell. Thus they can be divided further into (i) self supporting or electrolyte-supported designs, where the electrolyte, usually with thickness of a $110\text{--}250\ \mu\text{m}$, forms the structural element and (ii) supported or electrode-supported designs, where the electrolyte is deposited as a thin layer ($<50\ \mu\text{m}$) on porous support structures and the electrode (anode or cathode) plays the role of the supporting component of the cell [16].

2.4.1 Electrode-supported Solid Oxide Fuel Cells-Design and Fabrication

These aforementioned cell designs are currently under development. In electrolyte-supported cells, the thickness of the electrolyte, typically yttria-stabilised zirconia (YSZ), is larger than $150\ \mu\text{m}$, with thin electrodes screen-printed on it. Such cells are favourable only at high operating temperatures $\sim 1000^\circ\text{C}$ due to the high ohmic resistance of electrolyte materials at lower temperatures.

However, in order to reduce materials cost and improve component durability the operating temperature should be lowered from 1000°C to around 750°C . Since the

chemical and conduction processes in solid oxide fuel cells are thermally activated, a reduction in operating temperature suggests a strong increase in ionic resistance of the electrolyte, and thus losses within the cell. To achieve low electrolyte resistance, either new electrolytes have to be developed, with much higher ionic conductivity than YSZ even at the reduced temperatures or the thickness of this component must be decreased.

In recent years research and development have focused on transforming the electrolyte from the supporting membrane (150 μm) to a film of few μm [17,18]. To reduce the thickness of the electrolyte, an increase in the thickness of one of the electrodes is required to support the thin electrolyte film. In cathode-supported cells, a 30–40 μm layer of YSZ is deposited on a porous Sr-doped LaMnO_3 (LSM) cathode of $\sim 2\text{ mm}$ thickness [19]. Similarly, in anode-supported cells, a YSZ layer of 5–20 μm thickness is deposited on a Ni + YSZ anode of 0.5–1 mm thickness [16,20].

For the fabrication of the anode porous substrates and the thin electrolytes used for the manufacturing of anode-supported solid oxide fuel cells, a number of ceramic processing techniques have been developed.

The anode substrates are predominantly produced by tape casting. Anode cermets fabricated by this method, have exhibited a largely uniform porous structure with high values of porosity and high gas permeability [21], whereas planar anode-supported cells, whose anode and electrolyte components were tape cast and cofired, have shown high flexibility and strength with power densities greater than 1 W cm^{-2} at 810°C [22]. Whereas tape casting is the method usually employed for the fabrication of anode substrates (and calendaring as well), screen printing is a widely used deposition technique for thin anode, electrolyte and cathode layers.

Besides the above standard processing techniques, alternative methods like warm pressing, tape calendaring and wet powder spraying for the support are under investigation [23]. In general, pressing processes are very rarely applied for fabrication of substrates. The reason for that may be that the substrates in such processing routes cannot easily be fabricated thinner than 1 or 1.5 mm and most of the developers aim at substrates with thickness of around 0.5 mm . In a few cases wet

powder spraying [24] and slip casting [25] are applied for layer deposition. The advantages of slip casting as a forming method is that complex geometries can be shaped and good material (slurries) homogeneity can be generally achieved.

All these wet ceramic shaping techniques, which are based on shaping a paste or suspension of ceramic components and organic additives, are attractive due to low cost and the potential for effective scale-up. In addition, there are advanced gas phase and plasma techniques for depositing thin films on porous substrates such as the physical vapour deposition (PVD), electrochemical and chemical vapour deposition (EVD and CVD) or ion beam deposition. Although these techniques do not require subsequent sintering at high temperatures, they are considered to be expensive, time consuming and not easily scalable. Thus, these techniques, commonly applied for tubular systems in the past, are being increasingly replaced by slurry processing.

With respect to the anode as support compared to using the cathode as a support, an anode supported design coupled with planar geometry, offers the benefits of lower materials cost, greater strength and higher conductivity and also allows the application of cost-effective conventional ceramic processing techniques.

Additional information and recent developments of processing technology and fabrication techniques used for the manufacturing of cell components for the different types of solid oxide fuel cells have been surveyed by Tietz et al. [26].

2.4.2 Main Developers of Electrode-supported Designs of Solid Oxide Fuel Cell

Several industrial companies and research groups from the United States, Canada, Japan and Europe are currently pursuing electrode-supported cells, and anode-supported cells in particular. Again, developers aiming at 5-250 *kW* range, prefer the anode-supported solid oxide fuel cells because of their potential of lowering the operating temperatures.

In Canada, Global Thermoelectric Inc. is a leading developer of planar SOFC systems. Since 1997 Global Thermoelectric, using a three-step fabrication process,

has developed anode-supported planar cells. The initial tape casting process step yields anode substrates approximately 1 *mm* in thickness [27]. Recent results have shown very high performance from IT-SOFCs (Intermediate Temperature Solid Oxide Fuel Cells) operating on hydrogen and air. Power densities of 1.2 *W cm⁻²*, at 0.7 *V* and at 800°C and 0.2 *W cm⁻²*, at 0.7 *V* and at 600°C have been reported [28]. The reduced operating temperature allows the use of standard materials and cost effective cell systems.

On the other hand, Siemens Westinghouse is the company which introduced the seal-less tubular cell design in the 1980s. The tubular design of Siemens Westinghouse is a characteristic example of a cathode-supported fuel cell. Siemens Westinghouse is the market leader for tubular cells and the technology of that design has substantially progressed from 30 *W* per cell in the mid 1980s to the 250 *W* per cell in the late 1990s. The stack and power systems technology has advanced from a 3kW-unit operated on hydrogen/carbon monoxide initially, to 220 *kW* hybrid system (solid oxide fuel cell and a gas turbine). The high performance and efficiency of its tubular SOFC systems has encouraged Siemens Westinghouse to launch a plan for a series of prototype hybrid systems (300 *kW* or 1 *MW*) since such tubular SOFC designs remain closer to commercialisation [29].

In Japan, Tokyo Gas has designed and manufactured anode-supported planar cells with metallic interconnectors, which can be operated at reduced temperatures. These type of cells have a thin YSZ film of 25 μm thickness on a relatively thick Ni-YSZ anode substrate and are prepared by co-sintering a screen printed YSZ paste on the anode substrate [30].

Electric Power Development Co., (EPDC) and Mitsubishi Heavy Industries (MHI) are two of the leading fuel cell manufacturers and developers in Japan. Since 1989, they have focused on the development of tubular type solid oxide fuel cell modules and in the recent years they have been working on the pressurised 10 *kW* class module [31]. In addition, parallel attempts have been made by MHI to reduce the cell cost using the co-sintering fabrication method instead of the expensive plasma spray coating technique.

In Europe, Research Centre Jülich in Germany is renowned for its excellence in research and development of planar anode substrate solid oxide fuel cells. The anode substrate concept involves a thin electrolyte of about $15\ \mu\text{m}$, which is deposited on thick anode substrates of average thickness of $1.5\ \text{mm}$ [20]. The thin electrolyte film allows operation at lower temperatures which in turn lowers the costs of the interconnect and casing materials of the fuel cell stack. New materials and processing techniques are also under development in order to improve the reliability and further reduce the cost. Within the technology development program on kW-class cell stacks in Jülich, substantial work has been recently made on testing of short stacks in order to improve durability. Initial results have shown very small degradation rates after the first thousand hours of continuous operation [32]. Using the new materials developed and the results obtained from the $5\ \text{kW}$ short-stack testing, Research Centre Jülich is believed to begin operating a new $20\ \text{kW}$ stack by 2004.

The Danish consortium of Haldor Topsøe A/S and Risø National Laboratory (HTAS) are developing solid oxide fuel cell technology, which focuses on high performance, low-cost and durable anode-supported planar cells and stack components [33]. In particular, the Materials Department of Risø National Laboratory has been developing thin-electrolyte solid oxide fuel cells supported on porous anode supports, which have replaced the thick-electrolyte cells. The cells are fabricated by standard ceramic processes such as tape casting and slurry spraying, while a number of new, alternative materials are under development. So far results have shown that cells perform well with a typical ASR of about $0.35\ \Omega\ \text{cm}^2$ at 850°C [34]. By 2004 the Danish Solid Oxide Fuel Cell program aims at the demonstration of SOFC and systems in the $5\ \text{kW}$ size range operating at 850°C [33].

Sulzer Hexis has been designing, developing and manufacturing solid oxide fuel cells for stationary and low power applications since the late 1980s. The company Sulzer Hexis AG was established in 1997, as a subsidiary of the Sulzer corporation. An initial research stage with subsequent laboratory cell stack tests resulted in recent development of field test plant for long-term trials [35]. In Sulzer Hexis, solid oxide fuel cells are manufactured using the screen-printing fabrication technique. This technology developed for the first laboratory fabrication of cells has now been scaled

up to pilot production with competitive production costs [36]. As a result Sulzer Hexis entered successfully the fuel cell market with 1 *kW* system for residential applications at the end 2001.

There are also a number of other companies and research groups, which currently carry out research and development on electrode-supported solid oxide fuel cells. Once this small-scale technology has demonstrated its reliability, low production costs and high performance, then larger units of integrated power systems can be expected to be gradually introduced in the market, for stationary power and mobile applications.

2.4.3 Intermediate Temperature Solid Oxide Fuel Cells

A solid oxide fuel cell can, in principle, be designed to operate within a broad temperature range (500-1000°C). It is necessary, therefore to select the desired temperature of operation. This, in turn, is influenced by the specific application, the type of the fuel and the properties of the electrolyte component. The latter plays the biggest role on stack design and materials selection.

Operation at elevated temperatures poses problems, particularly for planar solid oxide fuel cell configurations. These problems are related to the high cost of materials, component durability, and the stability of the electrode-electrolyte interface [37]. In order to overcome these problems, it is necessary to reduce the operating temperature as far as possible without compromising the electrode kinetics or the internal resistance of the cell, as mentioned earlier.

One of the most important factors, in order to achieve low internal cell resistance, is the thickness of the electrolyte. The use of thinner electrolyte films would allow the operating temperature to be lowered. At present it seems that the minimum thickness for dense impermeable films that can be reliably mass-produced using relatively cheap ceramic fabrication techniques is around 15 μm . The use of a thinner electrolyte film requires this component to be supported on an appropriate substrate. Thus, the substrate functions as the main structural component in these cells, and it is necessary to optimise the opposing requirements of mechanical strength and gas permeability.

As discussed in the previous sections, there is an increasing interest among many companies (e.g. Global Thermoelectric, Sulzer, Ceramic Fuel Cells, etc.) in IT-SOFC systems operating at or below 800°C. Rolls-Royce has been developing an IT-SOFC configuration [38], which combines the advantages of the both tubular and planar designs. This integrated planar solid oxide fuel cell (IP-SOFC) concept incorporates multi-cell membrane assemblies connected in series with the electrolyte films, YSZ, of 10-20 μm in thickness supported on porous composite Ni-YSZ or Ni-CGO (Gadolinia doped Ceria) anodes. Experimental results [39] has shown that both types of anode have performed equally well and displayed similar behaviour.

Although most development work on planar IT-SOFC systems has involved thick-film YSZ electrolytes and Ni-YSZ anode substrates, research and development efforts have focused onto alternative anode and substrate compositions in an attempt to replace the common Ni-YSZ anode material. Rolls-Royce Strategic Research Centre has been investigating new anode substrate materials that could replace the existing ones for their IP-SOFC design. New alternative materials such as CSZ (Calcium stabilised zirconia) and MMA (Magnesia magnesium aluminate) have been tested and evaluated.

The Rolls-Royce IP-SOFC concept has been developed within the framework of current research projects, which are supported by UK and European programme funding. Key subcontract support has been provided over the years by many universities in Britain. At Imperial College, our research group in the Chemical Engineering Department has also participated in this project by evaluating and testing the new ceramic materials supplied by Rolls-Royce, and used as anode substrates for the construction of supported solid oxide fuel cells. This work constitutes one of the main objectives of this thesis. The results obtained have given insight into the development and exploitation of these new materials and have demonstrated the potential for the new materials to function effectively as part of the IP-SOFC design.

2.4.4 The Issue of Concentration Polarisation

There are three types of polarisations that limit the performance of the electrode-supported solid oxide fuel cells, namely ohmic, activation and concentration. In the electrode-supported designs the ohmic resistance is lower than that in the electrolyte-supported cells because thinner electrolyte films can be employed.

As well as lower ohmic resistance these designs are expected to have the advantage of lower activation polarisation, particularly with the use of the composite electrodes. The composite electrodes consist of a mixture of an ionic and electronic conductor and their role is to spread out the reaction zone so that the charge transfer process occurs over some distance from the electrolyte-electrode interface into the electrode. In this way, the electrolyte-electrode interface is a functionally diffuse interface. The latter has been verified by the findings of analyses carried out on composite electrodes [40,41]. It is worth noting that the process of the charge transfer on electrochemical systems had been first investigated by Newman and Tobias [42], whose original work provides a lot of useful information on composite electrodes and the processes involved.

The contribution of the concentration polarisation to voltage losses, at high current densities, is expected to be significant. The concentration polarisation problems result from the resistance to gas transport through the anode porous support. In such thick, porous anodes the fuel supply to the electrolyte is carried out mainly by diffusion of the gaseous species. Accordingly, the electrode reaction at the electrolyte-anode interface is governed by the rate of the reactant gas diffusion when the current density and the fuel utilisation are high. Since the diffusion rates of the reactant gases in the anode are affected by the structure of the anode, then the concentration polarisation, related to the transport of gaseous species through the porous electrodes, will in turn be related to the microstructure of the electrodes; specifically the volume percent porosity, the pore size, and the tortuosity factor.

The problem of the concentration polarisation in relation to gas transport through the porous media in electrode-supported solid oxide fuel cells has been examined by many researchers in recent studies. Kim et al. [43] and Virkar et al. [44] investigated the polarisation effects in intermediate temperature anode-supported fuel cells. They

fabricated anode-supported fuel cells and tested these over a range of temperatures. Their performance was explained in terms of concentration and activation polarisations. The results also showed that the polarisation effects could be minimised through a microstructural optimisation of the electrodes. In addition, a theoretical model, in which the binary diffusion is considered to be the dominant mode of gas transport through the porous electrodes [44], was given in order to further describe the fuel cell performance.

Chan et al. [45] proposed a generalised polarisation model that can be used to characterise the operation of a solid oxide fuel cell. Unlike the previous theoretical analysis given in Kim's study, in this model the general form of the Butler-Volmer equation is used to describe the activation polarisation rather than its simplified expressions. As for the concentration polarisation both ordinary and Knudsen diffusions are considered to allow for a different range of porous electrode designs.

In research work carried out by Marumoto et al. [46], the gas transport through the porous support and the electrodes of a solid oxide fuel cell was examined. A binary gas permeation method was proposed for the characterisation of the cell porous components, where the properties of porous media were obtained from the measured transport parameters of two different gases. That also allowed the estimation of the concentration polarisation caused by the porous layers (support and electrode), which eventually demonstrated the need for the improvement of the microstructure of the porous support tubes of the cell.

As these studies have shown, the diffusion process is the dominant type of transport of gaseous species through the porous support and it remains the most important contribution to concentration overpotential of the cell. Thus understanding of this interaction between gas transport and concentration polarisation is of prime importance with regard to the fuel cell performance. The study of the gas phase diffusion requires the determination of the gas transport properties and particularly the measurement of the effective diffusion coefficients of gases relevant to solid oxide fuel cell anode operation. Only when these transport parameters are accurately determined, can losses arising from the diffusion process be quantified. It is therefore clear that an improvement in cell performance will be achieved only by

minimising the voltage losses through the optimisation of the design specifications of the porous support and electrodes.

2.5 Diffusion of Gases in Porous media

The previous part provided an introduction to ceramic fuel cells and a detailed review of the research and development in the area of electrode-supported solid oxide fuel cells. It also introduced issues arising from this type of cell designs such as the problem of concentration polarization.

Diffusion is the dominant transport mechanism of the gas within the porous support and electrodes, playing a key role to the concentration polarisation of the electrodes and therefore influencing the performance of the fuel cell. In order to investigate the impact of gas phase diffusion within the porous ceramic materials on the performance of the solid oxide fuel cell, it is necessary to determine gas transport parameters such as the gaseous effective diffusion coefficients.

This part of the literature review will examine the experimental methods that have been employed for the measurement of the diffusion coefficients of binary gas mixtures through porous media. It will review relevant details of the fundamental principles of gaseous diffusion as well as issues related with complex phenomena of different modes of diffusion in porous structures.

2.5.1 An Initial Approach to Diffusion Process

Diffusion is caused by random molecular motion that leads to complete mixing. It can be a slow process. This slow rate of diffusion accounts for its importance. In many cases, diffusion occurs sequentially with other phenomena. When it is the slowest step in the sequence it limits the overall rate of the process. For example, diffusion often limits the efficiency of commercial distillations and the rate of industrial reactions using porous catalysts [47]. It also controls the growth of microorganisms producing penicillin, the rate of the corrosion of steel and the release of flavour from food.

The description of diffusion involves a mathematical model based on fundamental hypothesis or "law". Interestingly, there are two common choices for such a law. The

more fundamental, Fick's law of diffusion uses a diffusion coefficient. This is the law that is commonly cited in descriptions of diffusion. There is also a second one that has no formal name and involves a mass transport coefficient, a type of reversible rate constant. Choosing between the two models is the critical point. For fundamental studies where a function of the concentration versus position and time is required, the use of diffusion coefficient is more appropriate. On the other hand, there are cases when the experimental results dictate a more approximate and phenomenological approach. This suggests the use of mass transfer coefficients [47].

2.5.2 Analysis of Gaseous Diffusion: systems with or without walls

Diffusion primarily involves molecular motions that take place over small distances. In the case of gases, diffusion depends on molecular collisions.

The molecules of a gas collide frequently and so are constantly exchanging kinetic energy. The pressure a gas exerts on a surface (real or imaginary) is the average effect of the collisions of the molecules with the surface (if the surface is imaginary then one portion of the gas can be considered to exert pressure on the adjacent portion). The more frequently the collisions occur, the greater the pressure, so that the pressure increases as the number of molecules per unit volume increases. Unless the molecular concentration is very high, the most probable type of collision is that of two molecules, usually called a binary or simple collision. [48]

2.5.2.1 Systems without Walls

For a more detailed description of the phenomenon of gas diffusion, systems of molecules with or without walls can be introduced. If a concentration gradient exists for one of a species in a system that consists of two or more species, then there will be a net molecular flux of the molecules of that species from the more concentrated region to the less concentrated one. The molecules of that species are said to be diffusing and the flux of the species is regarded to be a diffusive flux.

The diffusion of a given component of a gas is resisted by collisions of the molecules of that species with the other molecules. In consequence, the diffusive flux of a given component in that system depends on two factors:

- the number of molecules of the given component per unit volume (the molecular flux of a given component increases as its concentration increases)
- the number of molecules per unit volume of the other species (as the concentration of the other species increases, the collision frequency increases, the molecular flights between collisions become shorter and so there is more resistance to diffusion and a lower diffusive flux of the given species).

Since there is conservation of momentum in molecule-molecule collisions, and there are no walls to which momentum can be transferred, the diffusion takes place with conservation of the total amount of momentum. Because this kind of diffusion proceeds through molecule-molecule collisions (in contrast to molecule-wall collisions), it is called molecular diffusion [48].

2.5.2.2 *Systems with Walls*

On the other hand, the presence of wall gives rise to a new type of collision, the molecule-wall collision. The interaction between the molecule of a gas and a solid wall is more complex than that between two molecules, as the molecule may be retained by absorption on the wall. In this case where the molecule is absorbed by the wall surface, the molecule transfers momentum to the wall. If the binding energy (the amount of energy released on absorption) is not too great the molecule can migrate over the surface, colliding with wall molecules and giving rise to the phenomenon of surface diffusion. When the absorbed molecule acquires a momentum normal to the wall surface large enough to exceed the attractive force of the wall, it will be emitted [48].

2.5.3 Mechanisms of Flux

The modes of transport are analysed in more detail along with the mathematical equations in section 6.3.1. Here, however, a comprehensible idea of the phenomena associated with the gas phase diffusion in porous media is presented. It is important to study the flux mechanisms (modes) in a system with walls. It is also convenient to represent the walls of the system as suspended particles distributed throughout the rest of the gas molecules. The "wall" particles are assumed to be spherical and be at rest in the reference coordinate frame. This system of molecules and particles displays three characteristic lengths:

- 1) the mean distance between two molecular collisions, called the mean free path λ ,
- 2) the average distance λ_p between two neighbouring particles,
- 3) the particle diameter d_p

2.5.3.1 Viscous Flux

In viscous flux, if $\lambda \ll \lambda_p$ and $d_p \gg \lambda$, there will be an enormously large number of molecules in the neighbourhood of a particle. Some of these molecules will be colliding with other molecules and some will be colliding with the particle. Under these conditions all molecules rebounding from the particle will collide with molecules in the immediate vicinity of the particle.

Considering the evolution of this system of gas and particles as a pressure gradient is applied, the rebounded molecules are diffusely reflected. Therefore they lose, on average, the component of their momentum along the direction of the flow of the gas produced by the pressure gradient. These molecules, through collisions, tend to decrease the average velocity of the molecules surrounding the particle. There is thus a damping effect on the boundary layer surrounding the particle and this effect continues until the boundary layer reaches the same velocity as the particle (motionless). As a result, it is necessary to apply a constant pressure gradient in order to keep the flow of gas constant [48].

The phenomenon described above differs from molecular diffusion in the following respects: the gas molecules lose momentum as a whole, there is no segregation of species and the mechanism of resisting the flux is that of molecule-wall collision.

When all molecules rebounded from a wall collide with the surrounding molecules, it can be said that the molecule-wall collision is a *viscous collision*. When the momentum exchange is progressively and smoothly transferred to the bulk of the fluid, then the *viscous regime* of flow is established which is the most common case in the porous media [49]. If the progressive transference is interrupted by vortexes then the so-called *turbulent regime* is obtained. The possibility of building up either the viscous or turbulent regime depends on the feasibility of dissipation of

momentum and this, in turn, depends on the intrinsic resistance of the fluid to this dissipation, the degree of influence of the wall and the flow rate [48].

2.5.3.2 Knudsen (free-molecule) Flux

In terms of the so-called Knudsen number, $K_n \approx \frac{\lambda}{\lambda_p}$, the opposite condition where $\lambda \gg \lambda_p$, means that $K_n \gg 1$. In this case the probability of a molecule-molecule collision is negligible compared to that of a molecule-wall collision. Those molecules rebounded or re-emitted by the wall do not collide with other molecules and the particles can thus only influence those molecules that collide with it. This kind of molecule-wall interaction is termed a Knudsen collision and the corresponding phenomenon will be called the Knudsen regime [48].

It is possible to distinguish molecular diffusion from viscous flux using different parameters such as the loss of momentum. For a system in the Knudsen regime, there are as many individual fluxes present as there are species (as in molecular diffusion) and these fluxes are independent of each other (in contrast to molecular diffusion) [48].

2.5.3.3 Nonequimolar Flux

In a system with walls the flux due to a pressure gradient can obviously be eliminated if the system is forced to remain at uniform pressure. This can only be achieved by external means and the net molecular flux will then no longer be zero. Once the flux due to a pressure gradient has died out only the diffusive components of the flux will remain. However, there is an evident contradiction: The diffusive fluxes are expected to be equal and opposite in a binary system, but in this system there are diffusive fluxes exclusively and yet the net molecular flux is not zero. In order to make these characteristics compatible a diffusive (nonsegregative) flux is introduced. This flux is called *nonequimolar* because it arises as a result of a difference in concentration (nonequimolarity) of species [48].

The nonequimolar flux occurs because, (1) the species have different molecular masses- the different masses of the molecules results in a different average velocity of the molecules and this difference in velocity is what tends to produce a pressure

gradient and (2) the system has walls. If the molecular velocities did not depend on the molecular masses, the nonequimolar flux would not exist.

Thus, in a system with walls the total diffusive flux of a given species consists of two components: the segregative one and the nonequimolar, nonsegregative one. The sum of these two components gives the total diffusive flux of the species: diffusive flux + nonequimolar flux equals the total diffusive flux.

2.5.3.4 Surface Flux

So far the movement of molecules in the gaseous phase has been taken into account. However, there is the possibility that a molecule will be adsorbed by the walls of a system and held for a given retention time $t_R > 0$. Only when the adsorbed molecule acquires an energy exceeding the energy barrier, equal to the energy developed during the adsorption, will it be able to return to the gaseous phase. When this happens, the molecule escapes from the surface in a random direction.

The picture of the surface flux is then the following one. A gas molecule is adsorbed on a low-energy site. After vibrating for a certain time, the molecule acquires an amount of energy Q_a sufficient to allow the molecule to hop to another adsorption site, where it will begin to vibrate again. The molecule makes a certain number of hops until it acquires an amount of energy sufficient to escape from the surface returning to the gaseous phase. The existence of the net flux on the surface is thus a probabilistic phenomenon that depends on the existence of the surface concentration gradient of the hopping molecules [48,50].

According to this scheme, each species transported along the surface is assumed to behave independently of the other species, so its flux can be taken to be proportional to its own surface concentration gradient. Also another assumption is that the adsorbed layer does not interact with the gas phase, except to maintain a rapid local adsorption equilibrium for each species [49].

2.5.3.5 Transition Regime

As it has been already discussed, the diffusion velocity of a given species is limited by the two resistances to diffusion, namely molecule-molecule collisions and molecule-wall collisions. In the molecular diffusion regime, the resistance due to

molecule-wall collisions is extremely low, while in the Knudsen regime, it is the resistance due to molecule-molecule collisions that is extremely low. It is apparent that a region will exist in which the diffusive process is intermediate in nature between these two extremes [51].

The transition from Knudsen to molecular diffusion (ordinary) encompasses a great range of mean free paths. This intermediate or transitional diffusive behaviour is of considerable practical interest, as it includes a range of pore sizes encountered in many commercial solid and pellet catalysts [51,52].

2.5.4 Gas Diffusion in porous media-A more focused analysis

Since a first approach of the fundamental principles of gaseous diffusion process has already been provided, a more specific investigation will be attempted with regard to the complex phenomena of diffusion in porous structures (porous materials, capillaries, etc.). The main aspects of gas phase diffusion (especially the mechanisms of gas transport) will be considered in terms of the structural characteristics of porous media.

Diffusion of gases and vapours in porous solids has not been definitely resolved. Part of the reason for this is that the diffusion flux may include a contribution from several mechanisms including bulk, Knudsen or even surface diffusion. Moreover, the wide variations in pore structure in terms of pore shapes and sizes makes it impossible to have a satisfactory geometric model of general applicability [53].

These variations in structure influence, to a great extent, the experimental methods commonly used for obtaining values of diffusivities. Consequently, the establishment of standardised techniques for providing diffusion coefficients will require structural parameters to be allowed for. An understanding of the influence of microstructure would be the first step in attempting to interpret diffusion of gases in porous media [54].

2.5.4.1 Basic Considerations

Diffusion in porous media can occur via three paths: through the pore volumes, along pore surfaces and through the solid matrix material of the media. The relative

importance of these paths depends on many factors, but a large fraction of the diffusion at ordinary and high temperatures will occur in the pore volumes unless the porosity and permeability of the medium are very low.

A generalised treatment of gas transport in porous media is the dusty-gas model developed by Mason and Malinauskas [49]. In this theoretical approach, the system is visualised as a "dusty" gas in which the dust particles are held stationary. By formally considering the dust particles as giant molecules, which are merely one more component of a multicomponent mixture, it is possible to treat the system by a means of the classical kinetic theory of multicomponent mixtures. Then, many of the usual results of diffusion in porous media can be derived very simply as special cases of standard kinetic theory [55,56].

Two limiting cases are usually distinguished: Knudsen diffusion (or free molecule flow) and normal (molecular or ordinary) diffusion. In Knudsen diffusion the limiting mechanism is the collision of the gas molecules with the solid walls of the porous medium, while the collisions between gas molecules have negligible effect. In normal diffusion it is the gas-gas collisions, which are limiting and the gas-wall collisions are negligible. The usual rough criterion for Knudsen diffusion is that the mean free path of the gas molecules be much larger than the size (diameter) of a pore. On the other hand, if the diameter is large relative to the mean free path of the molecules, transport occurs by normal diffusion [51,55,57].

2.6 Methods of Measuring Diffusion Coefficients

There are a great number of mathematical descriptions of diffusion within porous solids, but the ability of these models to interpret real experimental data is limited. Often too many unknown, or inaccurately known, parameters are present and the experiment can seldom be conducted with sufficient accuracy or discrimination to define them. As the theoretical prediction of effective diffusivity of gases in porous solids and catalysts is often not sufficiently accurate, there is a demand for simple and accurate experimental methods to evaluate effective diffusivities.

Effective diffusivities can be required for several reasons. They may be needed so that during catalyst formulation active species can be laid down precisely or with

specified concentration profiles on a porous matrix or support. In experimental work on heterogeneous reactions an effective diffusivity will be needed to determine the intrinsic reaction kinetics. Finally in reactor design the diffusivity will be needed to evaluate the Thiele modulus, which can then be an aid in predicting reaction rates for heterogeneous systems [60].

The work, which has been carried out for the measurement of effective diffusivities in the area of catalysis, can be applied to other areas as well. Thus established measuring techniques can be adopted for the measurement of the binary diffusion coefficients in ceramic porous materials such as the fuel cell support and electrodes.

Several experimental techniques have been used for the determination of effective diffusion coefficients of gases and vapours and can be broadly divided into steady and unsteady state methods. A description of such methods is given in the following sections.

2.6.1 Steady State Methods

A commonly used method for the characterisation of diffusion and adsorption of pure component systems is the diffusion cell method, which is used mainly with systems containing two gases. The process involves the counter-diffusion of these two gases through a porous medium from one chamber to the other. Usually both of these chambers are open, but there are applications where one of the chambers is closed. There are two modes of operation of the diffusion cell method. One is the steady state diffusion cell and the other is the transient diffusion cell.

The steady state diffusion cell was first developed by Wicke and Kallenbach [61], who designed a steady state method that is now widely used for porous pellets with regular geometry. The method is based on steady state counter-current diffusion flux measurement under zero pressure gradient. The overall effective diffusion coefficient is determined from the known dimensions of the pellet, the concentration difference and diffusion rate.

2.6.1.1 Wicke-Kallenbach Technique

This open-system method involves a porous pellet or many pellets that are mounted in parallel between two open chambers, and it is usually conducted with a binary system with an aim of determining the binary diffusivity and Knudsen diffusivity in the pellet (or a porous medium). In this binary system one gas (labelled as A) is flowing into and out of one chamber and in the other chamber another gas (B) is also flowing into and out of that chamber. The residence time in these two chambers is usually much smaller than the diffusion time through the porous medium. The gas A diffuses through the porous medium in the opposite direction to the diffusion path of the gas B. Due to the concentration gradient imposed across the medium, a counter-current mass transfer will occur. The pressures of the two chambers are maintained at the same level, and hence the mechanism for mass transfer through the porous medium is due to combined molecular and Knudsen diffusion [62].

The fluxes of these components are calculated by simply measuring the concentrations of A and B in the exit streams of the two chambers. A schematic representation of the Wicke-Kallenbach diffusion cell is shown in Figure 2.4:

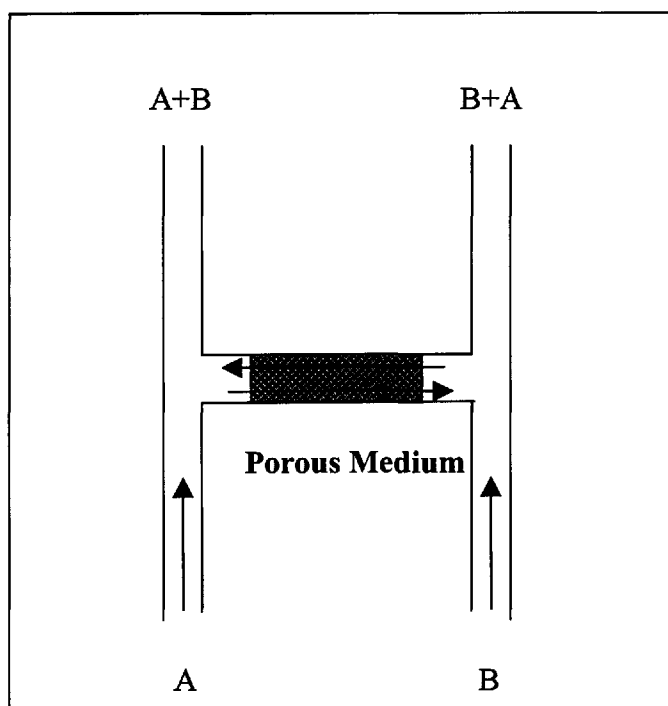


Figure 2.4: Wicke-Kallenbach diffusion cell [62].

The steady state method of Wicke-Kallenbach is relatively simple to carry out and provides a simple means to calculate steady state fluxes through porous media while it gives direct measurement of effective diffusion coefficients. However, it presents a number of disadvantages [54]. Results reflect only the flux through the major pores, which interconnect the flat end faces of the porous medium. Furthermore the tests cannot reflect the presence of any dead-ended or laterally distributed microporous structure around the major pores. Thus dead end pores are not characterised by the measurement of the steady state flux, as they do not contribute to the through-flux. In addition, the method is unable to identify anisotropic porous media [59].

Many variations on the basic technique have been developed but the Wicke-Kallenbach diffusion cell remains the essential ingredient of all steady state methods. An apparatus that has been devised by a group of researchers [57] is a modification of the common Wicke-Kallenbach apparatus. The diffusion cell consists of a hollow sphere of the solid under investigation sealed onto a “diffusion shaft” manufactured from hypodermic tubing to contain three separate passages.

2.6.2 Non-steady State Methods

Unlike the steady state diffusion method, dynamic methods based on transient diffusion flux measurement give effective diffusivities, which account for micropores and dead end pores in the solid. Among the unsteady state methods, pulse response measurements on single pellets and in gas chromatographic columns are most widely employed.

The pulse technique in single pellets was first used for diffusion studies by Suzuki and Smith [63]. In their paper a dynamic method was presented, and tested experimentally, for using single pellet chromatography to evaluate effective diffusivities and adsorption data for porous catalysts. Dogu and Smith [64,65] developed the pulse-response method using alumina pellets. Lu et al. [66] revised the dynamic analysis of single-pellet cell for the measurement of diffusion and convection in porous catalysts. They were able to solve and propose a complete mathematical model for the “diffusion-convection” cell.

These studies showed that pulse response experiments of single catalyst pellets can be used to determine effective diffusion coefficients as well as adsorption equilibrium constants. Such quantities also can be determined from dynamic experiments in columns packed with catalyst pellets but interpretation of the measurements is less direct. This is because the concentration of tracer in the effluent from the packed column depends on the solution of two differential mass balances, one applicable within an individual pellet and the second for the interpellet space in the column. Hence, axial dispersion and fluid-particle mass transfer effects must be accounted for before intrapellet parameters, such as the effective diffusivity, can be evaluated. This procedure can lead to less accurate results in comparison with the single pellet method. Axial dispersion is eliminated if pulse response experiments are carried out with single catalyst pellets. Therefore, these tests should provide an improved approach for evaluating intrapellet rate parameters [65,67,68].

2.6.2.1 Pulse Response Technique on Single Pellet Cell

Several variations of pulse response experiments are possible. A procedure that is used widely, corresponds to a Wicke-Kallenbach experiment. An inert gas is usually passed through the two chambers of the Wicke-Kallenbach diffusion cell. Once this is achieved and the pressures of both chambers are equalised, an impulse of tracer, either non-adsorbing gas or adsorbing gas, is injected into one chamber and its concentration is monitored at the other chamber [16].

In the pulse injection method, the response curve contains information about the various processes occurring inside the pellet. The moment method is applied to analyse the response curve. The zero order moment gives the amount injected into the system while the first order moment contains information about the processes responsible directly to the through flux. These moments are sufficient to establish the effective diffusivity and adsorption constant of the tracer. These are also the moments that can be measured with reasonable accuracy. The second order moment contains information about the secondary processes occurring in the pellet [62,64,65].

Instead of injecting the tracer as a pulse, a step injection can be used. Similar to the pulse injection method, the response curve of the step injection method also contains

information about the processes taking place in the pellet. This curve is usually analysed by matching the time domain solution to the experimental data.

Despite the fact that the transient operation can provide additional information about the system, for example the dead end pores, it does suffer from a number of disadvantages. The major one is that the mathematical analysis in order to extract information, is more complex than the steady state analysis. A schematic of the transient operation of the diffusion cell is shown in Figure 2.5.

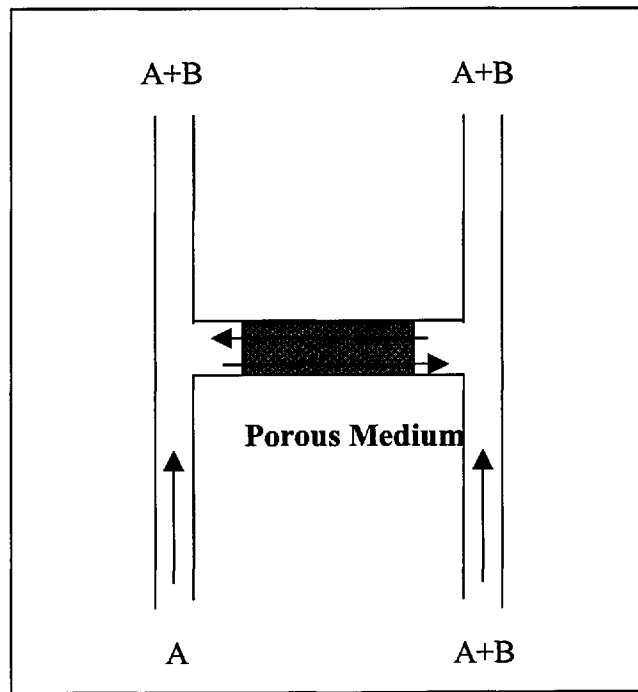


Figure 2.5: Transient operation of the diffusion cell

2.6.2.2 Chromatographic Pulse Response Technique

Many unsteady state testing techniques involve arrays or groups of particles. These are normally in small packed beds and are commonly referred to as chromatographic type tests. Many models have been developed to describe such systems and the tests are appealing in that they can be arranged so as to mimic closely the true conditions in which the porous solids will be used. Examination of the results produced shows that dispersion of a pulse of gas introduced into such beds is normally a weak function of the effective diffusivity. Also gas phase axial dispersion usually dominates as the pulse spreading mechanism, so that experimentally determined diffusivities are subject to large errors.

A promising variation on the chromatographic type tests is to employ a single pellet string reactor (SPSR), as described by Scott et al. [69]. This consists of a tube, only slightly larger in diameter than the pellet, which is packed with upwards of 50 pellets. Provided the tube-to-particle diameter ratio lies between about 1.1 and 1.4, it appears that the SPSR is in some respects equivalent to a packed bed of a more conventional aspect ratio. High superficial velocities can be used without introducing intolerable pressure drops and the result is that experimental conditions can be manipulated so as to minimise the gas phase axial dispersion term, which normally contributes so dominantly to the spreading of a pulse of diffusing species as it traverses the bed. As a result it offers an attractive way for determining effective diffusion coefficients [60].

At the moment, the chromatographic method is probably the most attractive dynamic technique for the evaluation of effective diffusivities in porous solids. The experiment is simple to carry out, can be conveniently used over a wide range of temperatures and the results are averaged over the number of pellets in the column. However, it has some shortcomings as the mathematical model used to determine the mean effective diffusion coefficient for a batch of pellets is complex and must account for other interacting factors such as adsorption and intraparticle diffusion. This means that some uncertainty in the results exists due to often ill-defined assumptions of some of the models [54,60,63].

2.6.3 Conclusion

From a comparison of the main methods for measuring binary diffusion coefficients, it becomes evident that the dynamic techniques provide us with effective diffusivities that account for the macropore as well as the micropore structure of the medium. They are also capable of providing more information on the processes taking place within the porous medium. Nevertheless, they present the drawbacks of the complex mathematical analysis in order to retrieve information from the obtained data, and of the need for more advanced instrumentation for conducting the diffusion experiments.

On the other hand, the method of the steady state diffusion cell constitutes an easy and a much simpler way to measure diffusion coefficients in porous media. The interpretation of the steady state diffusion measurements is straightforward and the effective diffusivities can be directly calculated by conducting a mass balance in the diffusion cell and applying the appropriate transport equations for diffusion through the porous sample.

In this work, for the reasons mentioned here, the steady state Wicke-Kallenbach technique was the obvious choice for the measurement of the binary gas diffusion coefficients.

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Chapter 3

Experimental Procedure

3.1 Introduction

The chapter outlines the experimental procedure for the measurement of the gaseous diffusion coefficients for binary mixtures through porous ceramic materials. The experimental apparatus and particularly the operation of the diffusion cell employed is also analysed in detail.

The main experimental techniques used for the investigation of the microstructure of the porous substrates are also summarised here. The morphological characterisation was achieved by scanning electron microscopy (SEM). The pore size distribution, the mean diameter as well as the open volume, the surface area and other physical properties of the materials were obtained by mercury porosimetry. To back up the mercury porosimetry measurements of the open porosity, water and methanol uptake tests were also conducted. For an additional estimation of the porosity of the samples and the mean pore diameter, image analysis was used.

As the gas chromatograph (GC) is the central part of the measurement system, a detailed description of the system is given here. The main components of the GC system are presented and details of the chromatographic columns along with the operating principles of the detectors are discussed. The applicability, the range and the sensitivity of the GC detectors and in turn of the system are also examined. The preliminary tests for the precision of the analysis and the preparation and the calibration of the GC before the sample analysis are also described in detail. The creation of the gas chromatographic methods for the detection of different gas pairs was a painstaking task that required a lot of effort and time. Therefore all the instrument parameters specified in each method for the different gas mixtures are explained.

3.2 Apparatus and Procedure

Several experimental techniques have been used to determine the effective diffusion coefficients of gases and vapours in porous materials and can be broadly divided into steady and unsteady state methods. A commonly used steady state technique is the

one developed by Wicke and Kallenbach [1]. This method involves the measurement of the amount of a gas diffusing from a gas stream flowing along one side of the porous material into another gas stream flowing on the opposite face of the material, under zero pressure difference across the two sides.

To apply the above method for the measurement of the gaseous diffusion coefficients through the porous ceramic materials, a test rig was built, shown in Figure 3.1. It was designed to provide measured flow rates to each face of the cylindrical sample and to analyse the composition of the inlet and outlet flow streams with a gas chromatograph. The apparatus consisted of the diffusion cell, flow and pressure metering and controlling, equipment and a gas chromatograph along with the data acquisition system.

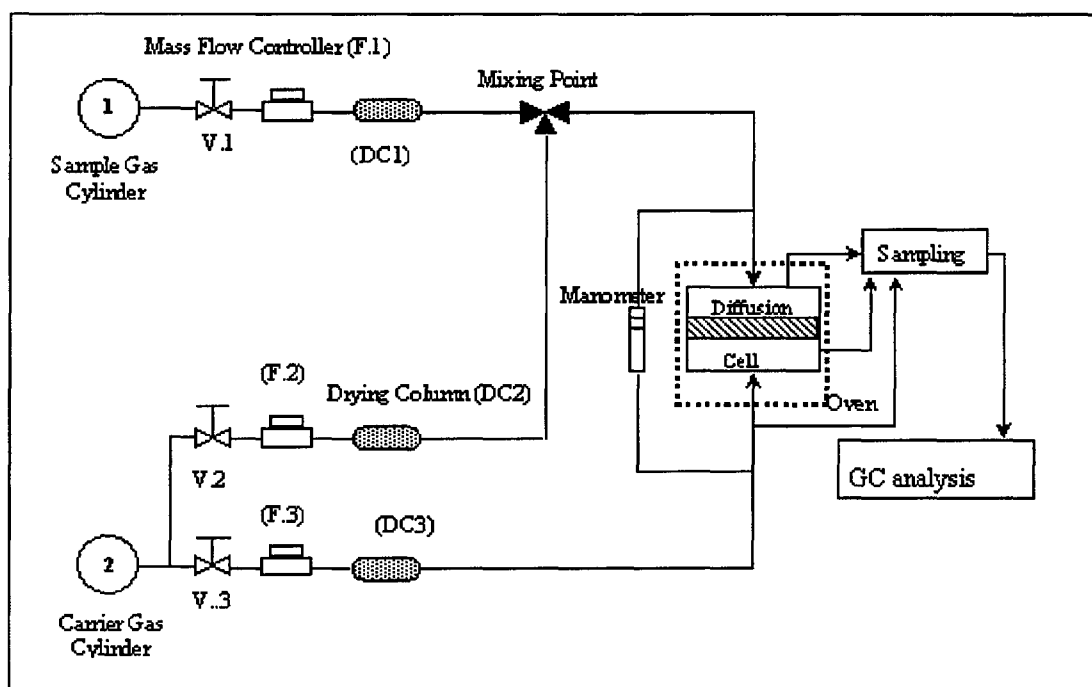


Figure 3.1: Schematic diagram of the apparatus

The main part of the experimental set-up is the diffusion cell. It consisted of a hollow, inner cylindrical chamber, which was designed to hold cylindrical samples up to 13 mm diameter, and which could be employed for steady state as well as dynamic measurements. The samples tested in these experiments had a diameter of 11.7 mm and a thickness 2 mm. A rubber O-ring supported the sample in the central part of the chamber and a cylindrical barrel sealed the chamber, holding the cylindrical disc in position. A cross section of the cell is illustrated in Figure 3.2. The

schematic shows more the orientation of the inlet and outlet gas streams and the position of the sample rather than describing in detail the cell inner configuration, i.e. the cylindrical barrel that holds the cylindrical sample.

Measurements were performed using nitrogen as the main carrier gas and a range of sample (trace) gases, such as hydrogen, carbon monoxide, carbon dioxide and methane. This type of gases were selected as relevant to solid oxide fuel cell anode operation. All the gases were supplied by BOC Ltd, (purity 99.998%).

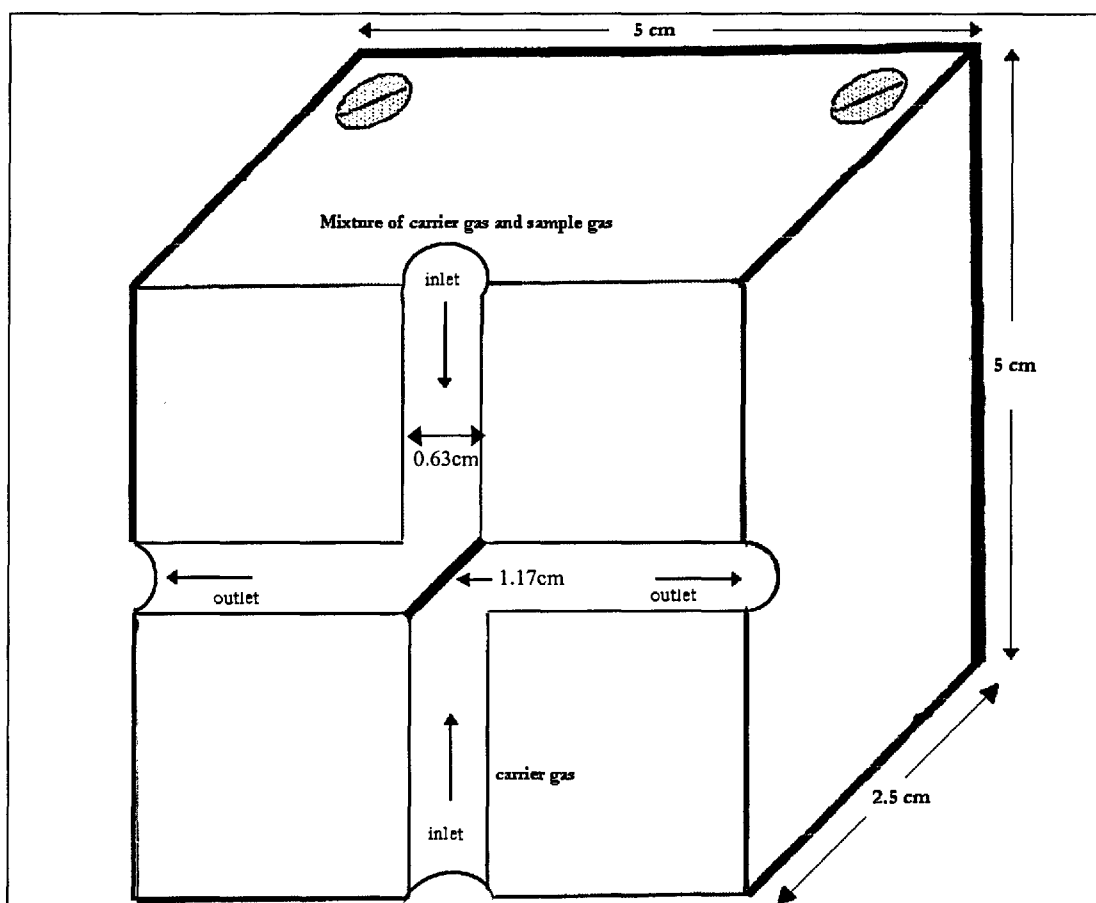


Figure 3.2: Cross section of the diffusion cell. The orientation of the gas streams and the position of the sample at a 45° angle are shown.

The carrier gas (nitrogen) was fed directly onto the lower end face of the sample at a known flow rate and a mixture of the sample gas and the carrier gas was passed directly along the upper side of the sample, as shown in the schematics of Figures 3.1 and 3.2. The design of the cell holder was made in such way that the porous sample would sit in an angle of 45°. That prevented the introduction of the carrier

gas and the mixture gas streams directly on the end surfaces of the sample and therefore reduced any errors due to the diffusion resistance in the gas space on either end of the sample. The direction of gas streams could be regarded as tangential to the sides of the porous sample.

The desired concentration of this mixture stream was obtained by mixing the carrier and the diffusing gas (sample gas) with the aid of a tee-junction, placed downstream. This is indicated as the mixing point in the diagram of Figure 3.1. The use of the gas mixture fed to one side of the porous sample was necessary to avoid any likely problems arising from use of pure gases such as H_2 and CH_4 (safety reasons) directly into one side of the sample. The flow rates of the inlet gas streams were accurately regulated by thermal-mass flow meters controllers (Bronkhorst Hi-Tech BV) operating at the range from 2 to 100 *ml/min*.

Pressure difference between the two sides of the sample was eliminated (in practice falling in the range 0-12 *Pa*) by controlling a needle valve connected at the end of one of the outlet stream lines. The pressure drop was monitored by a high precision differential digital manometer, Digitron 2080P, with an operating range 0-2500 *Pa*.

In order to maintain a near zero pressure drop across the sample and equal flow rates at both sides of the cell, the two inlet gas streams had to be directed at exactly equal volumetric flow rates. The volumetric flow rates used were 100 and 50 *ml/min*. The flow rate of 100 *ml/min* was used for the pair of H_2 - N_2 . For the rest of the binary gas mixtures, the analyses were carried out at 50 *ml/min*, except for the binary mixtures of CH_4 -CO and CO_2 -CO for which the runs were carried at a flow rate of 80 *ml/min*. The latter was dictated by the limitations of the measurement system. In order to obtain detectable amounts of the diffusing gas through the porous sample, lower flow rates had to be employed. The detection of diffusing gases such as CO and CH_4 through the porous sample can only be achieved at lower flow rate because of the lower diffusion rates (small diffusivities) of molecules such as CO and CH_4 .

Prior to any diffusion measurements, leak tests were carried out. This type of test involved blank runs in which a solid, impermeable pellet of the same dimensions as

the tested porous supports was placed inside the diffusion cell. Ar and N₂ were flowed past the opposite sides of the solid pellet and no measurable flux was detected through it. Therefore the sealing between the sample and the chamber holder, provided by the rubber O-ring, was regarded as being satisfactory.

Samples were taken from both inlet and outlet gas flow streams and analysed with a gas chromatograph (Ai Cambridge Q94 GC), which was configured with a thermal conductivity detector (TCD) and a flame ionisation detector (FID). The output signals from these detectors were recorded by the data acquisition system (JCL 6000 for Windows Chromatography Data system). All the experimental operating conditions such as temperature, pressure and flow rates were also recorded. Measurements were made in the temperature range of 23-27°C and 1 *atm* total pressure.

Steady state diffusion was reached when there was no change with respect to time in the outlet gaseous compositions. Preliminary tests with a mass spectrometer (MiniLab) confirmed that steady state conditions were established in less than 2 minutes for all the runs. An estimation of the time to reach steady state was also obtained by using one-dimensional, time dependent diffusion model for the flux through the porous sample. These calculations are described in more detail in the following section of the experimental design.

Drying columns (4214MS, Omnifit) were connected upstream to make sure that the gases were dry. They contained a general purpose 4A Molecular sieve with a moisture indicator changing from blue to white when exhausted. The system was also purged by nitrogen for 2 hours before the beginning of a new analysis to remove any impurities left in the tubing by previous runs.

3.3 Parameters of the Experimental Design

For the calculation of the effective diffusivities from the experimental data a number of assumptions and approximations were made. It is very important to ensure that for the chosen experimental conditions, these approximations were appropriate and valid for the current method. For instance, it is very important to become aware of the sensitivity of different parameters, such as the small pressure drop across the porous

sample, to the changing physical properties of the mixture. Although this technique required zero pressure difference, in practice the cell was operated under small pressure drops. Estimates were therefore made to determine any possible convective contributions to the diffusive flux.

Another experimental requirement of this method was that the steady state diffusion was reached. The effective diffusivities were calculated by equations that treated the experimental diffusion data under steady state conditions. The time required for the steady state conditions to be established was therefore first estimated by adopting a transient diffusion model.

The boundary layer was another factor that could affect the way in which the raw data were interpreted. The validity of the one-dimensional approximation for diffusion through the porous sample, and the assumption that the surface concentration on each side of the porous sample was equal to the bulk concentration of the gas on the bulk stream of the fluid, were all closely related to the boundary layer issue.

Calculations were first performed to characterise the bulk flow above the porous sample and then to estimate the mass transfer coefficient. The effect of the employed range of bulk flow rates on the mass transfer coefficient was also examined and conclusions were drawn. A comparison of the transport coefficients, namely the mass transfer coefficient and binary diffusion coefficient, was a means of evaluating whether diffusion was the dominant transport mechanism. These issues are explored in turn in the following.

3.3.1 Effect of the Pressure Drop

The main source of error in this method is the uncontrolled pressure difference between the two sides of the porous sample in the diffusion experiments. This total pressure difference may give a convective flow contribution to the diffusion flux. To eliminate this error the pressure drop was monitored by a differential monometer and was maintained close to zero by adjusting needle valves in the gas exit streams.

As mentioned previously, the experimental pressure drops observed were in the range of 4-12 Pa . For the isothermal mass transfer of a single gas driven by a pressure gradient ∇p (and for one dimension $\frac{dp}{dx}$), the flow rate through the porous medium can be described by Darcy's law [2]:

$$N = -\frac{k}{\mu} c \frac{dp}{dx} \quad (3.1)$$

where k is the permeability (m^2), μ the dynamic viscosity of the fluid ($N s/m^2$) and c the molar concentration ($kmol/m^3$). In the continuum region the flow through the pores of a porous medium can be assumed as laminar, which is justified considering the size of the pores. In this case Darcy's law has the same form as the Poiseuille equation for laminar flow in a cylindrical tube. Ignoring entrance and two-dimensional effects, the mean velocity V for Poiseuille flow [3] is given by:

$$V = \frac{1}{2} \frac{\bar{r}^2}{4\mu} \left[-\frac{dp}{dx} (p + \rho g z) \right] \quad (3.2)$$

with $\bar{r}$ the mean pore radius (m), μ the dynamic viscosity of the fluid ($N s/m^2$) and ρ the density (kg/m^3). The second term inside the parenthesis on the right hand side of the Equation (3.2) is the acceleration pressure drop. This can be ignored as in principle, its contribution is very small. Note that the pressure gradient is negative because pressure decreases with x .

For the flow through porous media, the Poiseuille equation takes the following form:

$$\frac{G}{\rho} = \frac{\varepsilon}{\tau} \frac{1}{2} \frac{\bar{d}^2}{16\mu} \left(-\frac{dp}{dx} \right) \quad (3.3)$$

where G is the mass flux ($kg/m^2 s$), and $\bar{d}$ describes the mean pore diameter (m). The porosity ε takes into account the volume of the pores that go from one face of the porous medium to the other. The tortuosity τ accounts for the irregular shape

and the actual length of the pores in comparison with the pores of a porous medium seen as a bundle of straight, parallel capillaries with constant diameter (detailed discussion for this porous model along with others is given in chapter 5). The Equation (3.3) can be used to calculate the mass flux through porous media induced by a pressure difference.

Equation (3.3) can be then applied to predict the pressure driven flux for a typical binary gas mixture such as that of hydrogen and nitrogen. The mean radius or diameter of the pores can be estimated by several techniques. It will be shown in chapter 5 that the pore size distribution yielded an average pore diameter of $2.0 \mu\text{m}$ and $2.1 \mu\text{m}$, for the CSZ and MMA materials respectively. The average values of the porosity and tortuosity were also found to be $\varepsilon = 21.56\%$ and $\tau = 3.30$ for the CSZ and $\varepsilon = 15.24\%$ and $\tau = 4.27$ for the MMA. For the calculation at one side of the porous sample $x = 0$, shown in the schematic in Figure 3.3, there is pure hydrogen with $\rho = 0.08078 \text{ kg/m}^3$, $\mu = 8.96 \times 10^{-6} \text{ kg/ms}$, while at the opposite side $x = L$, there is pure nitrogen with $\rho = 1.12330 \text{ kg/m}^3$, $\mu = 17.82 \times 10^{-6} \text{ kg/ms}$ (at 1 atm , 298 K) [4].

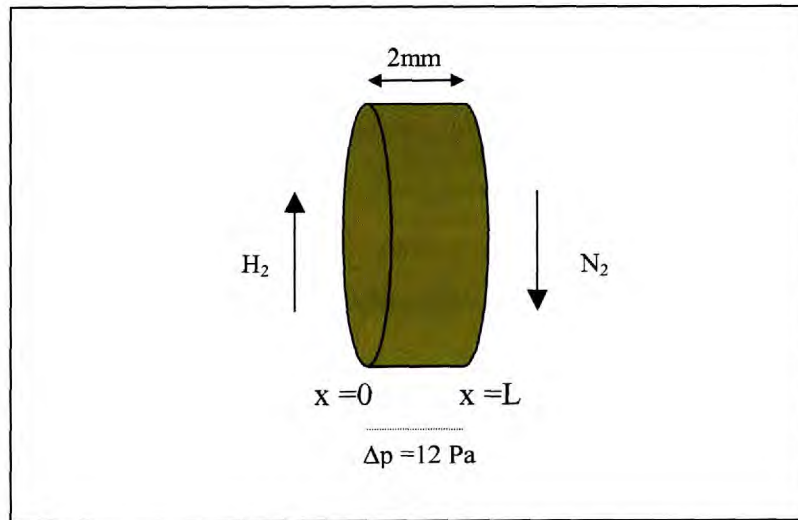


Figure 3.3: Schematic of the porous sample

Integration of Equation (3.3) gives a linear profile for the pressure drop:

$$G = \frac{\varepsilon}{\tau} \frac{1}{32} \frac{\bar{d}^2}{\mu} \rho \frac{(p_L - p_0)}{L} \quad (3.4)$$

or

$$G = \frac{\varepsilon}{\tau} \frac{1}{32} \frac{\bar{d}^2}{\mu} \rho \frac{\Delta p}{L} \quad (3.5)$$

Setting the pressure drop to be the maximum of the observed values, $\Delta p = 12 \text{ Pa}$ or kg/m s^2 and L to be $L = 0.002 \text{ m}$ predicts pressure driven mass fluxes for hydrogen and nitrogen of

$$G_{H_2} = 0.44 \times 10^{-6} \text{ kg/m}^2 \text{ s} ; \quad G_{N_2} = 3.09 \times 10^{-6} \text{ kg/m}^2 \text{ s}$$

The corresponding experimentally measured diffusion mass fluxes for the mixture of hydrogen 20% and nitrogen 80%, through the porous sample of CSZ were found to be:

$$G_{H_2} = 0.48 \times 10^{-4} \text{ kg/m}^2 \text{ s} ; \quad G_{N_2} = 8.39 \times 10^{-4} \text{ kg/m}^2 \text{ s}$$

It is evident from these results that the convective flux through the porous sample induced by a pressure difference of 12 Pa is at least two orders of magnitude smaller than the diffusive flux. The convective contribution to the diffusive flux is less than 1% and therefore can be ignored. Calculations for the MMA support showed the same difference between the fluxes, with the convective flux being two orders of magnitude smaller than the diffusion fluxes.

3.3.2 Time to Establish Steady State Diffusion

To estimate the time taken to reach steady state, a simple, one-dimensional, transient diffusion model was employed. The simplest case of transient diffusion which is amenable to analytical solution, is the one-dimensional mass transfer in a semiinfinite stationary medium with a prescribed mass concentration. This case is very common because any diffusion problem will behave as if the medium is infinitely thick at short enough times. Many actual processes are adequately described during their transient period by the resulting equation.

The diffusion in a semiinfinite medium [5] is schematically shown in Figure 3.4. A volume of solution, which starts at an interface and extends a very long way, can be considered. Such a solution can be gas, liquid or solid. The semiinfinite medium initially contains a uniform concentration of solute (c_{in}). At some time, chosen as

time zero, the concentration at the interface is suddenly increased (c_s), although the solute is always present at high dilution. The increase produces the time-dependent concentration profile that develops as solute diffuses into the medium.

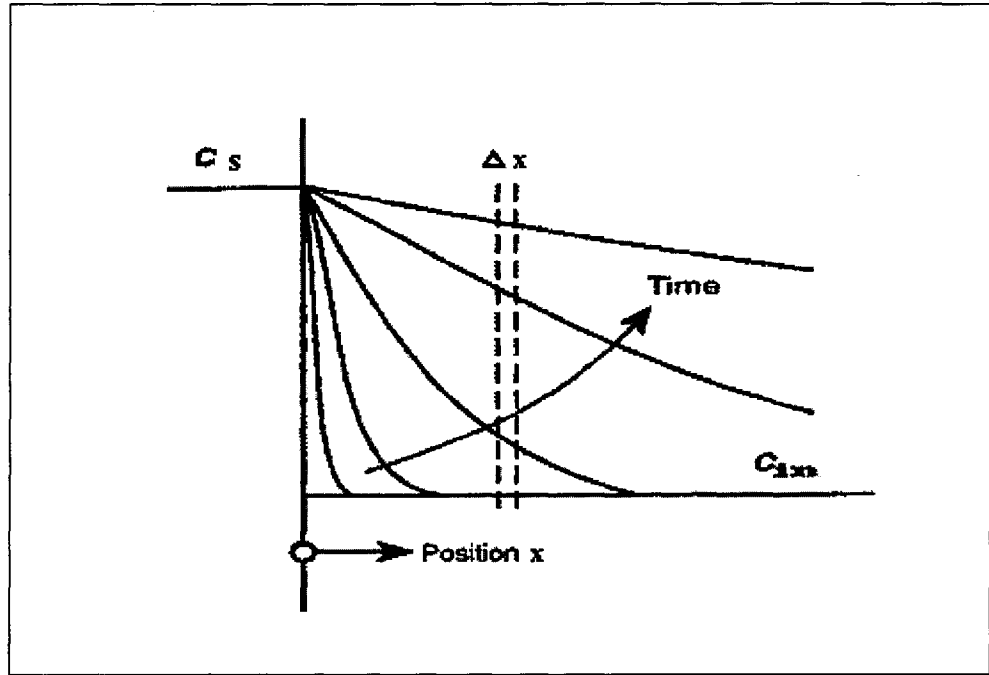


Figure 3.4: Diffusion in a semiinfinite medium. c_{in} is the initial concentration, and the concentration at the left is increased to a higher constant value (c_s). Diffusion occurs in the region on the right

The mathematical statement of the time-dependent diffusion problem already defined above is as follows:

$$\frac{\partial c}{\partial t} = D_{AB}^{eff} \frac{\partial^2 c}{\partial x^2} \quad (3.6)$$

This partial differential equation is Fick's second law. In this case, it is subject to the following conditions:

$$\text{Initial condition:} \quad \text{at } t = 0, \text{ all } x, \quad c = c_{in} \quad (3.7)$$

$$\text{Boundary conditions:} \quad \text{at } t > 0, \quad x = 0, \quad c = c_s \quad (3.8)$$

$$x = \infty, \quad c = c_{in} \quad (3.9)$$

An analytical solution for Equation (3.6) for the prescribed initial and boundary conditions can be obtained by recognising the existence of the similarity variable n :

$$n = \frac{x}{\sqrt{4 D_{AB}^{eff} t}} \quad (3.10)$$

The concentration distribution in the final solution has the following form:

$$\frac{c - c_s}{c_{in} - c_s} = \frac{2}{\sqrt{\pi}} \int_0^n e^{-\xi^2} d\xi = \text{erf} \left(\frac{x}{\sqrt{4 D_{AB}^{eff} t}} \right) \quad (3.11)$$

where the Gaussian error function, $\text{erf} \left(\frac{x}{\sqrt{4 D_{AB}^{eff} t}} \right)$, is a standard, tabulated, mathematical function. An estimate of the time constant for steady state conditions to be reached can be obtained from the similarity variable, Equation (3.10), in which the time constant can be considered to be proportional to the ratio x^2 / D_{AB} . Therefore for a thickness of the porous support $L=0.002 \text{ m}$ and $D_{AB}^{eff}=5.30 \times 10^{-6} \text{ m}^2/\text{s}$ (see Table 5.16) and the gas pair of hydrogen and nitrogen, the time constant is calculated to be,

$$\tau \sim L^2 / D_{AB}^{eff} = (0.002)^2 / 5.30 \times 10^{-6} = 0.76 \text{ s}$$

This predicted time to reach steady state diffusion is even shorter than the time found experimentally. For the other binary mixtures longer times were found especially in the case of MMA support ($t=6.67 \text{ s}$). In practice, a time of twenty minutes was allowed for the system to reach steady state before measurements were made.

3.3.3 The Effect of the Concentration Boundary Layer

When a binary mixture of chemical species of A and B (such as a binary mixture of hydrogen and nitrogen) flows over the surface of a pellet or a cylindrical porous disc and the concentration of species at the surface $c_{A,s}$ differs from that in the bulk stream $c_{A,\infty}$ a concentration boundary layer will develop [4], as shown in Figure 3.5. It is this region in which concentration gradients occur.

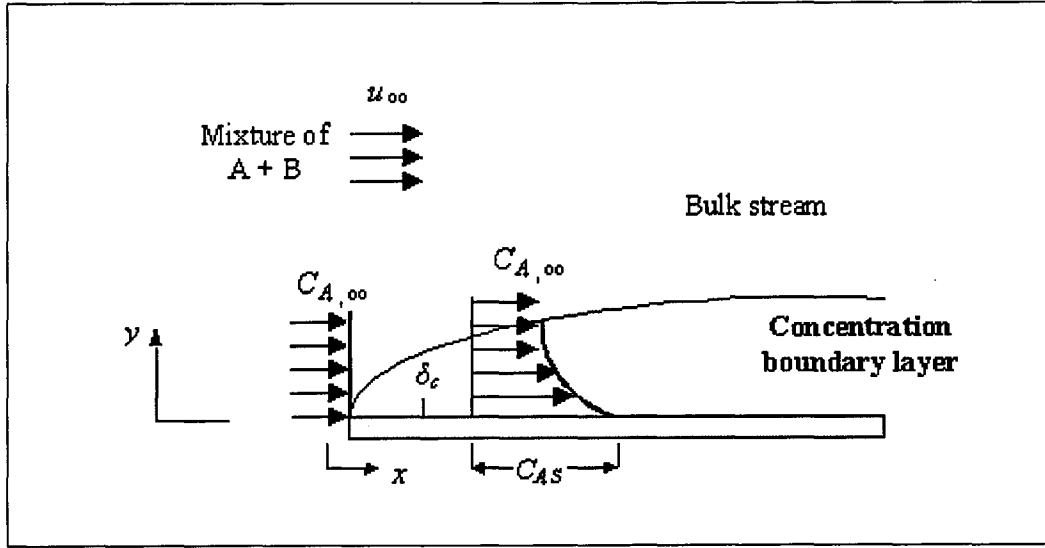


Figure 3.5: Concentration boundary layer development on a flat surface.

At any point corresponding to $y > 0$ in the concentration boundary layer of Figure 3.5, species transfer is due to both the fluid motion and diffusion. However, at the surface $y=0$ there is no fluid motion because the velocity is zero and species mass transfer takes place only by diffusion. Applying Fick's equation at $y=0$, the species flux at any distances from the edge is given by:

$$N_A = -D_{AB} \left. \frac{\partial c_A}{\partial y} \right|_{y=0} \quad (3.12)$$

Introducing the equation that relates the molar flux of species A to the product of a mass transfer coefficient and a concentration difference between the bulk stream and the surface, Figure 3.5, the molar flux may be also expressed as [4]

$$N_A = h_m (c_{A,S} - c_{A,\infty}) \quad (3.13)$$

where h_m (m/s) is the convection mass transfer coefficient, while the molar concentrations $c_{A,S}$, $c_{A,\infty}$ have units of kmole/m³. From Equations (3.12) and (3.13) it follows that

$$h_m = \frac{-D_{AB} \left. \frac{\partial c_A}{\partial y} \right|_{y=0}}{c_{A,S} - c_{A,\infty}} \quad (3.14)$$

The conditions in the concentration boundary layer, which strongly affect the surface concentration gradient, will also affect the convection mass transfer coefficient and hence the rate of the species mass transfer into the boundary layer.

3.3.3.1 Flow Regime

It is important to become aware of the internal flow geometry before any calculations are to be made to characterise the bulk stream flow and estimate the convection mass transfer coefficient.

Referring to the cell internal configuration, shown schematically in Figure 3.2, the internal flow geometry above the surface of the porous support can be simulated as a tube of noncircular cross section or duct. The dimensions of the duct can be approximated by the size and the characteristics of the internal geometry of the cell. Therefore for the duct, shown schematically in Figure 3.6, the width W , length L and height H are 4.0 mm, 11.7 mm and 0.8 mm respectively, as taken from the dimensions of the cell design.

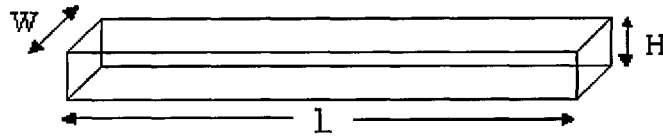


Figure 3.6: Dimensions of the duct.

In addition, analysis of flow in noncircular tubes utilises the concept of equivalent circular tube flow. An effective diameter may be used as the characteristic length. Such dimension is the hydraulic diameter, which is defined as

$$D_h \equiv \frac{4A_c}{P} \quad (3.15)$$

where A_c and P are the flow cross sectional area and the wetted perimeter, respectively. It is this diameter that should be used for calculating parameters like the Reynolds number. For flow in a circular tube the dimensionless Reynolds number is defined as

$$Re \equiv \frac{\rho u_m D}{\mu} \quad (3.16)$$

where u_m is the mean fluid velocity over the tube cross section, D the tube diameter and μ and ρ the dynamic viscosity of the fluid and its density respectively. In the case of noncircular tube, the hydraulic diameter D_h , is used instead of diameter D .

For the dimensions given above, the cross sectional area and the wetted perimeter are, $A_C = 3.2 \text{ mm}^2$ and $P = 9.6 \text{ mm}$. From Equation (3.15), the hydraulic diameter is found to be, $D_h = 1.33 \text{ mm}$. The binary gas mixture of hydrogen 20% and nitrogen 80% flowing over the surface of the porous support is considered again. With a volume feeding flow rate (Q) of $100 \text{ cm}^3/\text{min}$ and with the estimated value of wetted perimeter, $A_C = 0.032 \text{ cm}^2$, the mean velocity can be calculated by the following equation,

$$u_m = \frac{Q}{A_C} \quad (3.17)$$

Thus the mean velocity is $u_m = 0.52 \text{ m/s}$. It is important to characterise the flow inside the duct by calculating the Reynolds number. With the mean velocity known, the diameter D being $D_h = 0.00133 \text{ m}$ and with $\rho = 1.12330 \text{ kg/m}^3$, $\mu = 17.82 \times 10^{-6} \text{ kg/m s}$ (at 1 atm, 298 K) for nitrogen, the Reynolds number can be calculated from Equation (3.16), $Re = 43.6$. Thus the internal flow is laminar.

Note that in this case the boundary layer fluid is a binary mixture of hydrogen and nitrogen and its properties should be those of the mixture. However, in these calculations only the properties of nitrogen are involved rather than those of the binary mixture, since nitrogen is assumed to be in large excess.

3.3.3.2 Estimation of the Convection Mass Transfer Coefficient

For laminar flow the use of circular tube correlations in order to find the convection mass transfer coefficient is not very accurate since the cross sections of ducts are generally characterised by sharp corners. In such cases the Nusselt number corresponding to fully developed conditions may be obtained from the appropriate tables [4], for flow through non circular tubes of differing cross sections. These

numbers have been tabulated for conditions of uniform surface flux and uniform surface temperature (in the case of heat transfer). Note that the dimensionless Nusselt number mentioned here is defined as

$$Nu \equiv \frac{hD_h}{k} \quad (3.18)$$

where h is the heat transfer coefficient, D_h is the hydraulic diameter and k is the thermal conductivity. The Nusselt number provides a measure of the convection heat transfer occurring at the surface.

Accordingly in mass transfer, the Sherwood number can be defined as

$$Sh \equiv \frac{h_m D_h}{D_{AB}} \quad (3.19)$$

where h_m is the mass transfer coefficient, D_h is the hydraulic diameter of the noncircular tube and D_{AB} is the binary diffusion coefficient. The Sherwood number provides a measure of the convection mass transfer occurring at the surface.

By heat and mass transfer analogy, the results tabulated for noncircular tubes of various cross sections for convection heat transfer may be used for convection mass transfer by simply replacing the Nusselt number with Sherwood number.

According to the dimensions of the duct shown in Figure 3.6, the cross section of the duct has an aspect ratio b/a ,

$$\frac{b}{a} = \frac{\text{width}}{\text{height}} = \frac{4.0}{0.8} = 5 \quad (3.20)$$

If an uniform surface concentration is maintained at the surface of the porous support, which is analogous to a constant surface temperature, the use of the appropriate table [4] with an aspect ratio $b/a=5$ yields the Nusselt number, $Nu=5.27$.

By applying the heat and mass analogy, the Nusselt number can be replaced by the Sherwood number, thus $Sh=5.27$. By substituting the “free” binary diffusivity for the mixture of hydrogen and nitrogen $D_{AB}^{free}=0.73 \times 10^{-4} \text{ m}^2/\text{s}$ (see Table 5.16 of chapter 5) and the hydraulic diameter $D_h=1.33 \text{ mm}$ into Equation (3.19) the convection mass transfer coefficient, h_m , can be obtained. It follows that,

$$h_m = Sh \frac{D_{AB}^{free}}{D_h} = \frac{5.27 \times 0.73 \times 10^{-4} \text{ m}^2/\text{s}}{0.00133 \text{ m}} = 0.29 \text{ m/s} \quad (3.21)$$

Moreover the Biot dimensionless parameter for mass transfer is defined as

$$Bi_m \equiv \frac{h_m L}{D_{AB}^{eff}} \quad (3.22)$$

where L is the thickness of the porous support material. The Biot number may be interpreted as the ratio of internal species transfer resistance to the boundary layer species transfer resistance. Although the Sherwood and the Biot numbers are similar in form, they differ in definition and interpretation. The Sherwood number is defined in terms of the ‘free’ binary diffusion coefficient while the Biot number is expressed in terms of the binary diffusivity in the porous support.

With the thickness of the CSZ support, $L=0.002 \text{ m}$ and the effective binary diffusivity for the mixture of hydrogen and nitrogen $D_{AB}^{eff}=5.30 \times 10^{-6} \text{ m}^2/\text{s}$ (see Table 5.16 of chapter 5), Equation (3.22) yields $Bi=109.4$. The last result shows that the Biot number is much larger than unity. In such a case the resistance to species mass transfer by diffusion in the porous support is much larger than the resistance to species mass transfer by convection to the surface across the boundary layer.

This can be also related to the concentration differences. By defining the resistance as the ratio of driving potential to the corresponding mass transfer rate [4], it follows that the mass transfer resistance for diffusion is

$$R_{m,diff} \equiv \frac{C_{A,S_1} - C_{A,S_2}}{\dot{N}_{diff}} = \frac{L}{D_{AB}^{eff} A} \quad (3.23)$$

where $\dot{N}_{diff}$ is the diffusive flow rate and A and L the cross sectional area and thickness of the porous support respectively. The mass transfer resistance by convection is defined in a similar way

$$R_{m,conv} \equiv \frac{C_{A,S_1} - C_{A,\infty}}{\dot{N}_{conv}} = \frac{1}{h_m A} \quad (3.24)$$

Equations (3.23) and (3.24) show that the Biot number can also be viewed as a measure of the concentration drop within the porous support relative to the concentration difference between the surface and the bulk stream of the fluid. A small resistance to convection compared to the large resistance to mass transfer by diffusion indicates that the concentration difference between the bulk stream concentration and the surface concentration is also small, as shown in the diagram in Figure 3.7. It is the concentration difference across the porous support, which is significant. It then follows that the bulk stream fluid concentration may be regarded to be approximately equal to the surface concentration.

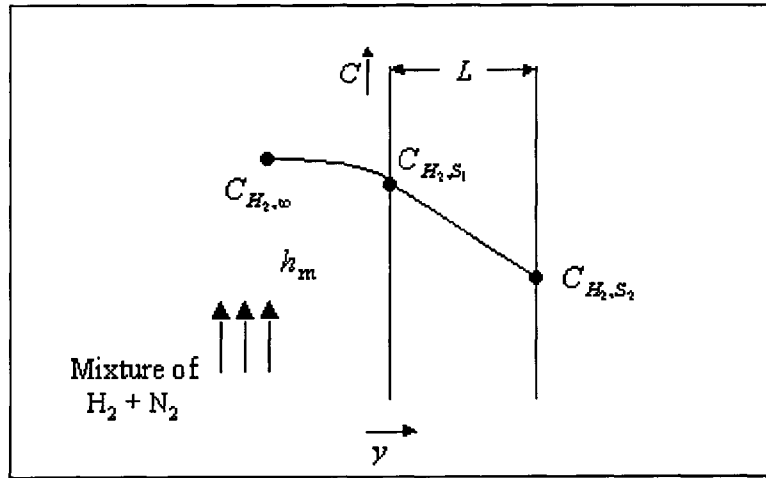


Figure 3.7: Effect of a large Biot number on steady state concentration distribution in the porous support of thickness L . The concentration difference between the bulk stream concentration and the surface concentration is very small compared to the concentration drop across the support.

The above conclusion verified the initial approximation adopted for the processing of the raw diffusion data in which the surface concentration of the porous support was actually taken to be that of the bulk stream.

The foregoing analysis explains also the effect of the flow rate on the mass transfer coefficient. It was shown that for laminar flow and fully developed conditions, the estimation of the convection mass transfer coefficient from the Sherwood number, Equation (3.21), is a constant, independent of parameters like the Reynolds number or the axial location. Since the Reynolds number does not influence the Sherwood number thus the feeding flow rate does not have any effect on the convection mass transfer coefficient too. Within the chosen range of flow rates from 50-100 cm^3/min the flow is in the laminar regime. Therefore the independence of the convection coefficient on the flow rate holds for the whole range of the selected feed flow rates.

According to the aforementioned discussion the one-dimensional approximation made is valid because the experimental conditions are controlled so that the concentration difference across the boundary layer remains small and the diffusive flux across the porous support small but measurable.

3.3.3.3 Boundary Layer Approximations

In the discussion made previously for the effect of the concentration boundary layer and the estimation of the convection mass transfer coefficient, the entry effects were neglected. The flow was analysed under fully developed flow conditions. Note that in the entry region h_m varies with x . Because boundary layer thickness is zero at the tube entrance the convection coefficient is extremely large at $x=0$. It drops rapidly as the boundary layer develops until it reaches a constant value at fully developed region.

In addition the two dimensional effects were ignored. The gradient normal to the surface is normally assumed to be much larger than that along the surface, which suggests that the diffusion rates for the y direction are much larger than those for the x direction. The assumption that the gradients in one direction only are considered to be significant is consistent with the one-dimensional approximation.

3.4 Materials and Investigation Methods

The porous ceramic materials tested in this work are calcia stabilised zirconia (CSZ) and magnesia-magnesium aluminate (MMA), and were supplied by Rolls Royce Research Strategic Centre in the form of approximately of 75mm x 75mm x 2mm plates. The CSZ samples, batch PCA1/98, had been fired at 1450°C for one hour and lapped, while the MMA samples, batch SP2/98, had been heated at 1550°C for one hour and also lapped.

The methods used within this work for the characterisation and the study of the structure of the porous materials are given in the following sections.

3.4.1 Scanning Electron Microscopy

Scanning electron microscopy (SEM) was performed for the investigation of pore morphology. Specimens of polished and unpolished surfaces, and cross sections of both ceramic materials, were first prepared and then observed using a scanning electron microscope. The unpolished surfaces were cold coated.

Typical micrographs were obtained under normal and higher magnification (400x), and revealed useful information about the microstructure of the porous samples. They are shown in chapter 5.

Prior to analysis, polished samples of the porous ceramics were prepared. These were first cut using a 10 *cm* diamond saw and water. The dry sample was then encapsulated in a 25 *mm* mould using Struers Specifix-20 epoxy resin. The section was removed from the mould and ground flat using a diamond grinder and a glass plate with 400 grit and 1000 grit aluminium oxide. The sample was then polished using 0.3 micron aluminium oxide with water on a Buehler Texmet cloth for 6 minutes followed by a final polish on Texmet cloth and 0-0.5 micron diamond paste and oil for 30 minutes.

3.4.2 Mercury Porosimetry

Mercury porosimetry is widely used to determine the pore size distribution of porous solids by the analysis of the mercury intrusion curve. It is performed nearly exclusively on automatic commercial instruments that differ mainly in the highest

operative pressure, which determines the size of measurable pores. In this method mercury, a non-wetting fluid, can be forced into the pores within the sample by application of pressure. This is described using Washburn's equation, which forms the basis of the data evaluation [6]:

$$P = \frac{-2\gamma \cos \theta}{r} \quad (3.25)$$

where P is the applied pressure, γ is the surface tension of mercury, θ is the contact angle between the mercury and the pore wall and r is the intrusion radius of cylindrical pores. As it can be seen from the above equation the applied pressure is inversely proportional to the radius of the pore or capillary through which the mercury must pass.

When the pressure is released after intrusion, the extrusion, i.e. retraction of mercury from the porous structure, reveals two phenomena: hysteresis between intrusion and extrusion and the entrapment of mercury when the pressure is reduced to one atmosphere. Furthermore, reintrusion from the entrapped state occurs when the pressure is again increased [7].

The total pore volume and the pore size distribution are determined by incrementally increasing the pressure of a mercury column above the sample and measuring the change in mercury height. Pressures of 33,000 *psia* or 227.50 *MPa* or even higher can be employed. The total intruded volume, the total pore surface area, the mean, mode, and median pore diameter, the material bulk density, the true density, and percent porosity can be determined by this method.

For the CSZ sample analysis, the Hg surface tension was 480.00 *erg cm⁻²*, the Hg contact angle was 130.00° and the applied pressure range during the intrusion was from 138.24 *kPa* to 207.04 *MPa*. In the MMA analysis the operation parameters were the same, with the applied pressure ranging from 138.10 *kPa* to 206.75 *MPa*. In this work the "PoreMaster® 33000" automated mercury porosimeter of Quantachrome Instruments was used. This pore size analyser achieves a maximum pressure 227.5 *MPa* for pore measurements in the range of 440 μm to 0.0064 μm pore diameter [8].

3.4.3 Archimedes Measurements

Immersing the porous sample in a liquid such as water causes the water to imbibe into all the open pores space. The sample is weighed accurately before and after immersion using an accurate laboratory balance. These two weights, coupled with the density of the water permit calculation of the pore volume. It is important to ensure that no air is trapped within the specimen. The bulk volume of the porous sample can be determined by simply measuring the dimensions of the plate. From the pore volume and the bulk volume the open porosity of the sample can be directly calculated. Similar tests were also carried out using ethanol.

3.5 Gas Chromatography

The analysis of the gas samples taken from both the inlet and outlet gas streams was made by a gas chromatograph, Ai Cambridge Q94 GC. The Q94 model is a high performance, modular instrument that contains precision ovens for the temperature control of the columns, the injection system and the detectors. Temperature programming of the column oven was also provided with a maximum of 4 different ramp steps in the program.

The instrument was controlled and its operation was monitored by an in-built Psion computer (94A). The various instrument parameters (oven temperatures, amplifier sensitivity settings etc) were set by means of 'direct' commands or by using stored methods. These methods consisted of complete assembled sets of commands required to run an analysis. Up to twenty methods in non-volatile memory could be stored in the Psion computer.

The output signals from the GC detectors were recorded by the data acquisition system, the JCL 6000 for Windows Chromatography Data System. Peak detection took place after data have been acquired. The detection proceeded according to the parameters defined in the integration parameters section of each method file. When the JCL 6000 for Windows performs its peak detection it passes through the chromatograph twice. First the peak detection routine determines peak start and maximum positions. Having passed through the whole chromatograph the routine then returns to the start of the chromatograph and begins to look for the peak end positions. To do this it starts at the first peak maximum (as detected in the first pass)

and moves down the falling edge of the peak looking for the point where the peak end criteria are met.

The peak identification was carried out on the basis of retention times. In order for the Chromatography Data System to recognise peaks of interest (and perform any concentration calculations), it was necessary to create a list of named peaks and the retention times at which they were expected.

3.5.1 Gas Chromatograph Components

A schematic diagram of the gas chromatograph used for the determination of gases such as H_2 , N_2 , CO , CO_2 and CH_4 , is shown in Figure 3.8. The GC was configured with a flame ionisation detector (FID) and a thermal conductivity detector (TCD). The instrument was also equipped with a 6-switch valve sampling loop for the injection of the sample. The volume of the sampling loop was 1 *ml*. Two columns were used for the separation of the gases: the porous polymer Porapak N and the molecular sieve 5A. An additional six-port switching valve was used for by-passing the molecular sieve.

The instrument also contains a precision oven for the temperature control of the column. The column oven temperature range is from 25°C to 450°C with the ability to cool from 250°C to 50°C in seven minutes. The minimum oven temperature allowed is normally 25°C. The maximum oven temperature is a function of the TCD detector current, the carrier gas and the detector type. For a given carrier gas, such as Ar or He used in these experiments, the relationship between the TCD maximum current and the temperature is linear.

In addition the Q94 GC has a number of gas control components. These are required to provide control of the column carrier gas flow, as well as of any additional gas flows required for the operation of the detectors. A soap bubble flow meter is used for measuring the flow rate of the carrier gas passing through the column and the flow rates of air and hydrogen necessary for the operation of the FID.

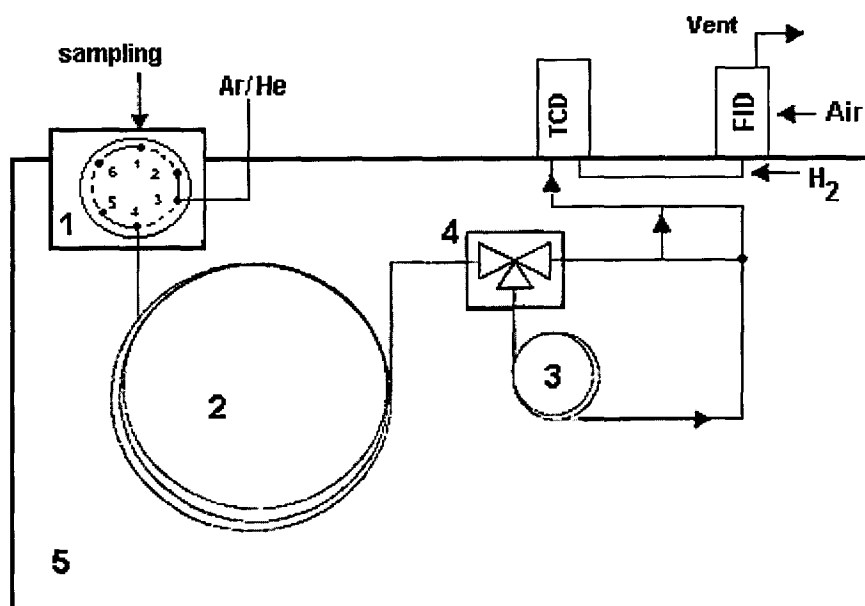


Figure 3.8: Schematic diagram of the Q94 gas chromatograph modified for determination of H_2 , N_2 , O_2 , CO , CO_2 and CH_4 . 1, 6-switch valve sampling loop; 2, Porapak N porous polymer column; 3, molecular sieve 5A column; 4, switching valve; and 6, oven.

3.5.1.1 GC Columns

The chromatographic columns configured in this instrument were a 3 m x 3.1 mm (1/8") I.D. stainless steel column packed with 80/100 mesh Porapak N (Waters Associates), and a 1.5 m x 3.1 mm I.D. stainless steel column packed with 40-60 mesh molecular sieve 5A.

The porous polymer column was mainly used for the separation of CO_2 , CH_4 and other hydrocarbons in combination with the FID. On the other hand the molecular sieve was suitable for the separation of the rest of the gases, H_2 , N_2 , O_2 , CH_4 , CO and H_2O using the TCD detector.

3.5.1.2 GC Detectors: FID

The Q94 gas chromatograph was equipped with flame ionisation (FID) and thermal conductivity (TCD) detection systems. The FID is by far the most widely used detector in gas chromatography. The FID responds to virtually all organic compounds but does not respond to water or inorganic gases such as He, Xe, H_2 , N_2 , O_2 , CH_4 , CO , SO_2 and NO_x .

The FID operation is based on a small jet through which passes the carrier gas flowing from the end of the column, mixed with hydrogen. Air is passed into the detector around the jet and the hydrogen is burnt as a small flame. A polarising voltage of 160V is applied to the jet above which is mounted a cylindrical collector electrode. The electrical current flowing between the jet and the collector electrode is amplified by the FID amplifier. When only carrier gas flows into the FID very little current flows between the electrodes. If an organic compound elutes from the column, this is ionised in the flame and produces an increase in current, which is then displayed as a peak.

The FID exhibits very good sensitivity and linear response characteristics. The FID used in this instrument has a sensitivity of $\sim 10^{-13}$ g solute/ml of carrier gas. The sensitivity or detection limit is defined as the minimum detectable concentration which the detector can detect a compound or as the amount of the sample in which the peak height is two or three times the noise height. The detector also has a very good linear dynamic range, 10^7 . This is the range where the peak area is directly proportional to the amount (concentration) of the compound and it lies between the minimum detection limit and detector saturation. This allows the quantification of the known samples using a multipoint calibration curve.

For the runs carried out in this work the FID operated at the following flow rates:

Carrier gas (Ar or He): 25-20 ml/min

Hydrogen: 30 ml/min

Air: 300 ml/min

3.5.1.3 GC Detectors: TCD

The thermal conductivity detector is widely used as a general purpose detector in gas chromatography. The TCD responds to any substance, which has a thermal conductivity different to that of the carrier gas. The detector is easy to use and only require a supply of the carrier gas.

The TCD of the Q94 GC model consists of a stainless steel block containing a number of passages through which the carrier gas can flow and into which are fitted four tungsten/rhenium filaments. These four filaments are electrically connected in a Wheatstone Bridge arrangement. Two of the filaments are mounted in connected

chambers, through which the carrier gas flows after passing through the GC column. The other two are mounted in connected passages through which a reference flow of the carrier gas flows.

The TCD is mounted on the lid of the column oven (see Figure 3.8) in a special oven designed to provide optimum temperature control for the detector. The two carrier gas inlets to the TCD are mounted on a bracket inside the column oven. The fittings mounted on this bracket are designed for use with 1/8" O.D. columns. The TCD may be used with two columns, one providing the reference flow while the other is being used for analysis. A single column may be used provided that a reference flow of gas is passed through the second channel of the detector.

It is essential that carrier gas flows over the detector filaments when electrical power is applied to the filaments. A flow rate of 25-40 *ml/min* of helium or argon through each side of the TCD is ideal. This flow rate is measured by attaching the bubble flow tube to the detector outlet pipe. A pressure sensitive switch is incorporated in the carrier gas inlet connection. This switch is designed to turn off the electrical power to the filaments if the carrier gas inlet pressure drops below 10 *psi*. Therefore before the current is switched on, it is always necessary to check that the carrier gas is passing through both channels of the detector and supplied at a pressure of 60 *psi* (4 *Bar*).

Apart from the flow rate of the carrier gas, the column and the detector temperature should also be established. The TCD should not be operated above 350°C. As mentioned above the TCD is mounted in an oven with a high thermal mass in order to ensure high thermal stability and it should be noted that it takes 1-2 hours for the detector to achieve its optimum thermal stability from switch on. The detector is used with the TCD amplifier, which provides the filament current for the TCD and controls the output signal.

The detection limit of the TCD detector is 1×10^{-7} *g/ml* of carrier gas (100 *ppm*), for gases like N₂, O₂, CO₂, CH₄. The linear dynamic range is in the order of 10⁶. The factors that affect the detector sensitivity are mainly the filament current and the difference in thermal conductivity between the sample compounds and that of the carrier gas. As the current increases the sensitivity increases too. Helium as a carrier

gas permits the use of the highest current and that will normally give the highest sensitivity.

But the sensitivity is also affected by the detector temperature, since the maximum filament current which can be used, given the choice the carrier gas, is a function of the detector temperature. The maximum filament current increases with the temperature of the detector block dropping, as shown in the plot in Figure 3.9.

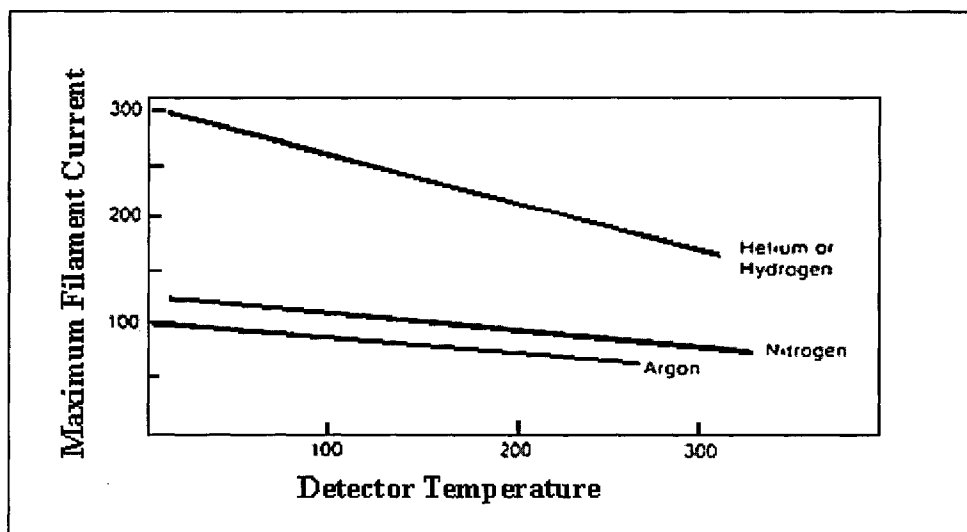


Figure 3.9: Maximum filament current as a linear function of the TCD temperature.

The advantage of the TCD is its simplicity, its large linear range, its general response to both organic and inorganic species, and its advantage over the FID that it is not destructive to the sample. The disadvantage of the detector is its limited sensitivity.

3.5.2 Preparation of the GC

Before a method could be run the preparation of the gas chromatograph had to be made. The first stage involved setting up the flow rates of the carrier gas and the gases necessary for the operation of the two detectors. Firstly the flow rate for the carrier gas was set up. This was usually adjusted at 25-27 *ml/min*. Then the hydrogen flow was set to 30 *ml/min* and finally the airflow to 300 *ml/min*. The flow rates were measured by removing the igniter cap from the top of the FID and inserting the bubble flow tube connecting adaptor into the top of the collector electrode.

Once the flow rate of the carrier gas was set the instrument could be switched on. At the next stage the temperatures of the column oven and the detectors were chosen. A typical value for the temperature of the column oven was 90°C while those for the FID and TCD were set at 150°C and 75°C respectively. The temperatures could be also entered when a method was loaded into the GC. A method consists of a list of parameters, including column and detectors' oven temperatures, which are specified for a particular analysis.

After measuring the gas flow rates, and as long as the FID temperature had reached the selected temperature (150°C), the FID was ready to switch on. The latter was done by reducing the air flow while pressing the “ignite” button on the status panel of the Q94 GC. A slight ‘pop’ was the indication that the flame had lit. Then the air pressure was turned back to the pressure required to give 300 *ml/min* flow. The flame was checked by holding a cold, bright spanner near one of the gas exit holes at the top of the detector. Condensation on the cold surface was the indication that the flame was alight.

The TCD was the next to be switched on. Through the menu in the in-built computer was possible to access the direct commands, set the temperature of the TCD oven and select the sensitivity of the detector amplifier and other parameters. The current of the TCD was specified to be 70 or 100 milliamps, the range was set to 10 the most sensitive, while the polarity was turned into positive. Again by loading the appropriate method for the particular analysis, these parameters could be directly entered.

The final step of the starting procedure involved the setting of the two valves fitted to the instrument. These are mechanisms that control the loading of the sample loop and the injection of the sample into the columns. They can be accessed by the DIRECT command in the top level menu of the software and the valves submenu is offered under the name VLV/ACC. The first valve was changed into ‘fitted’ and then two new parameters appeared that referred to the positions of the valve. The first state was set to ‘Load’ and the second state to ‘Inject’. The second valve was also set to ‘fitted’ and the two positions of this valve were selected to ‘Series’ and ‘By-pass’

For the analysis of the samples particular methods should be loaded. These GC methods had to be created by selecting the appropriate set of parameters and this task constituted the most important stage for the development of the GC operation. The basis under which the different parameters of each method were specified for the particular binary gas mixture is described in the next sections.

3.5.3 Creating the GC Methods

The Q94 GC is primarily controlled by the GC methods. A method consists of a set of parameters, including oven temperatures and amplifier sensitivity settings that determine the operating conditions of the instrument for a particular analysis. The method files can be stored for future use in the GC computer. On activation of a method, the instrument progresses through a series of states, which can be monitored in the different menus of the software.

As different gas pairs were used in the diffusion experiments, a number of different method parameters files had to be created. For each method file the desired parameters were selected in relation of the gases that consisted the binary mixture.

3.5.3.1 *H₂-N₂ GC Method*

The first binary mixture to be analysed was that of H₂-N₂. Ar was the carrier gas used in this method. It can be seen from Table 3.1 that the thermal conductivity of argon is much different from that of hydrogen while there is not such great difference from that of nitrogen.

Thermal Conductivities of Gases (at 100°C), $\frac{\text{cal}}{\text{s cm}^2} \times \frac{^\circ\text{C}}{\text{cm}} \times 10^{-5}$	
Hydrogen	45.9
Helium	36.9
Methane	8.6
Oxygen	6.6
Nitrogen	6.4
Carbon Monoxide	6.2
Water	4.5
Argon	4.4
Carbon dioxide	4.2

Table 3.1: Thermal conductivities of typical gases used in these analyses at 100°C [10].

For this reason the system is mostly selective to hydrogen and this was confirmed by the sharp, high, symmetrical response peaks obtained for it. The same chromatographs indicated that the right hand side, falling edge of the nitrogen eluted peaks would end in a tail which would cause a slight unsymmetry of its peaks. This is indicative of the poor adsorption of the nitrogen by inner walls and it may be attributed to the overloading of the column itself. However the binary mixture was well separated and that suggested that the choice of argon for the separation of these two gases was the appropriate one.

As mentioned previously the TCD maximum filament current which can be used is governed by the choice of the carrier gas and detector temperature. The range of currents offered by the instrument is 0, 70, 100, 125, 175-275 milliamps. With argon as a carrier gas, the above range of maximum filament currents is restricted to two choices 70 and 100 milliamps, clearly shown in the graph of Figure 3.9. In order to prolong the detector's filament life it is advisable to use the minimum filament current consistent with the necessary sensitivity for the application. Therefore a 70

milliamps filament current was selected in the method file and the corresponding TCD temperature was 75°C.

Table 3.2 gives the method file for the separation of the binary mixture of H₂-N₂ with all the necessary parameters defined.

Hydrogen-Nitrogen GC Method	
No of ramps	0
Equil time	0
Run temp	90°C (column oven temperature)
Run time	6:00
FID temp	150°C
TCD temp	75°C
FID/A Range	1 (1 is the most sensitive and 1000 the least)
Autozero/A	Yes (this option checks the temperature and adjusts the detector's output to be from 0-1V if temperature changes during the run)
ChartMK/A	No
TCD/C Range	10
TCD/C Current	70 milliamps
Carrier gas	Argon
Autozero/ C	Yes
ChartMK/C	No
TCD/C Polarity	+ve (change -ve if the peaks appear inversely)
Polarity events	None
Valve	Series
No of events	0
Inj time	0:00
V1 State	Load
No of events	1 (up to 8)
Inj time	0:10

Table 3.2: The set of the parameters of the method file for the mixture of H₂-N₂.

Although the TCD was the detector of choice for all the binary mixtures used in these analyses, the FID was recommended to be set. For this reason the parameters

related to FID operation were also specified in the method file as shown in the above table.

3.5.3.2 $\text{CH}_4\text{-N}_2$ GC Method

In the case of the binary mixture of methane and nitrogen a problem was experienced with regard to the co-elution of two components. The separation of the peaks of the two components can be achieved either by decreasing the temperature of the column oven or by reducing the flow rate of the carrier gas. Since the change of the carrier gas flow rate did not have any effect, the separation of the two peaks was made possible by decreasing the temperature of the column. The latter was changed from 90°C to 60°C. As a consequence the resolution was improved but the retention times became longer since species eluted more slowly.

Not only was the separation of the substances difficult to achieve but the detection of methane, especially in the gas stream which contained the uptake of diffusing gas through the porous support, was very poor. In order to get detectable amounts of methane, the sensitivity of the TCD detector had to be increased.

The choice of helium as a carrier gas permits the use of the highest filament current and this in turn will normally give the highest sensitivity for the TCD. It is evident from Figure 3.9 that the use of helium as carrier gas permits the application of filament currents up to 300 milliamps. Also helium gives a great difference in thermal conductivity with almost any of the typical gases except for hydrogen. Therefore the use of helium as a carrier gas in combination with the increase of the concentration of methane in the mixture under analysis resulted in sufficiently measurable amounts of methane diffusing through the support.

All the parameters configured in the new method file for gas pair of $\text{CH}_4\text{-N}_2$ are presented in the Table 3.3.

Methane-Nitrogen GC Method	
No of ramps	0
Equil time	0
Run temp	60°C (column oven temperature)
Run time	5:00
FID temp	150°C
TCD temp	75°C
FID/A Range	1 (1 is the most sensitive and 1000 the least)
Autozero/A	Yes (this option checks the temperature and adjusts the detector's output to be from 0-1V if temperature changes during the run)
ChartMK/A	No
TCD/C Range	10
TCD/C Current	100 milliamps
Carrier gas	Helium
Autozero/ C	Yes
ChartMK/C	No
TCD/C Polarity	+ve (change -ve if the peaks appear inversely)
Polarity events	None
Valve	Series
No of events	0
Inj time	0:00
V1 State	Load
No of events	1 (up to 8)
Inj time	0:10

Table 3.3: The set of the parameters of the method file for the mixture of CH₄-N₂.

3.5.3.3 *CO-N₂ GC Method*

For the binary mixture of CO-N₂, helium was also used as a carrier gas and the procedure related to the column oven temperature and the sensitivity of the TCD detector was also followed in this case. There was no need for a new method to be created because the same parameters specified in the method file for the binary mixture of methane and nitrogen applied to this binary mixture. The same method file was also used for the analysis of gas pairs that consisted of combinations of these gases such as that of methane and carbon monoxide.

For these mixtures the resolution was sufficient while the quantitative determination of the amount of methane diffusing through the porous medium provided adequate results.

3.5.3.4 *CO₂-N₂ GC Method*

The method for the analysis of the binary mixture consisting of carbon dioxide was based on the methodology that has already been explained in the above sections. The only difference in the specified parameters of this method was the use of the by-pass state for the switching valve. The latter was necessary because of the presence of the carbon dioxide in the mixture.

Carbon dioxide is retained by the porous polymer column enabling its separation from the other component, nitrogen, while the molecular sieve column permanently absorbs the carbon dioxide and this makes its detection not feasible. Since the two columns are connected in series (porous polymer column is the first followed by the molecular sieve) the components will pass eventually through both the columns. Therefore carbon dioxide is retained permanently by the molecular sieve. This also degrades the resolution of nitrogen or of other components if there are present in the mixture. The solution to this problem is the change of the state of the switching valve from series into by-pass for by-passing the molecular sieve so that no more the components pass through the second column.

In Table 3.4 all the parameters of the method file for the gas pair of CO₂-N₂ are shown.

Carbon Dioxide-Nitrogen GC Method	
No of ramps	0
Equil time	0
Run temp	60°C (column oven temperature)
Run time	5:00
FID temp	150°C
TCD temp	75°C
FID/A Range	1 (1 is the most sensitive and 1000 the least)
Autozero/A	Yes (this option checks the temperature and adjusts the detector's output to be from 0-1V if temperature changes during the run)
ChartMK/A	No
TCD/C Range	10
TCD/C Current	100 milliamps
Carrier gas	Helium
Autozero/ C	Yes
ChartMK/C	No
TCD/C Polarity	+ve (change -ve if the peaks appear inversely)
Polarity events	None
Valve	By-pass
No of events	0
Inj time	0:00
V1 State	Load
No of events	1 (up to 8)
Inj time	0:10

Table 3.4: The set of the parameters of the method file for the mixture of CO₂-N₂.

It was also necessary to ensure that changing from series to by-pass position would not affect the pressure in the columns. Thus the flow rate of the carrier gas was first measured with the valve in series state and it was measured again with the valve in by-pass position. Any differences were corrected by adjusting the needle valve located on the box on the left hand side of the instrument. This made sure that the flow rate of the carrier gas was the same all the way through the two columns. Therefore no major deviations in the retention time of carbon dioxide would occur.

It should be noted that the change of the switching valve position from series to by-pass did not require specifying any events in the corresponding parameters in the method file. This was because the mixture consisted of two components. However in the case of a ternary mixture, for instance one including N_2 -CO-CO₂, the above procedure would be different.

The analysis of such a mixture should consist of successive changes of the valve position such as series/by-pass/series and in the method file the number of events should be switched on to two. The first series would enable components like CO and N_2 to be directed to the molecular sieve column.

Having noticed the retention times of these components the valve should then switch to by-pass position (first change-event) for the separation of CO₂, at a shorter time than their retention times. The by-pass state would allow CO₂ to be retained by the porous polymer column and elute.

The final stage would involve the change of the valve back to the series position. The second change-event should take place after the retention time of CO₂. This final change would allow N_2 and CO to be retained by the molecular sieve column and finally elute at different retention times.

An alternative option could be the use of a methaniser. This converts compounds like CO and CO₂ into CH₄ which then pass through both columns and they are detected by the FID. The use of the CH₄ converter is necessary, as the FID does not respond to inorganic compounds and gases like CO and CO₂. It is important to mention that all the gas analyses involved the use of the TCD. The FID was not used

for any gas detection, though it was set up from the beginning mainly to burn out any impurities in the gas streams.

3.5.4 Calibration of the GC

The calibration procedure involved the analysis of a number of standard samples for each binary gas mixture of interest. The standard binary mixtures were prepared with the aid of the thermal-mass flow meters controllers mixing the selected gases of known concentrations. At least three or four composition levels covering the range of suspected gas concentrations were prepared for each binary mixture.

At the initial stages, for a measurement of a binary mixture the calibration was performed twice a day. Subsequently the calibration was only repeated each time that the porous sample was changed.

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Chapter 4

Interpretation of Binary Diffusion Measurements

4.1 Introduction

Diffusion of gases in the fine pores and capillaries of porous media is important in many areas of physical and engineering sciences, such as that of the heterogeneous catalysis involving porous materials. A large part of the processes in the chemical industry involve catalytic reactions on porous solid catalysts. Furthermore the use of porous materials with catalytic properties is extended into other areas of interest like electrochemistry. Electrochemical devices such as fuel cells incorporate porous electrodes and substrates, which allow the transport of gaseous species in and out of the cell and the electrochemical reactions to occur.

Therefore diffusion experiments in porous media are needed in order to investigate the interaction between gas transport and the structure of such materials. These experiments are generally performed using an open or a closed system. A closed system is characterised by a closed volume at each end of the diffusion path. In an open system, the closed volume is replaced by gas streams that flow by each end of the diffusion path [1], such as the Wicke and Kallenbach diffusion cell. This technique has been used in this work for the measurement of the effective diffusivities and has been described in detail in the chapter of the experimental procedure.

This kind of experiment involves diffusion measurements, which allow the calculation of the effective diffusion coefficients of the gases in interest. The proper interpretation of diffusion data obtained by such experiments requires the detailed understanding of the dominant transport mechanisms and the right choice of appropriate transport equations.

In the case of the continuum region and when there is not a pressure difference across the porous medium, gas transport occurs only by ordinary diffusion. This transport mechanism has been well studied and the fundamental equations describing the diffusion of a binary gas mixture through a porous medium have been reviewed in a number of studies.

This chapter discusses the general approach and equations (mole conservation equations) used to analyse the steady, one-dimensional diffusion for a binary gas mixture in a porous medium. It also shows that the requirement of constant pressure results in equimass counterdiffusion rather than the widely assumed equimolar counterdiffusion. This also explains why Fick's Law used for such analysis gives the incorrect results. A solution for the equimass case is given for more general boundary conditions different from those usually taken. A limited case of the solution for the equimass situation is also provided.

4.2 Interpretation of Diffusion Measurements

The description of diffusion in the molecular or continuum region, as well as in other regions, requires careful attention to the use of the proper flux in defining the diffusion coefficient. It has been reported [2] that in general the Fick's first law often used, is not correct with respect to a system of fixed coordinates for ordinary diffusion in a small channel, when the total pressure is constant at both ends of the diffusion path. Therefore, it is necessary to know what the relative rates of transport of each gas will be, if the appropriate diffusion equations are to be applied.

4.2.1 General Equation of Diffusive Fluxes

Just as momentum and energy have two mechanisms for transport, molecular and convective, so does mass transfer. However, there are convective fluxes in mass transfer, even on a molecular level. The reason for this is that in mass transfer, whenever there is a driving force, there is always a net mass flux of a particular species, which results in a bulk motion of molecules (of course there can also be convective mass transport due to macroscopic fluid motion).

The flux of species defined with reference to fixed spatial coordinates, J_A ($\text{kmol}/\text{m}^2 \text{ s}$) is

$$J_A = c_A v_A \quad (4.1)$$

with v_A (m/s) the velocity of species A relative to fixed spatial coordinates

This could be written in terms of diffusion velocity of a species A , (i.e., $v_A - v$) and the average velocity of a mixture, v , as

$$J_A = c_A(v_A - v) + c_A v \quad (4.2)$$

The molar average velocity is defined as

$$v = \frac{\sum_{i=1}^N c_i v_i}{\sum_{i=1}^N c_i} = \frac{\sum_{i=1}^N c_i v_i}{c} \quad (4.3)$$

Therefore, equation (4.2) becomes

$$\begin{aligned} J_A &= c_A(v_A - v) + \frac{c_A}{c} \sum_{i=1}^N c_i v_i \\ &= c_A(v_A - v) + x_A \sum_{i=1}^N c_i v_i \end{aligned} \quad (4.4)$$

Considering a system containing two gaseous components A and B ,

$$\begin{aligned} J_A &= c_A(v_A - v) + x_A(c_A v_A + c_B v_B) \\ &= c_A(v_A - v) + x_A(J_A + J_B) = c_A(v_A - v) + x_A J_{tot} \end{aligned} \quad (4.5)$$

The first term on the right hand side of this equation is the diffusional molar flux of A and the second term is the convective molar flux (or bulk motion).

For a system containing two gaseous components A and B , Fick's Law, which gives the diffusional molar flux, is defined by

$$J_{diff,A} = -D_{AB} \frac{dc_A}{dz} \quad (4.6)$$

or

$$J_{diff,A} = -\frac{P}{RT} D_{AB} \frac{dx_A}{dz} \quad (4.7)$$

Note that the flux $J_{diff,A}$ is a local flux with respect to the molar average velocity v .

Substitution of the above expression of Fick's Law into Equation (4.5) yields the following relation,

$$J_A = -\frac{P}{RT} D_{AB} \frac{dx_A}{dz} + x_A J_{tot} \quad (4.8)$$

with $J_{tot} = J_A + J_B \quad (4.9)$

Again, it must be noted that the diffusional molar flux is with respect to the molar average velocity, while the flux J_A is taken with respect to fixed spatial coordinates. A similar expression can be written for the component B .

In describing measurements of steady counterdiffusion, for the study of diffusion of gases in porous catalysts and media, many investigators have assumed equimolar counterdiffusion:

$$J_A = -J_B \quad (4.10)$$

With this assumption, equation (4.8) reduces to Fick's first law. However this condition has not been verified experimentally, since equimolar fluxes have not been observed in experiments involving steady state, binary counterdiffusion. According to Rothfeld [3], the first to consider the fact that the net flux $J_{tot}=J_A+J_B$ was not zero in such experiments was Hoogschagen [4]. Previous workers had assumed (erroneously) that $J_A+J_B=0$, presumably by analogy with the closed vessel case. However even in a closed volume case and for uniform pressure, it will be shown in the analysis of the dusty gas approach in chapter 6 that there is a net flux contribution to the diffusive flux.

Hoogschagen [4] first observed that the fluxes are inversely proportional to the square roots of the molecular weights. This observation was explained by Hoogschagen [4,5] in terms of momentum transfer to the walls of the pores. This result was initially considered to hold for the Knudsen range, but it was shown by Dullien and Scott [6] that it also applies to the ordinary diffusion range as well as to the intermediate region. The broad range of validity of this relationship was also reported and confirmed by Hewitt et al [7] in a review of the various phenomena involved in gaseous diffusion in porous media.

Moreover a number of experimental investigations in the ordinary diffusion range as well as in the intermediate region have confirmed the relationship between flux and molecular weight. In studies by Remick and Geankoplis [1] and Scott and Dullien [2], measurements of both fluxes in steady state counterdiffusion experiments under uniform pressure in the transition region showed a reasonable agreement between the experimental binary flux ratios and the predicted square root relationship. In an investigation by Evans and co-workers [8], experiments carried out with helium and argon at uniform pressure in the ordinary diffusion range showed that the square root relationship was followed in every case.

In all these studies, Equation (4.8) has been used along with the relation between the fluxes J_A and J_B and the molecular weights,

$$\frac{-J_A}{J_B} = \left(\frac{M_B}{M_A} \right)^{1/2} \quad (4.11)$$

to treat the experimentally obtained diffusion data. For example the flux J_B , can be eliminated from Equation (4.8) with the aid of Equation (4.11), and the resulting equation can be integrated under the appropriate boundary conditions yielding a direct relation between the flux and the concentration gradient for the particular problem. If these quantities are measured in a diffusion experiment the calculation of the binary effective diffusion coefficient of the gas mixture is straightforward.

Hence for the boundary conditions of $x_A = x_{A0}$ at $z=0$ and $x_A = x_{AL}$ at $z=L$, the integration of Equation (4.8) gives:

$$J_A = -D_{AB}^{eff} \frac{P}{RTL\alpha} \ln \left[\frac{1 - \alpha x_{AL}}{1 - \alpha x_{A0}} \right] \quad (4.12)$$

with $\alpha = 1 + J_B/J_A$ and L being the thickness of the porous medium. It is easy to see that when the mole fraction of the species at the two end surfaces of a porous medium and the flux are measured, the effective diffusivity can be easily obtained.

As already mentioned above, Equation (4.6), Fick's Law describes the diffusional flux and a careful definition of the frame of reference is essential for its clear

statement. Generally the flow should have the same quantity reference as concentration and most importantly the volume should have the same length references as A and z (or y), the cross-section and the distance along the diffusion path respectively. For example the frames of reference in porous media usually are:

- i) the entire bulk porous medium (subscript, m)
- ii) fluid phase only (subscript, f)

For a fluid phase with no porous medium Fick's Law takes the form of,

$$F_A = -D_{AB,f} A_f \frac{dc_{A,f}}{dz_f} \quad (4.13)$$

Equation (4.13) and Equation (4.6) both refer to fluid phase only. In Equation (4.13) Fick's Law has been written for the flow F_A (kmol/s) with A_f (m^2) being the cross-section normal to direction of diffusion. Several changes to Equation (4.13) are necessary if the system now contains a porous medium. We can define the tortuosity τ and porosity ε as,

$$\tau = \frac{z_f}{z_m} \quad (4.14) \quad \text{and} \quad \varepsilon = \frac{A_f}{A_m} \quad (4.15)$$

where z_f is the effective gas diffusion path length, z_m is the external length of the porous medium (or its thickness), while A_f is the area of the pores or the effective flow area in the porous medium and A_m the bulk area of the porous medium.

Substituting Equations (4.14) and (4.15) in (4.13) yields:

$$F_A = -D_{AB,f} A_m \frac{\varepsilon}{\tau} \frac{dc_{A,f}}{dz_m} \quad (4.16)$$

The effective diffusion coefficient $D_{AB,m}^{eff}$ may be defined as,

$$D_{AB,m}^{eff} = D_{AB,f} \frac{\varepsilon}{\tau} \quad (4.17)$$

Equation (4.17) relates the molecular or free diffusion coefficient with respect to fluid phase to the effective diffusion coefficient which refers to the porous medium. The above equation will be revisited in chapter 5. It is now possible to write Fick's Law using as the frame reference the entire bulk medium:

$$F_A = -D_{AB,m}^{eff} A_m \frac{dc_{A,f}}{dz_m} \quad (4.18)$$

In Equation (4.19) F_A has units of $kmol/s$ and does not need to be referenced (i.e. subscripted), while concentration $c_{A,f}$ is expressed as $kmol$ per unit volume of gas fluid phase. It is important to note here that the concentration has not been written with reference to total volume of bulk medium as it is more common to express solute concentration as $kmol$ per unit volume of gas fluid phase ($c_{A,f}$) than to express it per unit total volume of porous medium. According to the above equation, the effective diffusion coefficient $D_{AB,m}^{eff}$ for the porous medium is defined as the ratio of flow F_A to the concentration gradient and the total cross section normal to direction of diffusion:

$$\begin{aligned} D_{AB,m}^{eff} &= \frac{kmol\ s^{-1}}{\left(\frac{kmol}{m^3\ of\ fluid}\right)\left(\frac{1}{m}\ of\ porous\ medium\right)\left(m^2\ of\ porous\ medium\right)} = \\ &= \frac{m^3\ of\ fluid \times s^{-1}}{m\ of\ porous\ medium} = m^2\ s^{-1} \end{aligned} \quad (4.19)$$

4.2.2 Equimass and Equimolar Counterdiffusion

The general set of equations seen in the previous analysis constitutes the common way of treating diffusion data obtained by diffusion measurements for binary mixtures in porous media under steady state conditions and uniform pressure. An alternative method for treating and processing diffusion data is introduced in these sections. It is shown that this type of experiment under constant pressure and temperature, should be analysed assuming equimass counterdiffusion rather than equimolar counterdiffusion, which eventually leads to incorrect results. This has been assisted by a few, recent studies [9,10], which have examined and clarified the

true nature of binary diffusion on mass and molar basis and the implications of a constant pressure on such a system.

Two cases of steady state, one-dimensional diffusion in an isothermal, inert binary gas mixture of components A and B are considered and J denotes the molar flux while G is the mass flux (both per unit area).

4.2.2.1 Equimass Counterdiffusion

On a mass basis the species and mass conservation equations, for the component A , reduce to:

$$G_A = m_A G_{tot} + J'_{diff,A} \quad (4.20)$$

or
$$G_A = m_A \rho v' + J'_{diff,A} = const. \quad (4.21)$$

and
$$G_{tot} = \rho v' = const. \quad (4.22)$$

where G_A is the absolute mass flux of component A (relative to stationary coordinate axes) in $kg/m^2 s$, m_A is the mass fraction, ρ is the density in kg/m^3 , v' is the mass average velocity in m/s and $J'_{diff,A}$ is the mass diffusion flux relative to v' in $kg/m^2 s$.

For a constant pressure system, the mass average velocity is zero. This follows from momentum equation (Newton's second law of motion). Hence $G_{tot}=0$ and introducing Fick's Law, Equation (4.20) becomes:

$$G_A = J'_{diff,A} = -\rho D_{AB}^{eff} \frac{dm_A}{dz} \quad (4.23)$$

and assuming an ideal gas mixture,

$$\rho = \frac{PM}{RT} \quad (4.24)$$

where
$$\frac{1}{M} = \frac{m_A}{M_A} + \frac{m_B}{M_B} \quad (4.25)$$

the following form of Equation (4.23) is obtained:

$$J'_{diff,A} = - \frac{PM_A M_B D_{AB}^{eff}}{RT [m_A (M_B - M_A) + M_A]} \frac{dm_A}{dz} \quad (4.26)$$

Taking as boundary conditions, $m_A = m_{A0}$ at $z=0$ and $m_A = m_{AL}$ at $z=L$, integration of Equation (4.26) yields for the diffusion flux:

$$J'_{diff,A} = - \frac{PD_{AB}^{eff}}{RTL} \frac{M_A M_B}{(M_B - M_A)} \ln \left[\frac{m_{AL} (M_B - M_A) + M_A}{m_{A0} (M_B - M_A) + M_A} \right] = -J'_{diff,B} \quad (4.27)$$

with L length of the pore tube of the porous medium. A zero mass average velocity means that there is not net contribution (convective flux) to the diffusive flux and $G_A = J'_{diff,A}$, $G_B = J'_{diff,B}$.

A limited case is identified for Equation (4.26) when the two components have identical molecular weights. For instance the gases CO and N₂ have the same molecular weights, molecular shape and size and electronic configuration; that is they are isosteric molecules. In this case the molecular weight for the mixture reduces to $M = M_A = M_B$ and Equation (4.19) takes the simple form,

$$J'_{diff,A} = - \frac{PD_A^{eff} M_A}{RT} \frac{dm_A}{dz} \quad (4.28)$$

Another characteristic of such a case is that the binary diffusion coefficient reduces to the self-diffusion coefficient. Equation (4.28) is easily integrated for the prescribed boundary conditions and gives a typical linear profile for the mass fraction of component A across the length L .

4.2.2.2 Equimolar Counterdiffusion

On a molar basis the governing species and mole conservation equations are,

$$J_A = x_A J_{tot} + J_{diff,A} \quad (4.29)$$

$$\text{or} \quad J_A = x_A c v + J_{diff,A} = \text{const} . \quad (4.30)$$

$$\text{and} \quad J_{tot} = c v = \text{const} . \quad (4.31)$$

where J_A is the absolute molar flux of component A (relative to stationary coordinate axes) in $\text{kmol/m}^2 \text{ s}$, x_A is the mole fraction, c is the molar concentration in kmol/m^3 , v is the molar average velocity in m/s and $J_{diff,A}$ is the molar diffusion flux relative to v in $\text{kmol/m}^2 \text{ s}$.

A solution of these equations is:

$$v=0, \quad J_{diff,A} = -c D_{AB}^{eff} \frac{dx_A}{dz} = -J_{diff,B} = \text{const} . \quad (4.32)$$

A conclusion cannot be made from this result that the pressure and molar concentration are necessarily constant (they are not). If pressure and hence temperature are assumed constant then from Equation (4.32),

$$\frac{dx_A}{dz} = \text{const} . \quad (4.33)$$

Again taking the boundary conditions, $x_A = x_{A0}$ at $z=0$ and $x_A = x_{AL}$ at $z=L$, integration of Equation (4.32) yields for the diffusion flux:

$$J_{diff,A} = \frac{c D_{AB}^{eff}}{L} (x_{A0} - x_{AL}) = -J_{diff,B} \quad (4.34)$$

Since $v=0$, there is no molar convective flux and $J_A = J_{diff,A}$, $J_B = J_{diff,B}$.

These results are now discussed with regard to the common diffusion situation of the two chambers containing with gases A and B and connected by a tube, as Figure 4.1 illustrates:

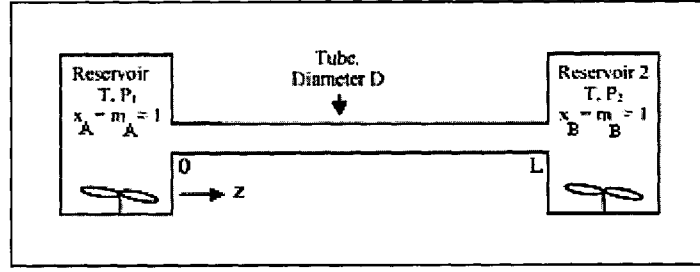


Figure 4.1: The diffusion problem of the two chambers connected with a tube for illustrating the equimolar diffusion problem [9].

Note that in the place of the two chambers can be gas streams. It is usually specified that the pressures in the two chambers or streams are equal and that the pressure is maintained constant everywhere. Therefore the pressure is constant in the connecting tube. Under such conditions, this situation is represented precisely by equimass counterdiffusion and its analysis.

However, standard texts [11,12] and studies have incorrectly assumed that the diffusion is equimolar. By studying the implications of equimolar counterdiffusion, it can be shown that the analysis under such conditions is not correct.

Although the molar average velocity v is zero, the mass average velocity v' is not zero, because

$$\begin{aligned} \rho v' &= G_A + G_B = M_A J_A + M_B J_B = M_A J_{diff,A} + M_B J_{diff,B} \\ &= M_A J_{diff,A} - M_B J_{diff,A} = J_{diff,A} (M_A - M_B) \end{aligned} \quad (4.35)$$

and

$$v' = J_{diff,A} \frac{(M_A - M_B)}{\rho} \quad (4.36)$$

Hence, Equation (4.36) shows that if $M_A < M_B$ the mass average velocity is in negative z -direction and increases in the direction of the flow. Therefore there must be a pressure gradient required to accelerate the flow. This can also be explained by considering the fact that the faster light molecules (M_A) tend to get through the tube more quickly than the slower, heavy ones (M_B). As a result of this the pressure rises on the side of the heavy gas (vessel 2 in Figure 4.1) until the viscous flow induced back through the tube (viscous flow caused by this temporal small pressure difference) is just sufficient to make the net flux zero again. Therefore the assumption of equimolar counterdiffusion does not agree with the specified constant pressure.

The situation in the connecting tube is even more complicated since the equimolar counterdiffusion cannot be one-dimensional. Due to the no slip condition at the walls the mass average velocity approaches the zero and the diffusion there is equimass and not equimolar. Thus Equations (4.30) and (4.31) do not apply and two-dimensional equations have to be written.

From the foregoing discussion it becomes apparent that the requirement of the constant pressure results in equimass rather than the equimolar counterdiffusion. It was proved why the equimolar counterdiffusion fails to describe correctly diffusion problems such as that of the two vessels or streams of gases connected by a tube and that the analysis made on a molar basis is inappropriate.

4.3 Conclusions

The general method of interpreting experimentally obtained diffusion data for binary gas mixtures through porous media was presented. An alternative approach to the problem of steady state, one-dimensional diffusion in an isothermal binary gas mixture under constant pressure was also shown. Under conditions of uniform pressure the equimass counterdiffusion is the correct approach. The discussion also demonstrated that the analysis of such diffusion problems under the assumption of equimolar counterdiffusion is inappropriate and incorrect.

In this work the interpretation of the data obtained by the diffusion measurements and presented in chapter 5 was made by applying the equimass counterdiffusion analysis. In particular the effective diffusivities were calculated by applying a mass balance in the diffusion cell and employing Equation (4.27). To the author's knowledge this is the first time that diffusion data from such measurements have been analysed on mass basis assuming equimass counterdiffusion.

4.4 References

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Chapter 5

Results and Discussion

5.1 Introduction

The structure of chapter 5 is divided into two major parts for clarity.

The first part of this chapter discusses the findings and the results of the microstructural investigation of the porous ceramic substrates. From previous work on porous ceramic materials, it has been observed that a number of parameters are necessary for the characterisation of the porous structure. These include the total and open porosity, the pore volume, the surface area, the bulk and apparent density as well as the pore size distribution.

The main characterisation techniques, employed within this work for the study of the porous substrates, were the following:

- (i) Scanning electron microscopy (SEM) is considered to be the primary tool for the visualisation of porous surfaces. It was used for the observation and assessment of the pore morphology and structure.
- (ii) Mercury porosimetry for the estimation of the open porosity, the pore volume, the surface area and the calculation of the mean diameter and of the pore size distribution.
- (iii) Water and ethanol uptake experiments for an estimation of the open porosity. The tests were carried out mainly to back up the mercury porosimetry measurements. The method is considered to be a crude approach of assessing the open porosity.
- (iv) Image analysis, for the estimation of total porosity and mean pore diameter. The procedure was applied to polished cross section of the porous substrates. The interactive UTHSCSA Image Tool for Windows was used.

The basic principles of the above investigation techniques were introduced earlier in chapter 3. Whenever it is necessary additional information is given here for the understanding of a technique. In particular, for the mercury porosimetry, which constitutes the main characterisation technique in this work, the theory along with the fundamental equations are explained further. This leads to the understanding and the interpretation of the plots generated by the porosimetry data.

In the second part of the chapter the results of the diffusion measurements are presented and analysed. First the precision of the measurement technique is discussed and sources of error are identified. Some basic statistical calculations on the data were performed to estimate the size of analytical errors.

Next the results of the experimental determination of the effective diffusion coefficients are given. Firstly the results of the measurements that were carried out on both porous substrates with binary gas mixtures are presented. These gas pairs consisted of nitrogen and the gaseous species relevant to solid oxide fuel cell anode operation (H_2 , CH_4 , CO_2 and CO) as well as different combinations of the gases with each other (i.e. CH_4 - CO).

The effect of the composition of the tracer gas and of the flow rate on the measured effective diffusion coefficients is established. Analysis of these findings attempts to correlate the observed trends and variations, employing the fundamental aspects of the kinetic theory of gases. The experimentally measured effective diffusivities are correlated with the physical properties of the porous materials. Comparisons were also drawn between the experimental data and existing theoretical models for diffusion in porous media (e.g. the dusty gas model) and this in turn enabled extraction of the tortuosity.

The results of diffusion tests, obtained from using different samples of the same porous substrate are also given. They are analysed and compared with those results taken from the measurements of the initial samples.

5.2 Microscopy

Typical micrographs of the CSZ and MMA porous substrates, obtained by the scanning electron microscopy are presented below. In Figures 5.1 and 5.2 the microstructure of the polished and the unpolished flat surface of the CSZ substrate is shown. The first micrograph revealed a surface with a number of big particles distributed randomly within a matrix of smaller grains. The pattern of the pores resembles a network of channels possibly interconnected. In Figure 5.2, a higher magnification (400 times) SEM image of the unpolished surface shows a different picture. As the surface is not polished, surface texture is less organised with much roughness.

An example of the cross section of a fracture surface is shown in Figure 5.3 and illustrates the fine microstructure of the CSZ substrate. This consists of rounded grains with an interior of rather large pores ($\sim 2.5\mu\text{m}$). The initial observation taken from the images of the flat surfaces of the sample is verified here. It is clear from this image that the void structure may be pictured as a series of interconnected channels. A close observation of the fracture surface reveals also useful information about the area of contact between the grains, which is an indication of the strength of the ceramic. The fracture surface of this sample showed close inter-grain contact areas.

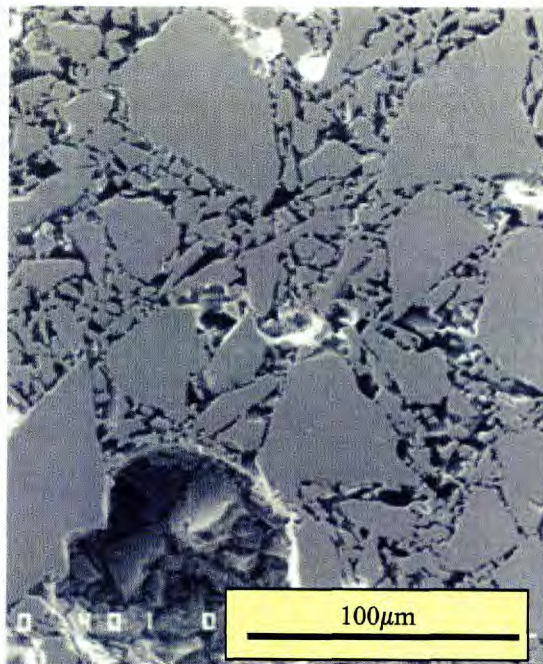


Figure 5.1: SEM micrograph of a polished surface of the CSZ substrate.

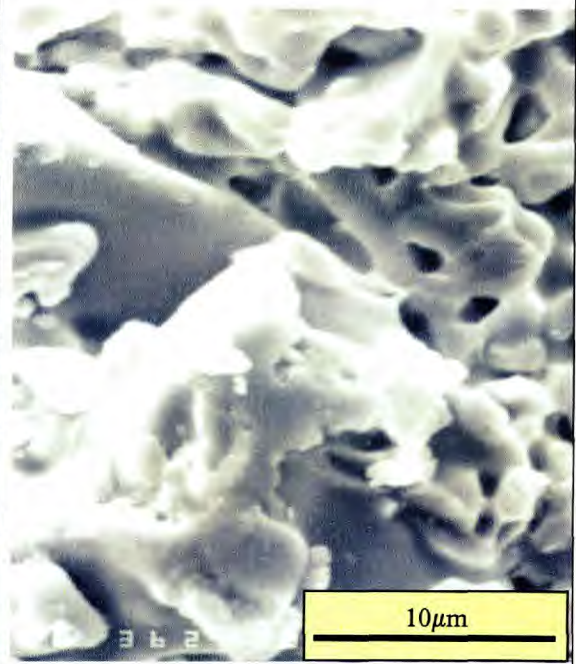


Figure 5.2: SEM image of the CSZ unpolished surface.

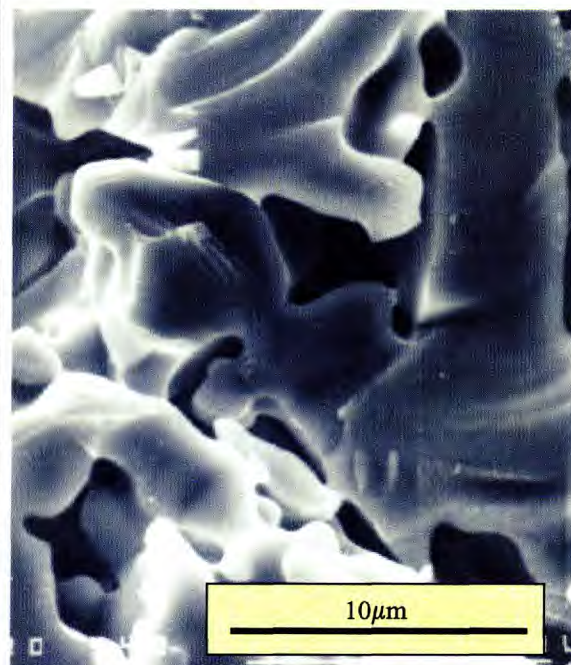


Figure 5.3: SEM micrograph of the unpolished fracture edge of the CSZ substrate.

Figures 5.4 and 5.5 show the SEM micrographs of the polished and the unpolished flat surface of the MMA substrate. The images revealed surfaces with smaller number of pores that tend to be nearly closed with a size of 2 to 3 microns. After careful inspection it was evident from the micrograph of the unpolished surface that there was, to some extent, coating of loose grains.

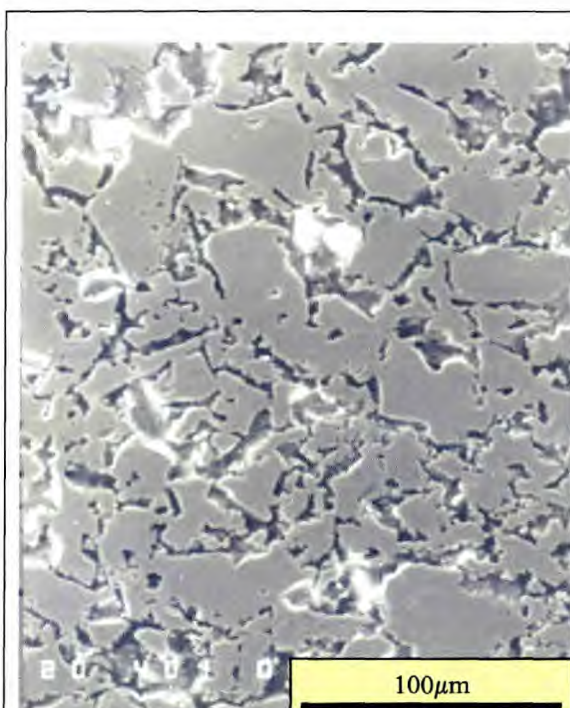


Figure 5.4: SEM micrograph of a polished surface of the MMA sample.

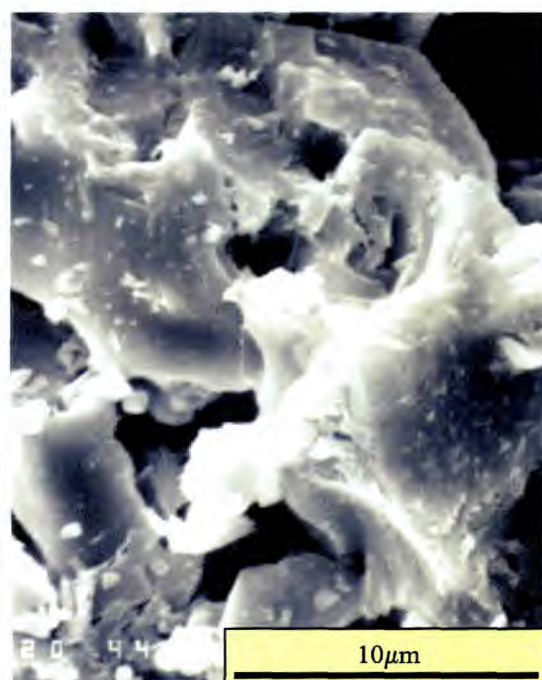


Figure 5.5: SEM micrograph of an unpolished surface of the MMA sample.

A comparison between the polished surfaces of the CSZ and MMA samples, Figures 5.1 and 5.4 respectively, shows a different pore structure. The pores of the CSZ look like a network of channels, which are well connected to each other. On the other hand, most of the pores of the MMA seem to be nearly closed and only partially connected to each other.

In comparison to the corresponding image of the unpolished surface of the CSZ of Figure 5.2, the MMA sample (Figure 5.5) exhibited less rounded grains and more surface roughness. This might be attributed to the irregular shape and size of the grains due to non-homogenous composition, obtained during the final stages of the production of the substrate. This generally involves various stages and by varying the parameters of the process e.g. binder content, the size and the distribution of the

tiny agglomerates can be changed [1]. The irregular shape and size of the aggregates might also explain the partial connectivity of the void volume in the MMA sample. In the following sections in this chapter (mercury porosimetry), this characteristic will be related to network models proposed by various researchers in an attempt to visualise and then describe the void structure of porous materials.

The microstructure of the MMA substrate, as illustrated in the cross sectional view of the fracture surface below, Figure 5.6, showed evidence of rather angular grains (at least less rounded than those of the CSZ substrate). This is consistent with the picture obtained from the flat surfaces.

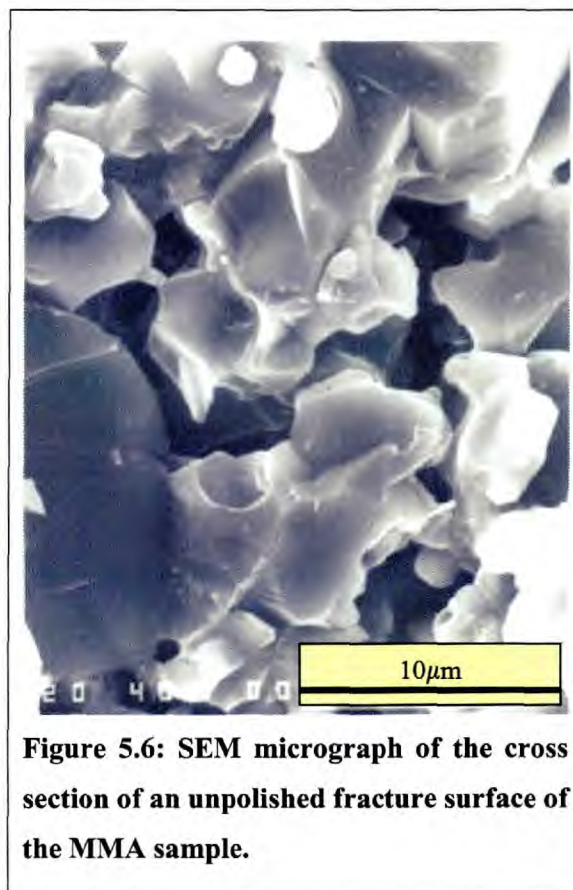


Figure 5.6: SEM micrograph of the cross section of an unpolished fracture surface of the MMA sample.

There was not strong evidence of close contact areas among the grains. It can be said that due to the angular shape of the grains, the MMA substrate showed weaker inter-grain contact areas than those of the CSZ sample. However this is not completely clear but it is the impression taken after an initial observation of the corresponding micrographs.

5.3 Mercury Porosimetry

The mercury-penetration is widely accepted as a standard method for measuring the distribution of pore volumes in a sample when the pores are in the macropore (pores $>50\text{ nm}$) or large mesopore range (pores between $2\text{-}50\text{ nm}$). It depends on the fact that the mercury has a significant surface tension and is a non-wetting fluid. Therefore the pressure required to force mercury into the pores of a porous sample depends on the porous radius. The pressure varies inversely with the radius according to the Washburn's equation [2] (introduced previously in the chapter 3 and revisited here):

$$P = \frac{-2\gamma \cos \theta}{r} \quad (5.1)$$

where P is the applied pressure, γ is the surface tension of mercury, θ is the contact angle between the mercury and the pore wall and r is the intrusion radius of the pore (assuming cylindrical pores). The above equation is derived from a force balance [2] on the fluid meniscus, where the force exerted at the perimeter of the meniscus by the surface tension $F = 2\pi r\gamma \cos \theta$, is balanced by the pressure force on the meniscus, $F = \pi r^2 P$. The Washburn equation dictates that, as the pressure is increased the mercury will intrude into progressively narrower pores, assuming that γ and θ are constant.

5.3.1 Pore Volume Distribution and Penetration Curve of the CSZ

Substrate

One of the most important characteristics of a porous structure is the pore volume distribution, which is the distribution of void volume according to the size of the pore. It is a very difficult problem to evaluate/calculate this distribution because the void spaces in a given particle are usually nonuniform in size, shape and length and normally are interconnected. These void spaces are usually simulated as cylindrical pores, and thus the size of the void spaces is interpreted as a radius of a cylindrical pore. Therefore the distribution of the pore volume is defined in terms of this variable [3].

In Figure 5.7, the pore volume distribution curve is shown for the CSZ sample as generated by the data obtained by mercury porosimetry.

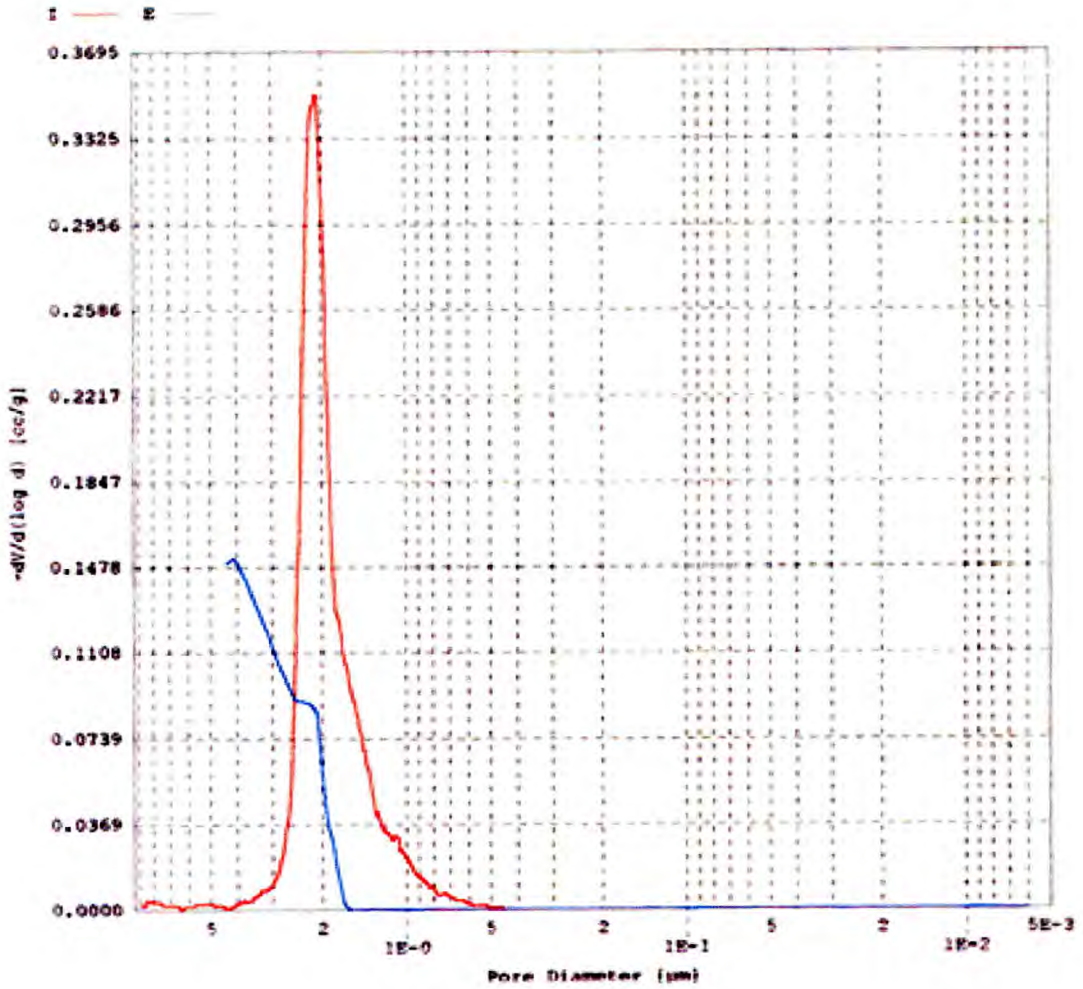


Figure 5.7: Pore volume distribution of the CSZ sample. The red line corresponds to the intrusion and the blue one to the extrusion.

The pore volume distribution is prepared from the mercury penetration curve, shown in Figure 5.8. First the mercury porosimetry data, consisting of the values of the raw volume of the intruded/extruded mercury and the corresponding pressures, are normalised by dividing the mercury volume by the sample weight (corrected to a basis of 1 g). Then from Equation (5.1) and the pressure, the radius corresponding to each penetration value can be calculated. The derivative of the penetration curve with respect to radius r , dV/dr , is the volume of pores between r and $r + dr$ divided by dr ; that is the pore volume distribution function,

$$D_V(r) = dV/dr \quad (5.2)$$

according to pore radius. Here in this graph the distribution function is given as a function of the pore diameter and this is found by dividing the $D_v(r)$ by 2. It is also customary to plot the pore radius or diameter in a logarithmic coordinate as shown above.

It can be seen from Figure 5.7 that the distribution is reasonably symmetrical, not bidisperse, with most of the volume to lie in a pore size range from 0.7 to 3.0 μm and with a most probable pore diameter of about 2.0-2.1 μm . No pore volume was observed below 0.5 μm .

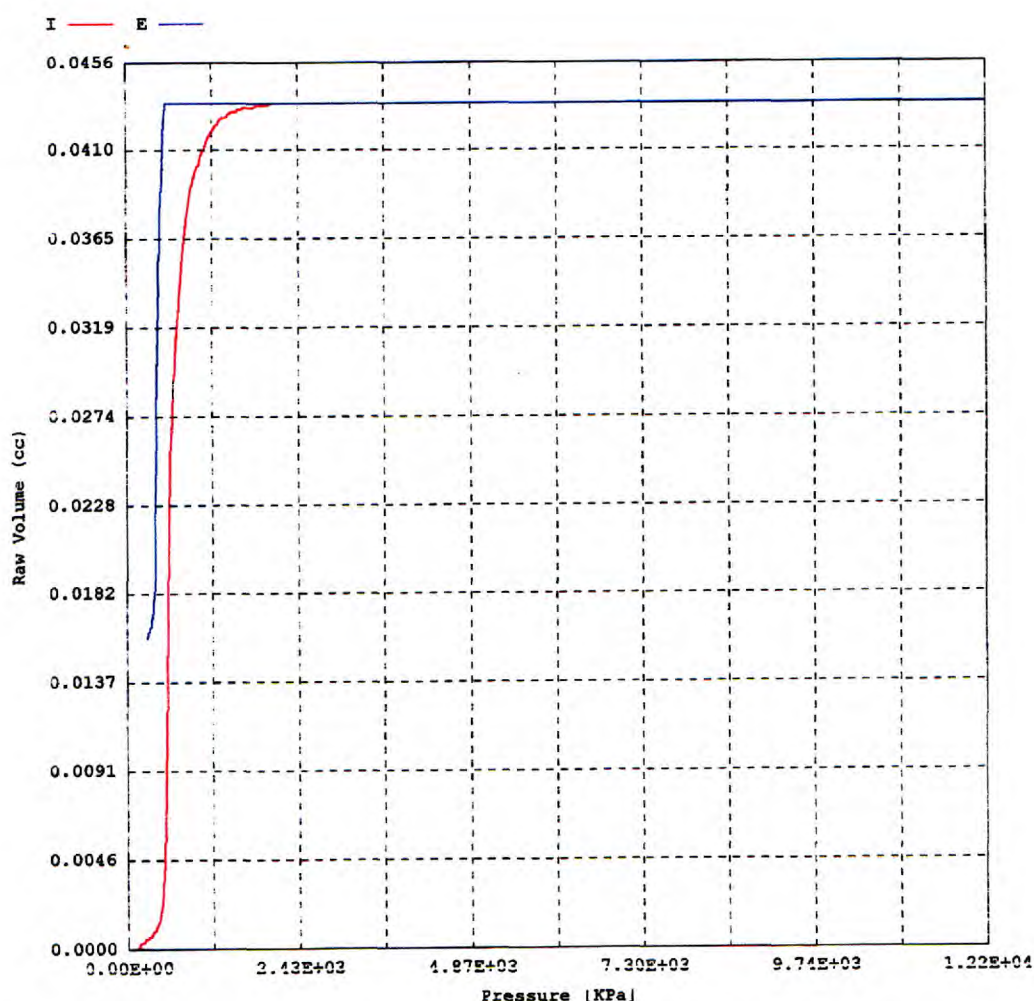


Figure 5.8: Porogram of the intruded and the extruded volume of mercury against pressure for the CSZ substrate. The red line corresponds to the intrusion curve and the blue one to the extrusion curve.

It is not easy to say whether the shape of the graph of intruded and extruded curves, shown in Figure 5.8, is a clear indication of a sample with controlled, open-ended pores. However, it is shown from the rather symmetrical shape of the pore volume distribution curve, in Figure 5.7, that the CSZ sample consists of pores of uniform diameter rather than possessing a wide range of pore sizes. It is evident from the intrusion curve that the majority of the pores are concentrated around the pore diameter of $2.0\mu\text{m}$ which appears to be the most probable pore diameter.

Moreover, a detailed observation of the intrusion and extrusion curves, shown in the above graphs (also called porograms), shows two features, which are very common in these plots. They all exhibit hysteresis [4]. This is always obtained when the extrusion path does not follow the intrusion curve. The depressurisation (extrusion) curve shown in blue in Figure 5.8 lies above the pressurisation (intrusion) red curve.

After the completion of an intrusion-extrusion cycle, usually the hysteresis does not close, indicating that, even when returned to ambient pressure, some portion of mercury is always retained by the sample (pore entrapment). This is evident here in both the porograms, as the extrusion curve (indicated with blue) never reaches the origin of the plot axes.

Because these phenomena have been attributed to a change in one of the parameters in the Washburn equation, the following explanations have been provided to account for the experimental observation of hysteresis.

Firstly, structural explanations [5,6] make use of the different controlling radii during the intrusion and extrusion. Such hysteresis was first attributed to “ink-bottle” shaped pores. For such pores, whose representation is shown in Figure 5.9, intrusion will occur at a pressure corresponding to radius R_i according to the Washburn equation. After the pore is filled, it can empty only at lower pressure that corresponds to radius R_e . The different controlling radius gives rise to the phenomenon of hysteresis which is always observed in the intrusion /extrusion cycle and constitutes the main difference between the intrusion and the extrusion process.

Various modifications of this theory have been proposed and included extension of the model pore structure to a three-dimensional network of interconnected voids [7,8,9]. These modifications have also suggested that it not necessary to use single access “ink-bottle” shaped pores to explain the phenomenon of hysteresis.

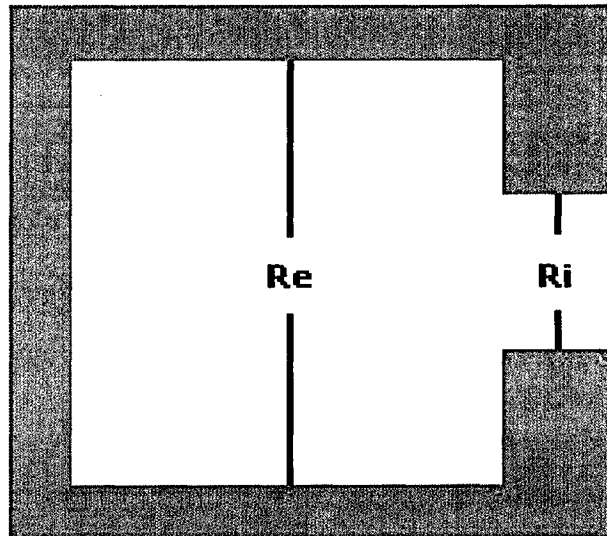


Figure 5.9: A schematic representation of an “ink-bottle” pore. Intrusion is controlled by the size of the opening R_i and extrusion is controlled by the size of the pore, R_e [7].

The second theory involves contact angle shift explanations [5,6]. According to this approach, there is a shift in contact angle between mercury and the solid. The contact angle of the advancing mercury interface during intrusion (θ_i) is larger than that of the receding interface during extrusion (θ_e). It has been suggested [3] that hysteresis gaps can be completely eliminated by modifying the extrusion contact angle. However this hypothesis has been open to debate as this theory relies on a model which assumes that the structure of the porous structure is made up of parallel, nonintersecting cylindrical pores. This theory has been shown by Conner et al. [7] to be inadequate in interpreting many of the phenomena associated with mercury porosimetry.

With respect to the structural explanation of the hysteresis phenomenon, it is more realistic to assume that the structure of a porous material can be viewed as a network of interconnected void spaces created by the interconnected network of the solid. This was first proposed by Conner and Lane et al. [9]. In their simulations, the porous solid was represented by a three-dimensional network of spherical pores

connected by cylindrical throats, as shown in Figure 5.10. This is a model of the void space only and the solid structure is not shown. The spheres represent the pores and the cylindrical shaped connections represent the void constrictions, that are the throats.

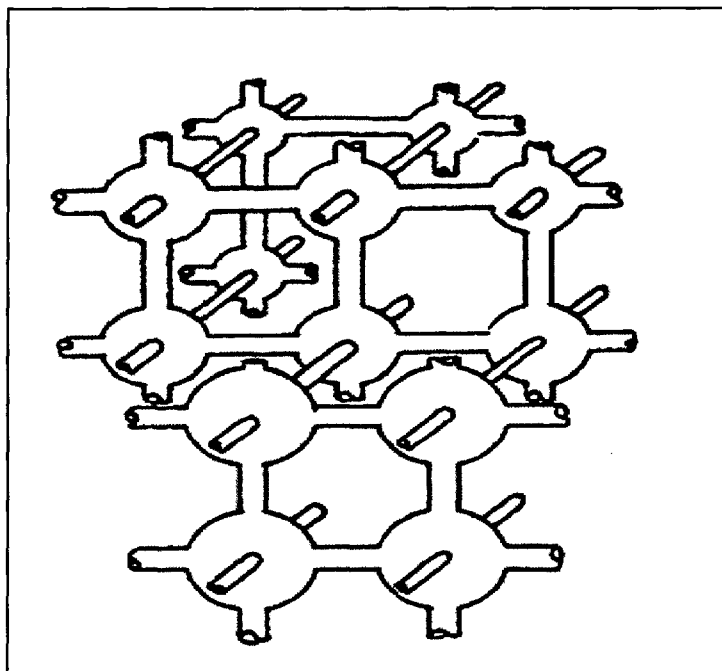


Figure 5.10: Three-dimensional pore-throat network [9].

Better information can be obtained from the mercury porosimetry by using the above representation of interconnected void structures. The model of the three-dimensional pore-throat network can explain both the phenomena of hysteresis and mercury retention. During porosimetry the size of the throats (constrictions) control the intrusion process, while the size of the pores (openings) control the extrusion process.

Therefore, it is always necessary to carefully analyse and comprehend the phenomena related to characterisation techniques such as the mercury porosimetry method, which is used as the basic tool for assessing and understanding the morphology and the geometry of interconnected porous structures. The model of the three-dimensional pore-throat network provides the theoretical basis for the understanding of such phenomena. The mercury porosimetry results are found to be consistent with the structural patterns suggested by the SEM micrographs in the previous section when seen in the context of this model.

5.3.2 Surface Area Distribution of the CSZ Substrate

The surface area distribution function as a function of the pore diameter is presented in Figure 5.11. This shows the change in surface area per unit interval of pore diameter.

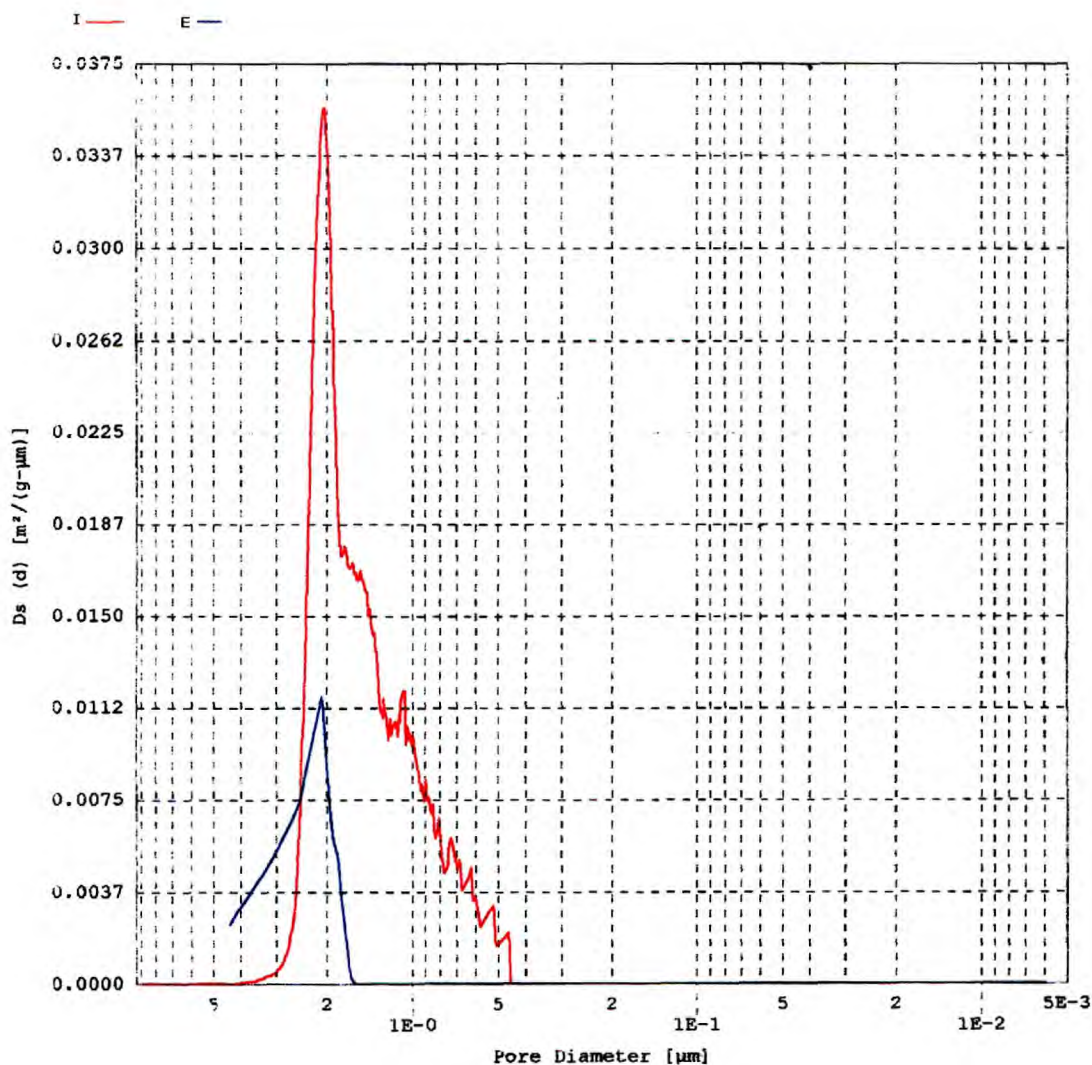


Figure 5.11: Surface area distribution for the CSZ sample. Intrusion is indicated by the red curve and extrusion by the blue curve.

From a first observation of the intrusion curve, it is evident that its shape is not symmetrical. There is a shift in the distribution curve and a number of slight variations appear in the direction of the smaller pore sizes.

A number of equations [10] may be written that lead to a relationship of the surface area distribution with the term dV/dP . As previously mentioned, the pore volume

distribution function, is given by $D_v(r) = dV/dr$, Equation (5.2). Differentiation of equation (5.1), with assumption of γ and ϑ being constant, gives:

$$Pdr + rdP = 0 \quad (5.3)$$

Combining equations (5.2) and (5.3) gives

$$-dV = D_v(r) \frac{r}{P} dP \quad (5.4)$$

and then,

$$D_v(r) = \frac{-P}{r} \frac{dV}{dP} \quad (5.5)$$

Since the change in volume is measured as a decreasing volume the negative sign can be dropped and finally obtain

$$D_v(r) = \frac{P}{r} \frac{dV}{dP} \quad (5.6)$$

Then the surface area distribution function is calculated by:

$$|D_s(r)| = \frac{D_v(r)}{r} \quad (5.7)$$

Substituting Equation (5.6) into (5.7) for $D_v(r)$ gives:

$$|D_s(r)| = \frac{P}{r^2} \frac{dV}{dP} \quad (5.8)$$

And substituting further for r gives:

$$|D_s(r)| = \frac{PP^2}{4\gamma^2 \cos^2 \vartheta} \frac{dV}{dP} \quad (5.9)$$

and the $D_s(d)$ is found by dividing (5.9) by 2.

It can be seen from the final relationship that the $D_s(r)$ or $D_s(d)$ data, at high pressures, are very sensitive to any slight fluctuation in the dV/dP term due to the PP^2 term. This might explain the variations observed on the surface area distribution curve. Some small fluctuations can be identified at the upper part of the penetration curve (higher pressures), in Figure 5.8. These high pressures correspond to small pore sizes, which is where these variations appear in the distribution curve.

Most of the surface area corresponds to a range of pores from 0.5 to $2.5\mu m$ in pore diameter. It is worth noticing that the interpretation of the results obtained by the mercury porosimetry including the surface area plot, are usually based on the intrusion. But this does not account for the pore size, only for the throat size according to the three-dimensional pore-throat network model. As a result of this the surface area will be calculated as smaller than the actual surface area.

5.3.3 Pore Volume Distribution of the MMA Substrate

The pore volume distribution curve for the MMA substrate is presented in Figure 5.12:

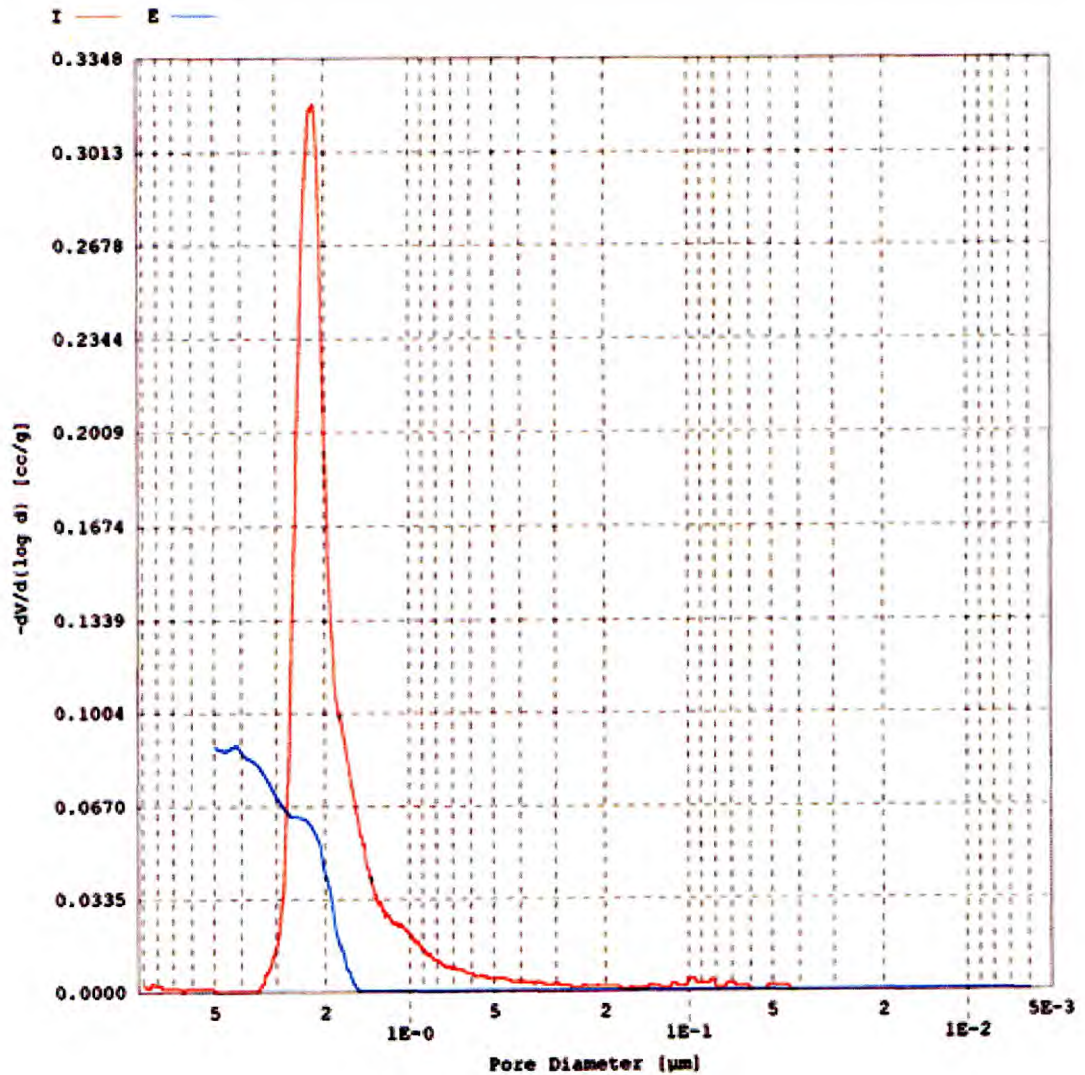


Figure 5.12: Volume pore size distribution of the MMA sample. Intrusion is indicated by the red curve while the blue one shows extrusion.

The distribution curve is quite symmetrical with most of the pore volume to be found in a pore diameter range from 0.5 to 3.0 μm with a most probable pore diameter of about 2.1 to 2.2 μm . The shape of the distribution curve of the MMA appears to be very similar to the corresponding plot of the CSZ sample. The pore sizes are equally similar, with that one of the CSZ to extend down to 0.7 μm . The characteristics of hysteresis and pore entrapment can also be observed here.

5.3.4 Surface Area Distribution of the MMA Substrate

In Figure 5.13 the surface area distribution function is shown:

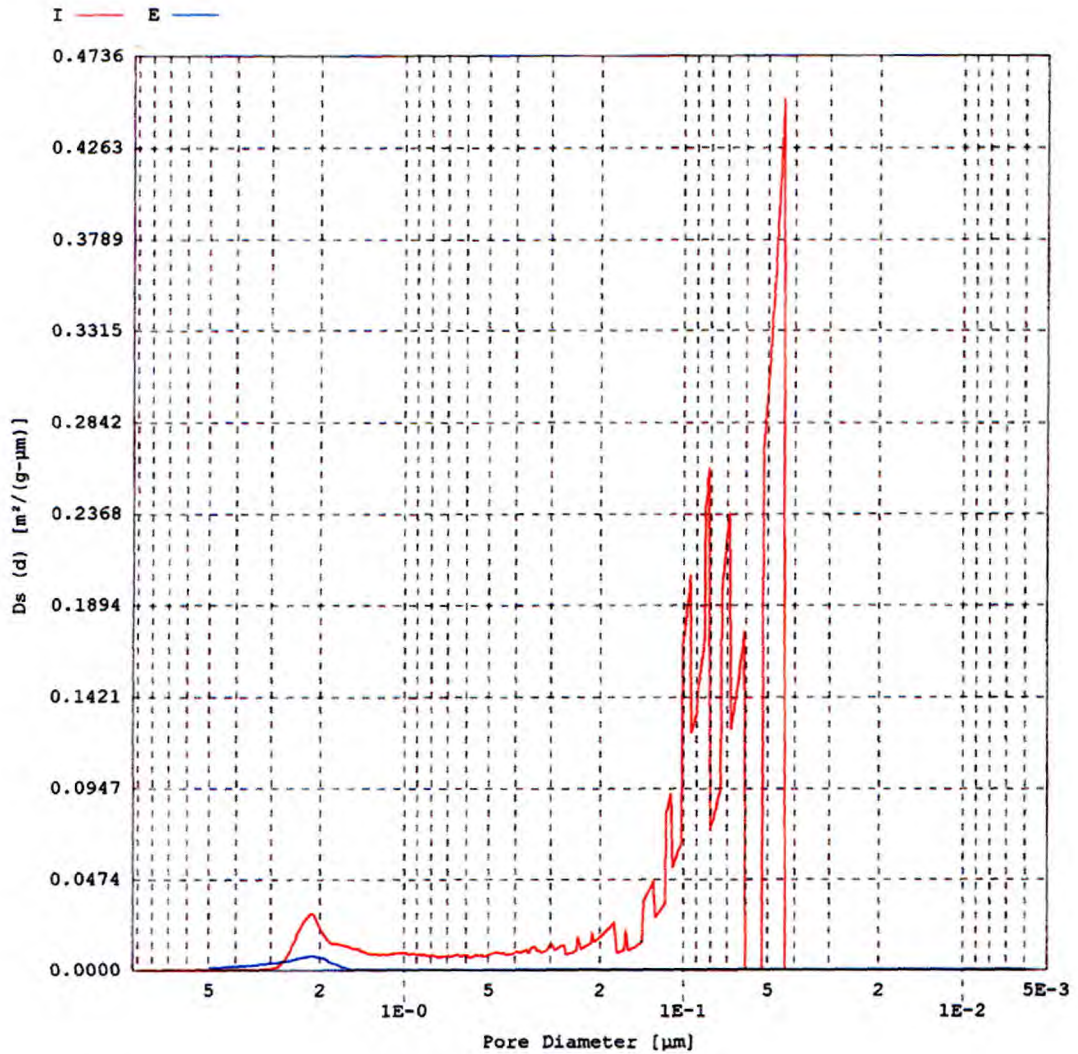


Figure 5.13: Surface area distribution for the MMA sample. Intrusion is indicated by the red curve and extrusion by the blue curve.

Like the case of CSZ sample, the shape of this intrusion curve is characterised from asymmetry. The same kind of variations are also present here, though in this case the shift in the curve advances further to even smaller pores sizes than in the case of the CSZ sample. The same discussion, used in the case of the CSZ sample, can be applied here to explain this shift.

5.3.5 Physical Properties of Porous Substrates

Apart from the mercury porosimetry method, nitrogen adsorption technique can also be employed to determine the physical properties of the porous solids. Although the physical interactions involved are different, both methods are based on surface tension, capillary forces and pressure. In particular for specific surface area measurements (BET method), nitrogen adsorption allows the entire surface to be probed, both external and internal, of the porous solid. In this work, mercury porosimetry measurements were backed up by BET measurements which gave close values for the specific surface area. However, the main difference between the two techniques is that the pore size range that can be determined by mercury porosimetry is wider (diameter $3\text{ nm} - 200\mu\text{m}$) than that of nitrogen adsorption ($0.3 - 300\text{nm}$). Mercury porosimetry can determine larger pores which are out of the detection range of nitrogen adsorption

Table 5.1, below, contains all the geometrical properties measured by mercury porosimetry for the two substrates.

Sample	Mean volume (m^3/kg) $\times 10^{-5}$	Total ^a intruded volume (m^3/kg) $\times 10^{-5}$	Mean ^a surface area (m^2/kg)	Total surface area (m^2/kg)	Bulk density (apparent) (kg/m^3) $\times 10^3$	True (skeletal) density (kg/m^3) $\times 10^3$
CSZ	3.92 at a diameter of $1.8\text{ }\mu\text{m}$	5.82	71 at a diameter of $1.8\text{ }\mu\text{m}$	127	3.74	4.78
MMA	4.98 at a diameter of $1.3\text{ }\mu\text{m}$	5.75	95 at a diameter of $1.3\text{ }\mu\text{m}$	176	2.75	3.27

Table 5.1: Structural properties of the porous substrates taken from the intrusion statistics. (a) Total intruded volume and total surface area values have been obtained from intrusion data.

It is observed that the CSZ sample has slightly greater total intruded volume than the MMA which presents bigger mean and total surface area per sample kilogram. The CSZ also has higher bulk and apparent density.

The bulk density is defined as the solid mass divided by the volume occupied by the solid, including pores and any interparticle voids. It is also known as apparent density and is less than the true density. The latter is defined as the ratio of the mass of the solid to the volume occupied by that mass excluding contributions from pores or internal voids. It is also called the skeletal density.

A series of additional results can be generated using the basic structure properties taken from the mercury porosimetry results:

a) Given the total intruded pore volume per gram and the sample weight, the pore volume can be calculated:

$$\text{pore volume} = (\text{total intruded pore volume per kg})(\text{sample weight}) = (5.82 \times 10^{-5} \text{ m}^3 \text{ kg}^{-1})(74.58 \times 10^{-5} \text{ kg}) = 4.34 \times 10^{-8} \text{ m}^3 \quad (5.10)$$

This value for the pore volume agrees with the total intruded volume shown by the penetration curve in Figure 5.8, as the maximum point of the curve corresponds to a raw volume value of about 0.043 cm^3 or $4.30 \times 10^{-8} \text{ m}^3$.

b) The void fraction or open porosity of the porous sample is obtained by applying the following equation:

$$\varepsilon_p = \frac{\text{pore volume}}{\text{total bulk sample volume}} = \frac{4.34 \times 10^{-8} \text{ m}^3}{19.94 \times 10^{-8} \text{ m}^3} = 21.77\% \quad (5.11)$$

When the bulk and true density of the material are known, an alternative expression for calculating the open porosity is the following:

$$\varepsilon_p = 1 - \frac{\rho_{\text{bulk}}}{\rho_{\text{true}}} \quad (5.12)$$

c) The solids fraction is given by the following equation:

$$\begin{aligned} \varepsilon_p + \varepsilon_s &= 100\% \\ \varepsilon_s &= 100 - 21.77 = 78.23\% \end{aligned} \quad (5.13)$$

d) The bulk density is easily determined by:

$$\rho_{bulk} = \frac{(\text{sample weight})}{(\text{sample bulk volume})} = \frac{74.58 \times 10^{-5} \text{ kg}}{19.94 \times 10^{-8} \text{ m}^3} = 3.74 \times 10^3 \text{ kg/m}^3 \quad (5.14)$$

The value of the bulk density is in exact agreement with that estimated by the mercury porosimetry.

e) Finally, the density of the solid phase (true density) can be calculated according to the expression:

$$\rho_{true} = \frac{(\text{sample weight})}{(\text{bulk volume} - \text{pore volume})} = \frac{74.58 \times 10^{-5} \text{ kg}}{(19.94 - 4.34) \times 10^{-8} \text{ m}^3} = 4.78 \times 10^3 \text{ kg/m}^3 \quad (5.15)$$

The calculated value agrees exactly with the value of the true density in Table 5.1, as measured by the mercury porosimetry method.

Performing similar calculations the corresponding properties of the MMA sample may be determined. All the values for the two samples are shown in Table 5.2.

Sample	Sample weight (kg) $\times 10^{-5}$	Bulk sample volume (m ³) $\times 10^{-8}$	Pore volume (m ³) $\times 10^{-8}$	Porosity	Solids fraction	Bulk density (kg/m ³) $\times 10^3$	True density (kg/m ³) $\times 10^3$
CSZ	74.58	19.94	4.34	21.77%	78.23%	3.74	4.78
MMA	89.13	32.40	5.13	15.83%	84.17%	2.75	3.27

Table 5.2: Structural properties of the porous substrates calculated using data generated by mercury porosimetry.

From the two porous substrates the CSZ has higher porosity than the MMA. Interestingly the values of bulk and true density calculated are in precise agreement with those ones measured by mercury porosimetry.

5.4 Water and Ethanol Uptake Tests

This method is based on the principle of fluid displacement. Immersing the porous sample in a fluid, such as water, will cause the water to flow into the open pore volume. The sample is weighed before and after immersion. These two weights, coupled with the density of water, permits calculation of the pore volume. The bulk volume of the porous sample can be determined by simply measuring the dimensions of the plate. From the pore volume and the bulk volume the open porosity can be directly calculated. Water and ethanol uptake tests gave the following porosities, Table 5.3:

Sample	Porosity (Volume %) Obtained by water uptake	Porosity (Volume %) Obtained by ethanol uptake
CSZ	22.1 ± 0.1	18.9 ± 0.9
MMA	17.0 ± 1.0	12.8 ± 0.2

Table 5.3: Porosity values as obtained by water and ethanol uptake tests.

The values of open porosity measured by water and ethanol uptake methods are either higher or lower compared to the values measured by mercury porosimetry. These methods are approximate. Water or ethanol cannot penetrate all the pores especially in cases when the structure of the material consists of “ink-bottle” pores, whereas mercury has a significant surface tension and is a non-wetting fluid. Moreover, there are issues on the excess of water or ethanol that remains on the sample surfaces, not easy to remove, and thus resulting in wrong measurement of the sample weight after immersion. The discrepancy in the porosity results obtained by water and ethanol methods may also reflect a difference in water and ethanol surface tensions.

These methods are mainly carried out to support the mercury porosimetry measurements. A more rigorous approach would involve image analysis measurements on SEM micrographs of the polished cross sections of the two samples. This can be automated by the use of suitable imaging software. This is done in the following section, where the measurements of porosities obtained from image analysis are discussed.

5.5 Image Analysis

Quantitative results for the total porosity were obtained by image analysis on polished cross sections of the porous substrates. The micrographs of the polished cross sections of the fracture surfaces of the CSZ and MMA are shown in Figures 5.14 and 5.15 respectively.

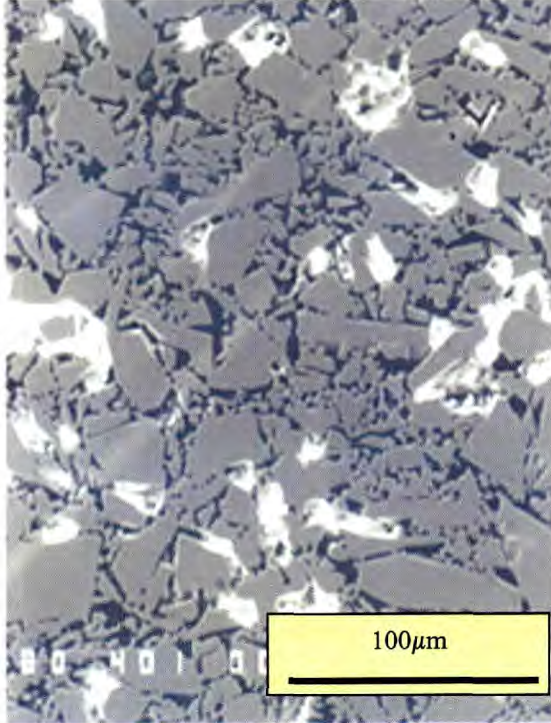


Figure 5.14: Micrograph of the cross section of the polished fracture surface of CSZ substrate.

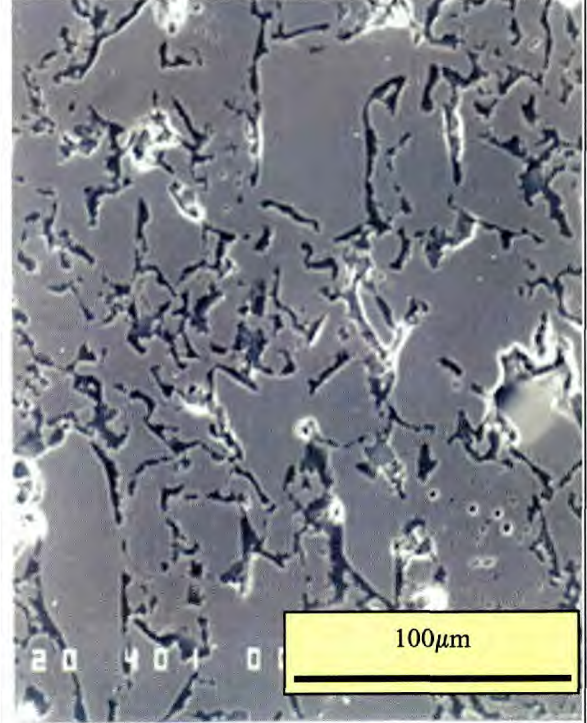


Figure 5.15: SEM image of the cross section of the polished fracture surface of the MMA sample.

The image analysis is applied to the SEM images of the porous samples and in order to determine quantitatively the porosity, it is necessary to know the relationship between surface and volume. From Exner and Hougardy [11] the following equation is available:

$$V_V = A_A = L_L \quad (5.16)$$

where $V_V = V/V_O$, V being the volume of the pores and V_O the reference volume of the sample; $A_A = A/A_O$, A being the surface of the pores and A_O the reference

surface of the sample and $L_L = L/L_O$, with L the sum of the length of the pores cut by L_O and L_O being the length between two points of the reference surface. The values of total porosity for the CSZ and MMA estimated by image analysis are given in the following table.

Sample	Porosity (Volume %)
CSZ	20.8 ± 2.0
MMA	12.9 ± 1.3

Table 5.4: Porosities estimated by image analysis method.

For both samples, it is observed that the values of open porosity measured by mercury porosimetry, given in Table 5.2, are a little higher than the estimated total porosities, shown above in Table 5.4. A possible explanation is that the samples were initially cut in order to fit into the cell of the porosimeter and this might have created additional porosity in the samples.

The estimation of the area of pores by image analysis have shown that the pore sizes of the two samples are shifted to larger pores (assuming pores of cylindrical shape) compared to the pore sizes obtained by mercury porosimetry. This is attributed partly to the mode of calculating the pore size with the two methods, and partly from the pore structure of the sample itself. Mercury porosimetry measures the pore diameter or radius as a function of the mercury volume intruded into these pores by a given pressure according to the Washburn equation, Equation (5.1). For “ink-bottle” pores, their volume corresponds to the intrusion radius which is the radius of the entrance of these pores, as this volume is filled under the corresponding pressure. On the other hand image analysis determines the radius of such pores by measuring the pixels on the screen of a pore cross section.

This comparison between the two methods provides useful information about the pore structure and pore size distribution. Because of the existence of “ink-pores” a significant amount of pores appears to have narrower entrances. Thus the pore volume in the area of $2.0\mu\text{m}$ (see Figures 5.7 and 5.12) might partially correspond to larger pore diameters or radii.

5.6 Diffusion Measurements: Results

5.6.1 Precision of the Measurement Method

Before the results of the diffusion measurements are given, it is necessary to determine the precision of the measurement technique. Because the diffusion coefficients measurements in this work involved a complex experimental procedure, including different systems and devices such as metering, controlling equipment and the gas chromatograph, they are inevitably subject to various kinds of error.

Imprecision errors (or random errors) occur differently for each measurement and create a distribution of values [12]. In these experiments one of the most important factors, which may cause an error in the results, is an undesired pressure difference between the two sides of the porous sample in the diffusion cell. This pressure difference may trigger a convective flux. Also possible non-homogeneity of the composition of gases in the streams flows may cause significant error in the results. The sources of this kind of error have been identified and discussed in detail, along with ways of reducing them, in the sections of the experimental procedure and gas chromatography in the second chapter.

In order to reveal the expected types of the analytical errors and in particular the random one, the selection of the appropriate experiment has to be made. The replication experiment is one way to estimate the uncertainty of an analytical method and increase the confidence in experimental data. It is performed by making repeated measurement of standard samples of known concentration under the same experimental conditions. For this purpose the binary gas mixtures of H_2-N_2 and $CO-N_2$ were selected. The binary mixture of hydrogen and nitrogen was the first to be analysed (shown in section 5.2.3) and gave consistent results at a flow rate of 100 ml/min, while the mixture of carbon monoxide and nitrogen was representative of the remaining gas mixtures analysed at a flow of 50ml/min. The same experimental conditions were used for the precision tests.

Precision is usually given in terms of standard deviation (SD) or as relative standard deviation (RSD) also known as percentage coefficient of variation (%CV) [13]. The standard deviation is a measure of the variability (scatter of a method). The RSD also

looks at the variability of data points and describes the SD as percentage of the average value.

The precision of this analysis was, in terms of RSD: $\pm 4.3\%$ for H_2 , $\pm 5.5\%$ for N_2 and $\pm 2.2\%$ for CO. For the case of H_2 , a RSD of 4.3% for precision is a prediction of the interval about the mean within which 68% of an infinite number of the replicate measurements of this quantity would be expected to lie: $\text{mean} \pm 4.3\% = 68.3\%$ of the results. Since it is important to have a better confidence interval, for 95% of the results we obtain :

$$\text{mean} \pm 8.6 \% \text{ for } H_2$$

$$\text{mean} \pm 11.0\% \text{ for } N_2$$

$$\text{mean} \pm 4.4\% \text{ for CO}$$

The compositions of the standard gas mixtures used were, 10% H_2 and 90% N_2 and 80% CO and 20% N_2 .

5.6.2 Diffusion Coefficients of Binary Mixtures of N_2 with H_2 , CH_4 , CO and CO_2 through CSZ and MMA Support Samples

Pairs of gases, consisting of N_2 with H_2 , CH_4 , CO and CO_2 were used for the measurement of the diffusion coefficients through the CSZ and MMA porous substrates. The diffusion experiments were analysed under conditions of one-dimensional diffusion in a isothermal, inert, binary gas mixture through a porous medium with zero pressure difference across it. Therefore, the diffusive flux through the porous plate is given by Fick's law equation expressed on mass fraction basis [14]. The theoretical treatment from which the adopted form of the flux equation is derived has been given in chapter 4.

To calculate the effective binary diffusivities, the diffusive flux through the porous support along with the concentrations of the gases at the two faces of the porous support are required. The compositions of the inlet and outlet gas streams were obtained by gas chromatography analyses, while the experiments were carried by feeding known inlet flow rates of the gases.

The processing of the raw data involved, first, comparison with the results from the calibration analysis and then normalisation to give 100%. Finally the diffusion fluxes of each gas in porous support were determined from mass balances on each stream.

The values of the effective diffusion coefficients for the gas mixture of H_2-N_2 are summarised in Tables 5.5 and 5.6:

CSZ support	
H_2 composition (volume %)	D_{eff} / H_2-N_2 (m^2/sec) $\times 10^{-6}$
5	4.83
10	5.30
20	5.65
Average value of D_{eff}	5.26

Table 5.5: Effective diffusion coefficient of H_2 in N_2 through CSZ (at $T=298K$, $P=1atm$).

MMA support	
H_2 composition (volume %)	D_{eff} / H_2-N_2 (m^2/sec) $\times 10^{-6}$
5	2.81
10	3.07
20	3.30
Average value of D_{eff}	3.06

Table 5.6: Effective diffusion coefficient of H_2 in N_2 through MMA (at $T=298K$, $P=1atm$).

The effective diffusion coefficients for the binary mixtures of CH_4-N_2 , $CO-N_2$, CO_2-N_2 were also measured and are given in Tables 5.7 and 5.8:

CSZ support			
Compos. of gas under analysis	D_{eff} / CH_4-N_2	$D_{eff} / CO-N_2$	D_{eff} / CO_2-N_2
(volume %)	(m^2/sec) $\times 10^{-6}$ at $T=301K$, $P=1atm$	(m^2/sec) $\times 10^{-6}$ at $T=297K$, $P=1atm$	(m^2/sec) $\times 10^{-6}$ at $T=300K$, $P=1atm$
60	1.06	1.13	1.07
70	1.19	1.14	1.09
80	1.25	1.21	1.11
90	1.19	1.14	1.13
Average of D_{eff}	1.17	1.16	1.10

Table 5.7: Values of binary diffusion coefficients of CH_4 , CO and CO_2 in N_2 through the CSZ support.

MMA support			
Comp. of gas under analysis (volume %)	$D_{\text{eff}} / \text{CH}_4\text{-N}_2$ (m^2/sec) $\times 10^{-6}$ at T=298K, P=1atm	$D_{\text{eff}} / \text{CO-N}_2$ (m^2/sec) $\times 10^{-6}$ at T=296K, P=1atm	$D_{\text{eff}} / \text{CO}_2\text{-N}_2$ (m^2/sec) $\times 10^{-6}$ at T=300K, P=1atm
60	0.60	0.59	0.58
70	0.71	0.57	0.61
80	0.69	0.58	0.63
90	0.72	0.65	0.68
Average of D_{eff} :	0.68	0.60	0.63

Table 5.8: Values of binary diffusion coefficients for CH_4 , CO and CO_2 in N_2 , in MMA support.

From the above values it is evident that the effective diffusivities of methane, carbon monoxide and carbon dioxide in nitrogen are lower than that of hydrogen. This is to be expected and can be explained in the context of the kinetic molecular theory of gases.

5.6.2.1 Interpretation of the Diffusion Results Employing the Kinetic Theory of Gases

The Boltzmann equation is the starting point in the kinetic theory of gases. Approximate solutions to that equation have developed by Chapman and Enskog [15]. The Chapman-Enskog kinetic theory for gases at low density provides molecular expressions for the transport properties.

On the basis of the elementary kinetic theory of gases, the self diffusivity as well as the binary diffusivity can be obtained by mean free path arguments with the assumption that the molecules are rigid spheres of equal mass m_A and diameter d_A . For different molecules A and B represented by rigid spheres of unequal masses and diameters, the formula for the binary diffusivity is [16]:

$$D_{AB} = \frac{2}{3} \sqrt{\frac{kT}{\pi}} \sqrt{\frac{1}{2} \left(\frac{1}{m_A} + \frac{1}{m_B} \right)} \frac{1}{\pi \left(\frac{d_A + d_B}{2} \right)^2} \frac{1}{n} \quad (5.17)$$

where m_A and m_B are the masses of molecules A and B , d_A and d_B their diameters, k is Boltzmann's constant ($1.38066 \times 10^{-23} \text{ J/K}$) and n is the so-called number density, which is the number of molecules per unit volume (in m^3).

But if more accurate results are to be obtained the Chapman-Enskog kinetic theory should be used. The theory is based on the Boltzmann equation. The development of the solution for this equation is mathematically complex and the reader is referred to well-known textbooks [15,16] in which the derivation of the equation and its approximate solutions by Chapman and Enskog are given. It is very important to note that in the solution process, molecular expressions for the fluxes and the transport properties are generated; the viscosity, the thermal conductivity and the multicomponent thermal and Fick diffusion coefficients appear in these expressions.

Thus the corresponding formula [15,16] for the binary diffusion coefficient obtained by the Chapman-Enskog theory is:

$$D_{AB} = 0.0018583 \sqrt{T^3 \left(\frac{1}{M_A} + \frac{1}{M_B} \right)} \frac{1}{p \sigma_{AB}^2 \Omega_{D,AB}} \quad (5.18)$$

where D_{AB} is the diffusion coefficient in cm^2/s , T is the absolute temperature in Kelvin, p is the pressure in atm, and M_A , M_B are the molecular weights of A and B . The dimensionless quantity $\Omega_{D,AB}$ is the diffusion collision integral. It is a function of the dimensionless temperature kT/ε_{AB} and depends on the choice of intermolecular-force law between colliding molecules. The parameter ε_{AB} is the characteristic energy, and σ_{AB} is the characteristic diameter of the molecules, often called the collision diameter, and it is given in $\text{\AA}$. This quantity also depends on the intermolecular-force law selected. These two parameters σ_{AB} and ε_{AB} are those that appear in the Lennard-Jones potential [15,16,17], when the Lennard-Jones potential is selected as the intermolecular-force law:

$$\phi_{AB}(r) = 4\varepsilon_{AB} \left[\left(\frac{\sigma_{AB}}{r} \right)^{12} - \left(\frac{\sigma_{AB}}{r} \right)^6 \right] \quad (5.19)$$

The Lennard-Jones potential is an empirical expression that relates the intermolecular potential energy $\phi(r)$ between two molecules A and B to the distance of separation r . It includes both the attractions and repulsions between the molecules A and B . The transport properties, according to Chapman-Enskog kinetic theory are given in terms of this function. The parameters σ_{AB} and ε_{AB} are estimated by the following combining rules:

$$\sigma_{AB} = \frac{1}{2}(\sigma_A + \sigma_B) \quad \text{and} \quad \varepsilon_{AB} = \sqrt{\varepsilon_A \varepsilon_B} \quad (5.20, 21)$$

where the parameters σ_A , σ_B and ε_A , ε_B are the characteristic diameters and energies of molecule A and B respectively.

In the light of the above predictions obtained from the kinetic molecular theory, the results of the diffusion measurements shown in Tables (5.5-5.8) can be now more clearly explained. Equation (5.17) and Equation (5.18) predict that the binary diffusivity is inversely proportional to the density of the gas and its mass or its molecular weight. It is also inversely proportional to the size of the molecule as this is expressed by the molecular diameters d_A and d_B and the quantity σ_{AB} in Equations (5.17) and (5.18) respectively. The effective diffusion coefficient of hydrogen in nitrogen is the greatest among the diffusivities of other gases in this study. Hydrogen is a light gas with the smallest molecular weight, therefore its diffusion rate and its diffusion coefficient in nitrogen must be higher than those of the other gases. Among the rest of the gases, methane with a low molecular weight, has a greater effective diffusion coefficient into nitrogen than carbon monoxide and carbon dioxide, for the case of the CSZ support. Accordingly, carbon dioxide is the molecule with the greatest molecular weight and size, among the other gases used in this analysis. As the molecular weight of a molecule increases the diffusivity decreases. Therefore carbon dioxide has the smallest diffusivity in nitrogen, relative to the other gases.

In the case of the MMA support, an inconsistency is evident from the observation of the carbon monoxide diffusion coefficient, which appears lower than that of carbon dioxide. However this variation is within the experimental uncertainty, which for this work was 11% (for nitrogen).

5.6.2.2 Effect of Composition on the Effective Diffusion Coefficient

To investigate the effect of mixture composition on the effective diffusion coefficient, the values are plotted against the mole fraction of the desired gas in the binary mixture. In Figure 5.16, the effective diffusivities of hydrogen in nitrogen are plotted against the hydrogen concentration in the mixture.

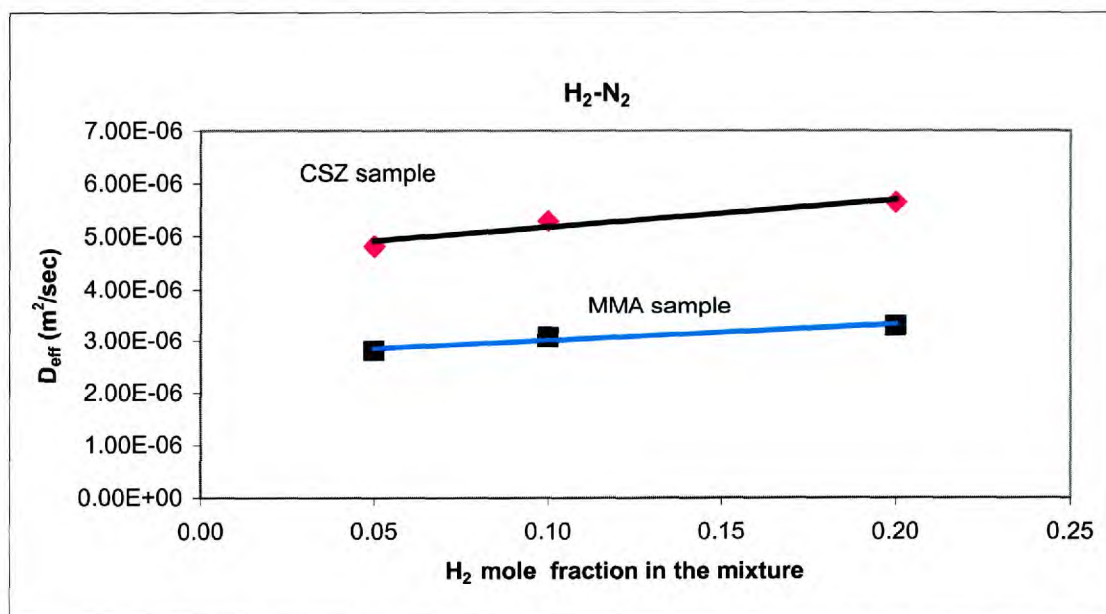


Figure 5.16: Effective diffusivities of H₂ in N₂ as a function of mole fraction of H₂.

In Figure 5.16, it is shown that the effective diffusion coefficient of hydrogen in nitrogen increases with the mole fraction of hydrogen. It appears to be a small, linear increase.

According to the Chapman-Enskog theory, the first approximation, $[D_{AB}]_1$, to the diffusion coefficient of a binary mixture results in Equation (5.18). In the form given by Equation (5.18) only interactions of the unlike species A and B enter and the mixture composition does not appear. Thus the effect of the composition is not predicted by this relationship. Higher approximations to the binary diffusivity are given by the following equation [15]:

$$[D_{AB}]_k = [D_{AB}]_1 f_{D_{AB}}^{(k)} \quad (5.22)$$

The function $f_{D_{AB}}^{(k)}$ is a function of the molecular weights, the mole fractions and the viscosities of the two components as well as the temperature. The exact relation for $f_{D_{AB}}$ is obtained only as a solution of an infinite set of simultaneous equations [15]. Chapman and Kihara [15,18], by using slightly different methods, have obtained approximations to this function, denoted as $f_{D_{AB}}^{(k)}$. The theoretical formulas of these approximations are quite complicated in form, especially the higher ones. Simpler expressions have been provided and discussed by Mason [19], who considered different extreme cases that should encompass most of the real cases and corresponded to the extremes of the mixture composition range.

It has been found that this function varies slightly from unity. For most binary mixtures where $M_A \approx M_B$, the function $f_{D_{AB}}$ lies within the range of 1.00-1.03 [17] for the Lennard-Jones potential regardless of the mixture composition or the intermolecular forces. Only when the molecular weights M_A and M_B differ significantly and the trace gas has nearly zero concentration is the value of $f_{D_{AB}}$ different from unity. But even in such cases the value of the function is between 1.0 and 1.1.

One of the marginal cases, is the so-called Lorentzian gas [19], which is characterised by $M_A \ll M_B$ and $x_A \ll x_B$, with A and B being the light and the heavier component respectively in the binary mixture. Under such conditions collisions among the molecules of the light gas have minor effect and only collisions of the (A,B) type are important. For a Lorentzian gas, the Kihara [19] second approximation factor to diffusion coefficient is given by the relation:

$$f_{D_{AB}}^{(2)} = 1 + \frac{1}{10} (6C_{AB}^* - 5)^2 \quad (5.23)$$

where C_{AB}^* is a function that can be found in tables [15] and is given by the ratio of the collision integrals $C_{AB}^* = \Omega_{AB}^{(1,2)*} / \Omega_{AB}^{(1,1)*}$. For the case of the binary mixture of hydrogen and nitrogen and for the Lennard-Jones potential, and at $T=298K$, C_{AB}^*

has a value of 0.92875. When this value is substituted in Equation (5.23), the Kihara second approximation is

$$f_{D_{AB}}^{(2)} = 1.033 \quad (5.24)$$

The opposite extreme of the Lorentzian gas case is the so-called quasi-Lorentzian gas. This case is characterised by $M_A \ll M_B$ as in the Lorentzian gas, but now it is the light component in excess, that is $x_A \gg x_B$. For this case the result obtained from the theoretical formulas for the function $f_{D_{AB}}^{(k)}$ is

$$f_{D_{AB}}^{(k)} = 1.000 \quad \text{for all } k \quad (5.25)$$

Therefore for the two extremes of the mixture composition range, the function $f_{D_{AB}}^{(2)}$ lies between the values of 1 and 1.033. Taking into account the last results, for diffusion of a binary mixture of a light gas and a heavy gas, the theoretical expression for the first approximation to the binary diffusivity will be exact when the light gas is present in excess and in this case no composition dependence is predicted. The second approximation will be quite accurate when the heavy gas is present in large proportion, as shown in the case of the Lorentzian gas above. For the rest of the cases that fall between these two extremes, the second approximation is expected to give adequate accuracy.

For these measurements, the binary mixtures of hydrogen and nitrogen ($M_{H_2} \ll M_{N_2}$) with compositions ranging from 5% to 20% for hydrogen and 95% to 80% for nitrogen, could be characterised as intermediate cases between the two marginal instances. Therefore the second approximation to the binary diffusion coefficient will be sufficiently accurate. However, a relatively simple, semiempirical equation for the function $f_{D_{AB}}$ has been obtained [20] which, in its range of validity, is consistent with the exact relations for $f_{D_{AB}}^{(2)}$ and $f_{D_{AB}}^{(3)}$ within 0.2% [20]. This expression is the following one:

$$f_{D_{AB}} = 1 + \frac{0.1}{3(M_A/M_B)^2 + 1.6M_A/M_B + 1} \frac{2x_B}{x_B + 1} (6C_{AB}^* - 5)^2, \quad (5.26)$$

with $(0 < M_A/M_B < 0.5)$

where x_B is the mole fraction of the heavy component of molecular mass M_B .

Substituting the values for σ_{AB} and $\Omega_{D,AB}$, at $T=298\text{K}$ and $p=1\text{atm}$, into Equation (5.18), the first approximation to binary diffusivity of hydrogen in nitrogen is obtained:

$$[D_{H_2 N_2}] = 0.74 \times 10^{-4} \text{ m}^2/\text{sec} \quad (5.27)$$

Also taking as x_B the mole fractions of nitrogen that correspond to mixture compositions from Table 5.5, the values of the function $f_{D_{AB}}$ can be calculated from Equation (5.26). Based on the result from (5.27) and the calculated values of $f_{D_{AB}}$, the second approximations to the diffusion coefficient can be found using Equation (5.22). These are presented in Table 5.9:

x_{N_2}	$f_{D_{H_2N_2}}$	$D_{H_2N_2} \text{ (calc)}$ (m^2/sec) $\times 10^{-4}$
0.80	1.026	0.759
0.95	1.028	0.761

Table 5.9: Values of the function f_D as obtained from Equation (5.26) using the Lennard-Jones potential and the corresponding calculated diffusion coefficients of the system H_2 - N_2 at $T=298\text{K}$, $P=1\text{atm}$.

From the calculated diffusion coefficients in Table 5.9, it is shown that the use of the semiempirical relation predicts very small composition dependence, less than 0.3 %, for the diffusion coefficient of the hydrogen and nitrogen, in the composition range 80-95 % of nitrogen. It is therefore evident that there is a variation of diffusivity with

the mole fraction of the lighter gas, which is also predicted by theory, but it was difficult to confirm within the given experimental uncertainty

It can be also seen from Figure 5.16 that the diffusion coefficient corresponding to a mole fraction of 0.05 for hydrogen departs to some extent from the other two values, in both cases of CSZ and MMA. This occurs very close to Lorentzian gas region where the greatest value of the function $f_{D_{AB}}$ was predicted by the theory, Equation (5.24). However, as the mole fraction of the light component increases, or that of the heavy component decreases, the value of the measured diffusion coefficient stabilises.

The literature shows only a few experimental investigations of the composition dependence of diffusion coefficient for binary gas mixtures. It worth noting that it is the molecular diffusion coefficients that are studied in these cases rather than the effective ones. In a study by Amdur and Schatzki [20], the composition dependence of binary diffusivity of a mixture of A-Xe was studied at the extremes of the composition range. A small dependence, less than 0.7%, of the diffusivity on the mole fraction of the tracer gas was predicted by the theory but the measured diffusion coefficients showed no composition dependence. Yabsley et al. [21] have reported binary diffusion coefficients for the system He-CCLF₃ as a function of concentration. They have shown that their data, represented by the above semiempirical relation, agree with concentration dependences predicted from the theory very accurately.

Returning to the rest of the binary mixtures, in Figure 5.17, the effective diffusivity of the methane versus its mole fraction in the binary mixture is shown.

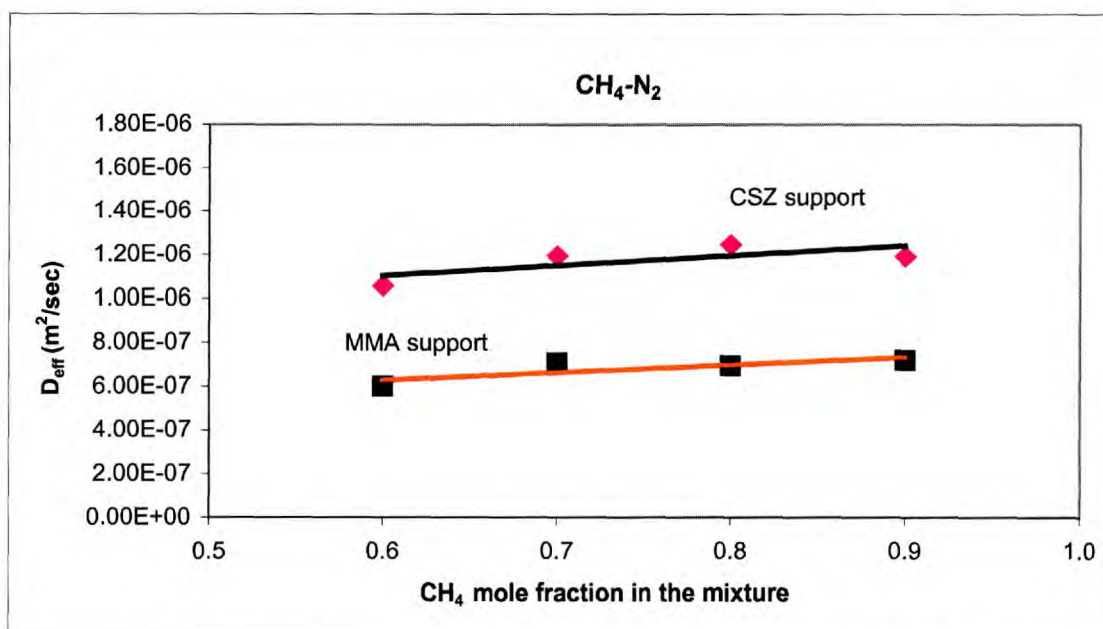


Figure 5.17: Concentration dependence of effective diffusion coefficient of CH₄ in N₂.

No obvious effect of the mole fraction of methane on the measured diffusion coefficients is shown in the range of the accepted experimental precision of 11.0% (as estimated for nitrogen).

Figures 5.18 and 5.19 show the plots of the effective diffusion coefficients of carbon dioxide and carbon monoxide in nitrogen as a function of their mole fractions.

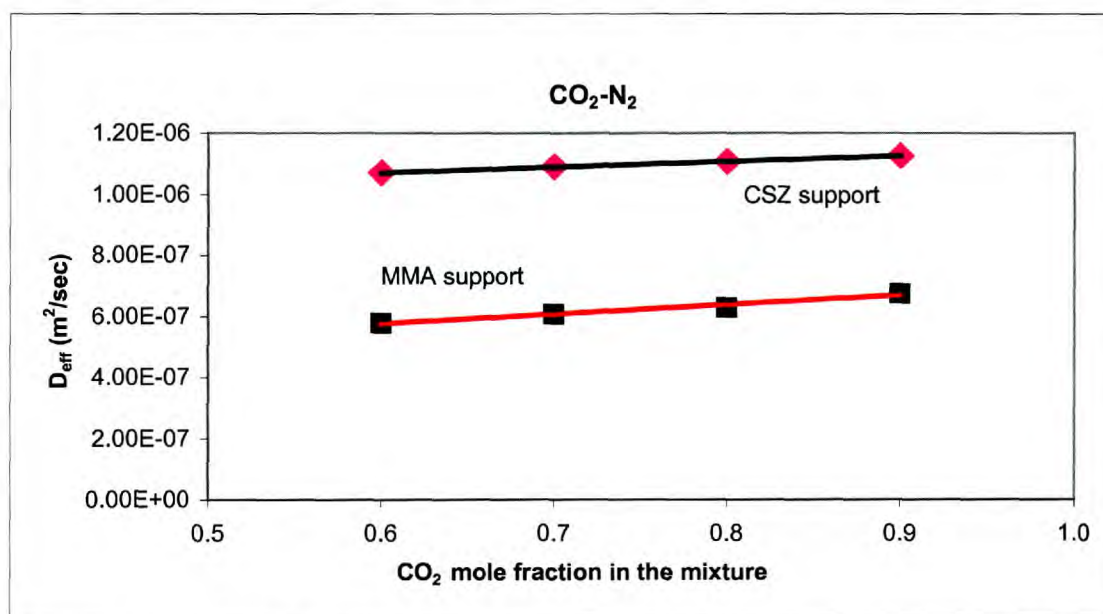


Figure 5.18: Binary diffusivities of CO₂ in N₂ as a function of mole fraction of CO₂.

Both the binary mixtures of CH_4 and CO_2 with N_2 are not represented by the two limits of the composition range that is the Lorentzian and the quasi-Lorentzian gas, since they do not satisfy the condition of $M_A \ll M_B$, with B being the heavier component of these mixtures. For this case, the molecular masses of the components (especially in the case of CH_4 and N_2) are not very different. As already mentioned before, when the molecular masses of the two components are quite similar the value of the function $f_{D_{AB}}$ falls between 1.0 and 1.03 regardless of composition and intermolecular forces. Therefore the composition dependence predicted by the theory is only minor. Also Figures 5.17 and 5.18 do not suggest any composition dependence, given the experimental uncertainty of 11%.

The binary mixture of carbon monoxide and nitrogen presents considerable interest. Because CO and N_2 have nearly identical molecular mass and the same molecular shape, size and electronic configuration they are isosteric molecules. In other words, this can be regarded to resemble the case of an isotopic mixture. This is another extreme case in which all the types of the molecular force laws are identical and the molecular masses of the components are approximately equal. In this case the binary diffusion coefficient reduces to the self-diffusion coefficient. It is more appropriate to consider this coefficient as a limiting case of the binary diffusivity. There is also no composition dependence and the self-diffusivity $[D]_1$ is only a function of the reduced temperature. The expression [15,16] for the self-diffusivity is obtained, if the Equation (5.18) is written for one component and the subscripts are omitted:

$$D = 0.0018583 \sqrt{T^3 2 \left(\frac{1}{M} \right) \frac{1}{p \sigma^2 \Omega_D}} \quad (5.28)$$

The different parameters in Equation (5.28) follow those defined for the binary diffusion coefficient, Equation (5.18). The higher approximations to the self-diffusion coefficient are given by:

$$[D]_k = [D]_1 f_D^{(k)} \quad (5.29)$$

The second approximation is only a function of the reduced temperature (kT/ε_{AB}). Therefore this limiting form of the binary diffusion coefficient is composition independent. This is demonstrated in Figure 5.19 in which the diffusion coefficient of CO in N_2 is shown.

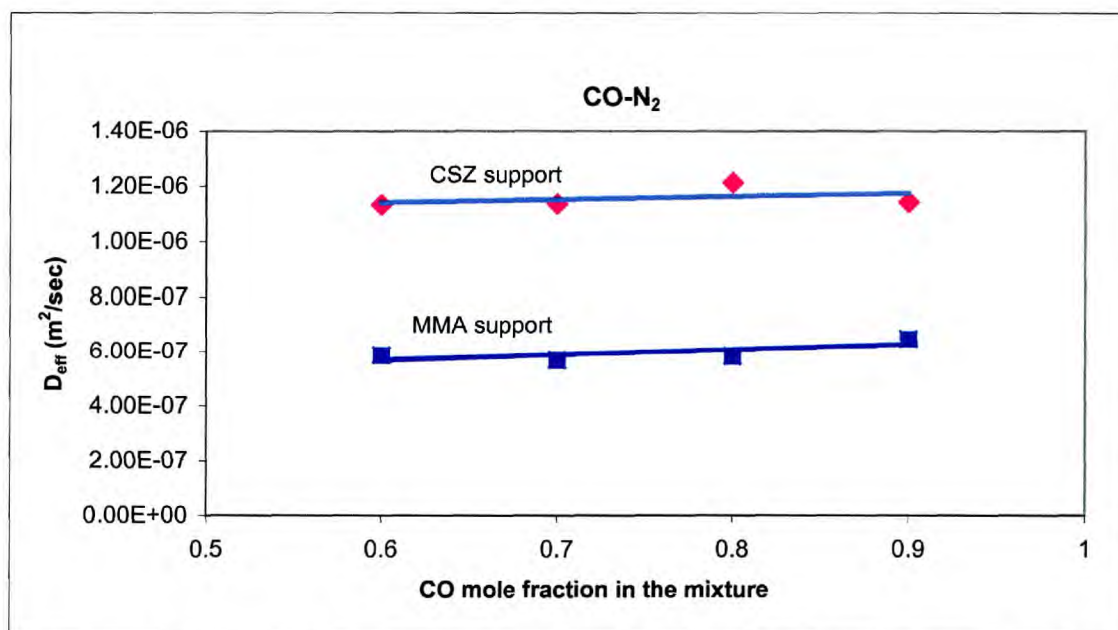


Figure 5.19: Binary diffusivities of CO in N_2 as a function of mole fraction of CO.

No obvious effect of the mixture composition on the measured diffusion coefficients is evident from the plots, in Figure 5.19. Therefore the prediction from the theory is consistent with the measured values of the binary diffusivity.

It has to be noted that the binary diffusion coefficients mentioned in the molecular theory are the “free” binary diffusion coefficients. On the other hand the experimental results refer to the effective diffusivities of the binary gas mixtures, that is the binary diffusivities through the porous ceramic supports. The values of the “free” diffusivities can be corrected by the tortuosity factor that accounts for the impact of the porous microstructure on the gas diffusion. Therefore the evidence presented above, using the kinetic theory, still holds. The meaning of the tortuosity factor with regard to the characterisation of a porous material is going to be described in detail in the section of estimation of tortuosity later in this chapter.

5.6.2.3 Effect of Flow rate on the Effective Diffusion Coefficient

A series of experiments were conducted to investigate the effect of the flow rate at which the gas streams flow across the two sides of the porous sample, on the measurement of the effective diffusion coefficients. In these experiments, a range of different flow rates was used, maintaining the composition of the binary mixture constant. For this type of test, the binary mixture of hydrogen and nitrogen was selected with a constant composition of 10% H₂ in N₂. The range of the flow rates used along with the values of the measured diffusivities are shown in Table 5.10:

Flow rate (ml/min)	CSZ Support $D_{\text{eff}} / \text{H}_2\text{-N}_2$ (m ² /sec) x 10 ⁻⁶	MMA Support $D_{\text{eff}} / \text{H}_2\text{-N}_2$ (m ² /sec) x 10 ⁻⁶
50	4.88	2.84
60	4.99	2.88
70	5.04	2.93
80	5.08	2.95

Table 5.10: Binary diffusion coefficients of H₂ in N₂ at different flow rates, through CSZ and MMA substrates (at T=298K, P=1atm).

The selection of the binary mixture of hydrogen and nitrogen was made because this mixture retains one of the conditions ($M_{\text{H}_2} \ll M_{\text{N}_2}$) of the special cases described in the previous section. The mixture also serves to simplify the experimental procedure, since the analysis of other gases such as CH₄ or CO is limited by the range of flow rates used. Figure 5.20 shows the effect of flow rate on the effective diffusion coefficient. Note that in chapter 3, the analysis on the estimation of the mass transfer coefficient concluded that the range of flow rates used had no apparent effect on the convection mass transfer coefficient.

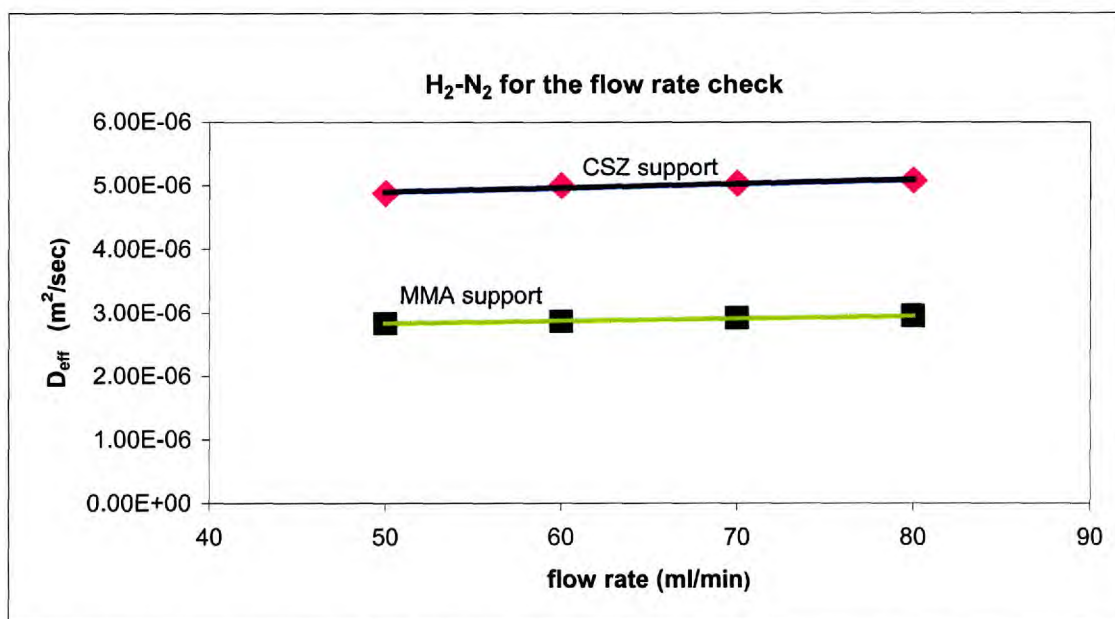


Figure 5.20: Effective diffusion coefficient of H_2 as a function of the flow rate.

The plot reveals no dependence of the effective diffusion coefficient of hydrogen on the flow rate, within the experimental uncertainty. This result also allowed the possibility of selecting a range of flow rates under which the measurements of the diffusion coefficients were carried out. Since no particular impact of the feed flow rate on the measured diffusivities was apparent, the only constraints imposed on this parameter were those originating from the measurement system. The effective diffusivity of the binary mixture of hydrogen and nitrogen was measured using a feeding flow rate of 100 ml/min , while for those of methane, carbon monoxide and carbon dioxide the desired flow rate was set at 50 ml/min . The use of a lower flow rate was made necessary by the limitations of the measurement system. Based on the detection limits of the gas chromatograph, low flow rate and high composition of the gas under analysis, were required to obtain detectable amount of gas through the porous samples.

5.6.3 Diffusion Coefficients of the Binary Mixtures in CSZ1 and MMA1 Samples-Effect of the Support Material on the Effective Diffusion Coefficient

In order to study the effect of taking different samples from the same substrate on the measured diffusivity, a repetition of the same series of the diffusion experiments, whose results were described in the section 5.2.2, were performed. For the purpose of this study these samples are called CSZ1 and MMA1.

In Table 5.11, the effective diffusion coefficients of hydrogen in nitrogen through the new samples of CSZ1 and MMA1 are shown.

H ₂ composition (volume %)	CSZ1 support $D_{\text{eff}} / \text{H}_2\text{-N}_2$ (m ² /sec) x 10 ⁻⁶	MMA1 support $D_{\text{eff}} / \text{H}_2\text{-N}_2$ (m ² /sec) x 10 ⁻⁶
5	4.88	2.62
10	5.18	2.84
20	5.92	3.12
Average value of D_{eff}	5.33	2.86

Table 5.11: Effective diffusion coefficient of H₂ in N₂ through CSZ1 sample (at T=292K, P=1atm) and MMA1 sample (at T=293K, P=1atm).

The values of the diffusion coefficients of hydrogen in nitrogen obtained for the initial samples of CSZ and MMA along with those ones for the new samples CSZ1 and MMA1 are shown in the same graph in Figure 5.21. In this way the comparison is better demonstrated.

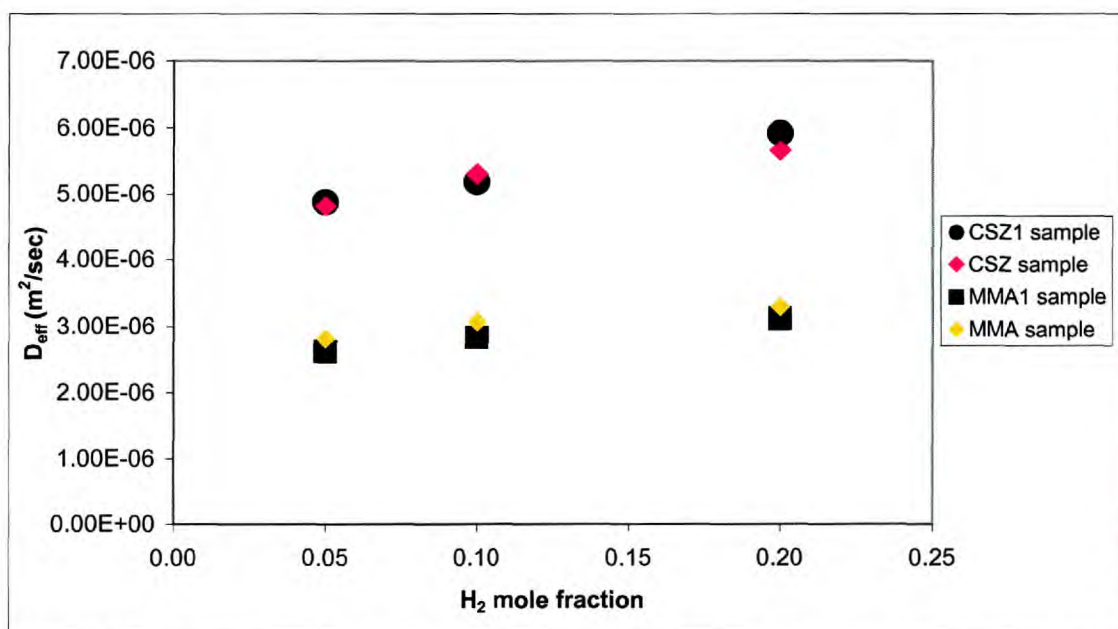


Figure 5.21: Comparison of H_2 effective diffusivities obtained using the initial samples CSZ and MMA with those obtained in CSZ1 and MMA1.

The above graph shows a very close agreement between the two sets of effective diffusion coefficients. The new values of the measured diffusivities are well within the experimental precision (11%) and this new series of experiments can be regarded as an indirect way to verify the precision of the experimental method, assuming that the physical properties are the same. The analysis given previously, in section 5.2.3.2, with regard to the composition dependence also applies here.

The new values of the effective diffusion coefficients for the binary mixtures of $\text{CH}_4\text{-N}_2$, CO-N_2 , and $\text{CO}_2\text{-N}_2$ are given in Tables 5.12 and 5.13:

CSZ1 support			
Compos. of gas under analysis (volume %)	$D_{\text{eff}} / \text{CH}_4\text{-N}_2$ (m^2/sec) $\times 10^{-6}$ at T=295K, P=1atm	$D_{\text{eff}} / \text{CO-N}_2$ (m^2/sec) $\times 10^{-6}$ at T=295K, P=1atm	$D_{\text{eff}} / \text{CO}_2\text{-N}_2$ (m^2/sec) $\times 10^{-6}$ at T=294K, P=1atm
60	1.20	1.15	1.08
70	1.28	1.15	1.09
80	1.31	1.15	1.18
90	1.37	1.16	1.21
Average of D_{eff} :	1.29	1.15	1.14

Table 5.12: The binary diffusion coefficients of CH_4 , CO and CO_2 in N_2 through the CSZ1 support.

MMA1 support			
Comp. of gas under analysis (volume %)	$D_{\text{eff}} / \text{CH}_4\text{-N}_2$ (m^2/sec) $\times 10^{-6}$ at T=293K, P=1atm	$D_{\text{eff}} / \text{CO-N}_2$ (m^2/sec) $\times 10^{-6}$ at T=293K, P=1atm	$D_{\text{eff}} / \text{CO}_2\text{-N}_2$ (m^2/sec) $\times 10^{-6}$ at T=295K, P=1atm
60	0.55	0.61	0.58
70	0.61	0.59	0.60
80	0.67	0.62	0.65
90	0.71	0.63	0.60
Average of D_{eff} :	0.64	0.61	0.61

Table 5.13: Values of binary diffusion coefficients of CH_4 , CO and CO_2 in N_2 , in MMA1 support.

A first inspection of the above tables reveals the same variations in the values as those observed in Tables 5.7 and 5.8 for the initial samples of CSZ and MMA. Again, the average value of the effective diffusivities confirms that methane, with smaller molecular mass displays greater diffusion coefficient in nitrogen than carbon monoxide and carbon dioxide. In the case of the MMA1 sample (Table 5.13), the average values of the diffusion coefficients of CO and CO_2 are equal and therefore

the irregularity that was present in the initial results (Table 5.8) cannot be seen this time.

Comparing the effective diffusivities obtained through the new samples with the corresponding ones taken for the initial samples, any likely effect of the different support sample can be recognised. This is done in a series of graphs shown in Figures 5.22-5.24.

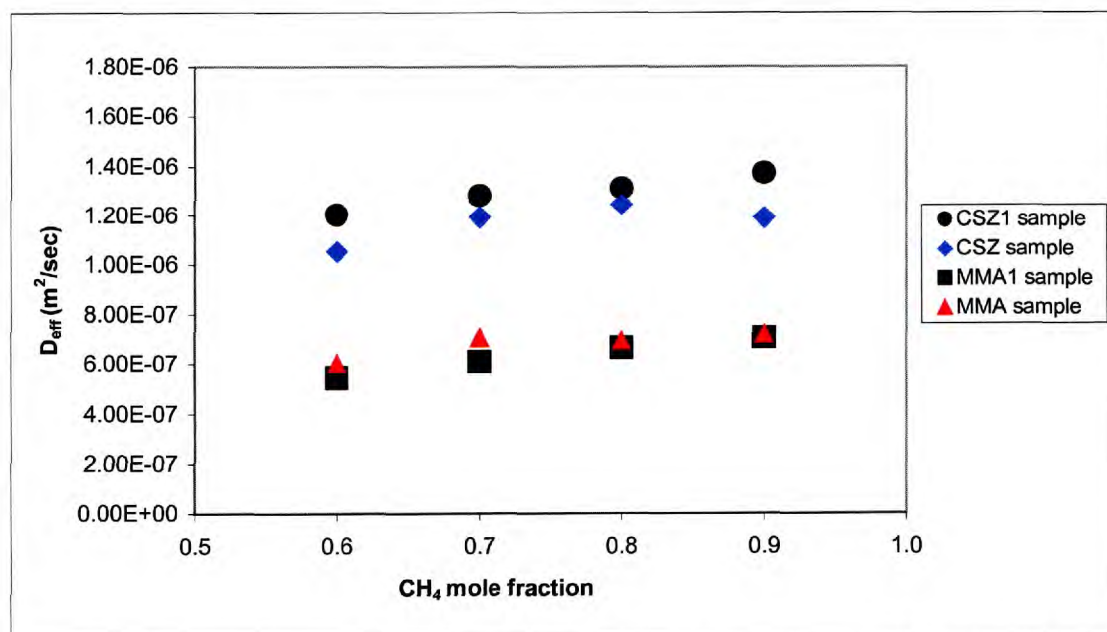


Figure 5.22: Concentration dependence of diffusion coefficient of CH₄ in N₂ and comparison of the values in CSZ1 and MMA1 with those in CSZ and MMA samples.

Figure 5.22 shows that the diffusivities are much closer for the case of MMA1 and MMA than for the case of CSZ1 and CSZ samples. Within the whole range of methane mole fraction, the effective diffusivities obtained with the CSZ1 sample are found to be a little greater than the corresponding ones in the CSZ case.

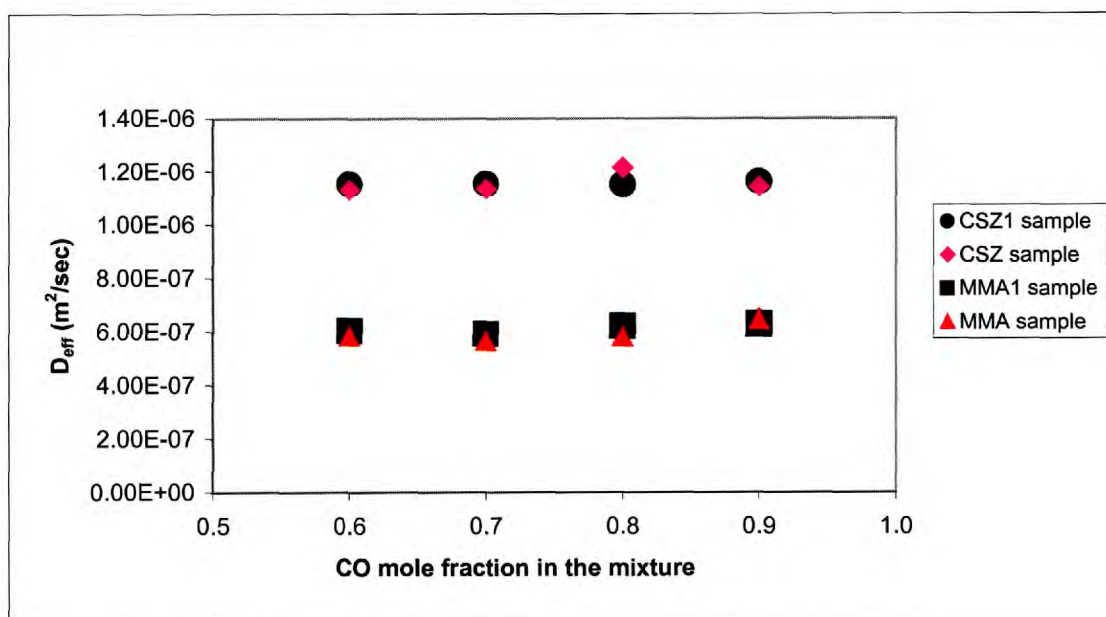


Figure 5.23: Binary diffusivities of CO in N_2 as a function of mole fraction of CO and comparison of the values for the two different support samples.

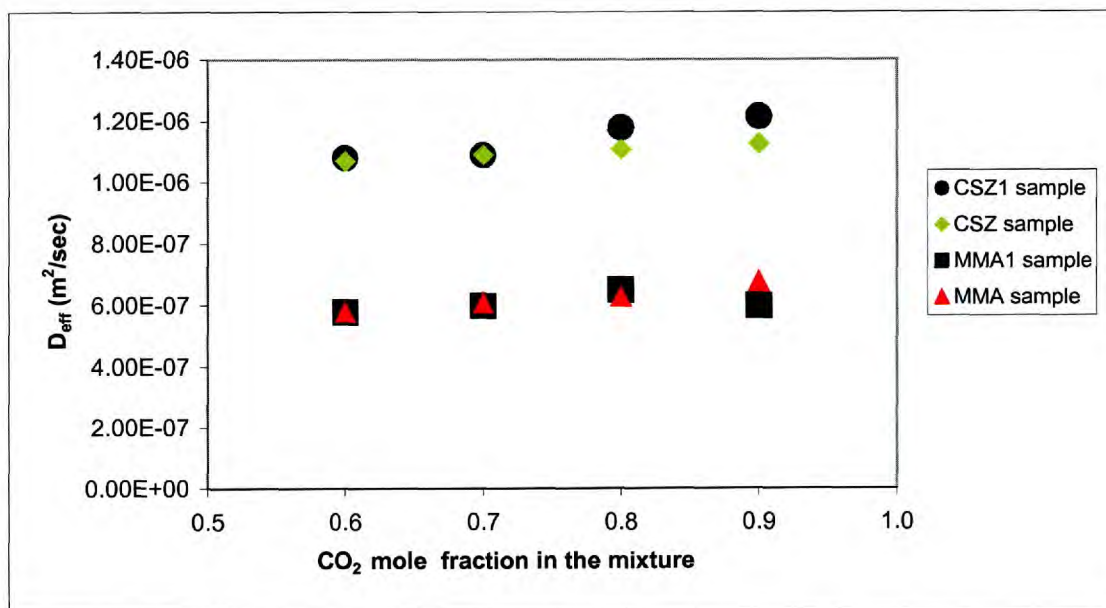


Figure 5.24: Binary diffusivities of CO_2 in N_2 as a function of mole fraction of CO_2 and comparison of the values for the two different support samples.

As shown in Figures 5.23 and 5.24, no significant difference is evident between the values of the diffusion coefficients measured on the initial samples (CSZ and MMA) and those measured on the new ones (CSZ1 and MMA1). It should be noted that,

while the measurements on the initial samples were carried out under slightly higher temperatures than those on the new samples, the impact of this was minimal.

The question that has been addressed in this section is whether different samples from the same support can have an impact on the measured diffusion coefficient. No dependence of the measured diffusivities on the different support samples has been suggested by the results derived from this comparative analysis.

5.6.4 Diffusion Coefficients of CH₄-CO and CO₂-CO Gas Pairs through CSZ1 and MMA1 Support Samples

In this section, the results of the effective diffusion coefficient measurements are given for typical binary mixtures encountered in the operation of anode supported solid oxide fuel cells. Not all the possible combinations of pair of gases were analysed. Limitations dictated by the existing measurement system made possible only the analysis of specific gas pairs.

In particular, the thermal conductivity detector (TCD), which was mainly used for these gas chromatography analyses, responds to any substance that has a thermal conductivity different to that of the carrier gas. In this work, helium was used as the carrier gas for the analysis of gases such as methane, carbon monoxide, or carbon dioxide. Helium gives a big difference in thermal conductivity with nearly any of the simple gases apart from hydrogen. Therefore it is not possible to detect hydrogen accurately in binary mixtures, which consist of one of the above gases, and hydrogen. On the other hand the use of an alternative carrier gas, like argon for instance, allows the detection of hydrogen but not the accurate determination of the rest of the gases. This inevitably excludes such mixtures from the analysis. But for those gas mixtures that the effective diffusion coefficient cannot be measured, it is possible to estimate it. Given that the ratio of the porosity to tortuosity is known and with the molecular diffusivity of the gases predicted by the theory or a semiempirical equation, the effective diffusivity can be obtained. This constitutes one of the main purposes of this work and it is extensively described in the next section.

In Tables 5.14 and 5.15, the effective diffusivities of the binary mixtures of CH₄-CO and CO₂-CO are shown respectively:

CH ₄ composition (volume %)	CSZ1 support $D_{\text{eff}} / \text{CH}_4\text{-CO}$ (m ² /sec) x 10 ⁻⁶ at T=298K, P=1atm	MMA1 support $D_{\text{eff}} / \text{CH}_4\text{-CO}$ (m ² /sec) x 10 ⁻⁶ at T=292K, P=1atm
62.50	1.30	0.71
68.75	1.42	0.76
75.00	1.41	0.79
Average value of D_{eff}	1.38	0.75

Table 5.14: The effective diffusion coefficients of CH₄ in CO through the CSZ1 and MMA1 supports.

CO ₂ composition (volume %)	CSZ1 support $D_{\text{eff}} / \text{CO}_2\text{-CO}$ (m ² /sec) x 10 ⁻⁶ at T=298K, P=1atm	MMA1 support $D_{\text{eff}} / \text{CO}_2\text{-CO}$ (m ² /sec) x 10 ⁻⁶ at T=298K, P=1atm
62.50	1.08	0.58
68.75	1.08	0.59
75.00	1.14	0.62
Average value of D_{eff}	1.10	0.60

Table 5.15: The effective diffusion coefficient of CO₂ in CO through the CSZ1 and MMA1 support.

It is obvious from the tables that the effective diffusivity of methane in carbon monoxide is greater than that of carbon dioxide. This is to be expected since methane is a smaller size molecule and has smaller molecular mass than the bigger molecule of carbon dioxide. The measured diffusivities of the two gas pairs are also plotted as a function of the composition and are shown in Figures 5.25 and 5.26:

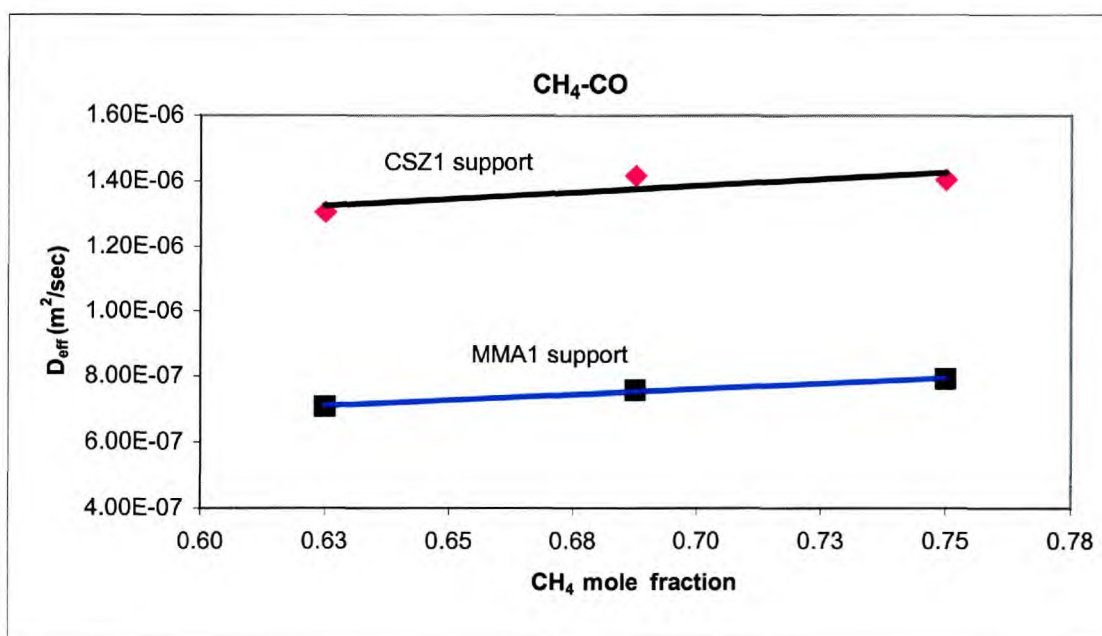


Figure 5.25: Effective diffusivities of CH₄ in CO as a function of methane mole fraction.

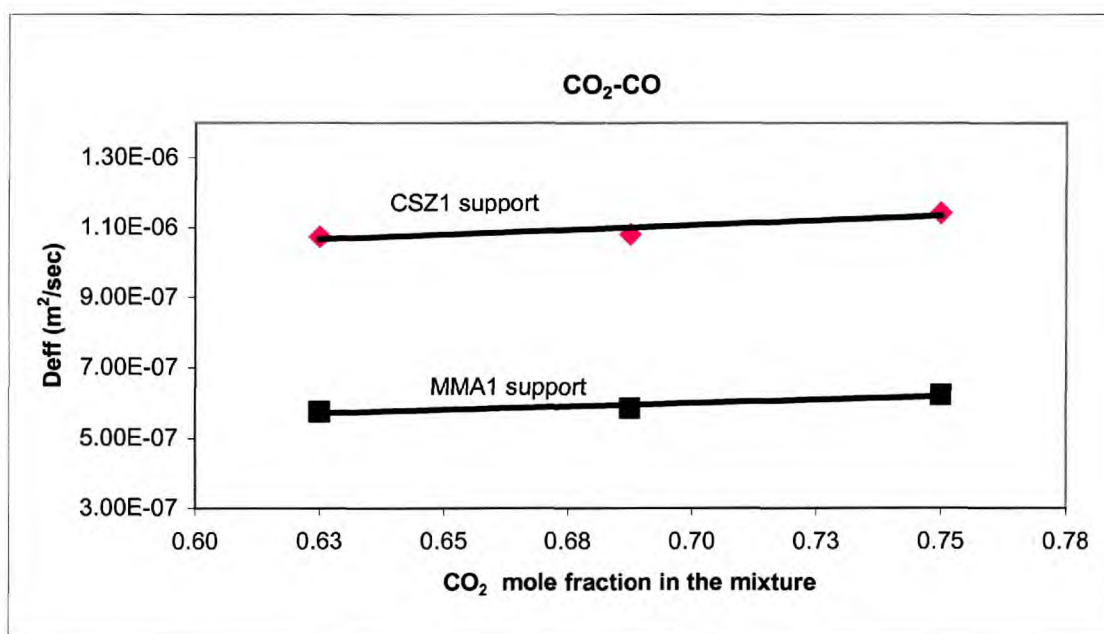


Figure 5.26: Effective diffusivities of CO₂ in CO as a function of CO₂ mole fraction.

For both the binary mixtures no composition dependence is observed within the estimated experimental uncertainty. It is important to distinguish the case of CO₂-CO gas pair. As previously mentioned (section 5.2.2.2) CO and N₂ are isosteric

molecules namely they have the same molecular shape and size. According to the kinetic molecular theory therefore, they should have nearly identical self-diffusion coefficients. Similarly the diffusion coefficients of CO and N₂ interdiffusing with nonpolar gases like CO₂ can also be expected to be very similar.

A close inspection of Tables 5.12 and 5.13 containing the effective diffusivities of CO₂-N₂ gas pair and Table 5.15 containing those ones of CO₂-CO gas pair shows that the values are very close. The average value of the effective diffusion coefficient for CO₂ in N₂ is only 3.5% greater than the average value for CO₂ in CO, through the CSZ1 support and under nearly the same experimental conditions of temperature and pressure. In MMA1 support the corresponding deviation reduces even further to 1.6%.

There is an excellent agreement of the average values for CO₂ in N₂ in CSZ and MMA supports (Tables 5.7 and 5.8) with those for CO₂ in CO through the CSZ1 and MMA1 supports. In the case of the CSZ and CSZ1 supports the average values are found to be exactly the same.

These results confirm the initial assumptions derived from the theory that these isosteric molecules should have similar values of diffusion coefficients when they interdiffuse with the same nonpolar gases, in this case CO₂. The last conclusion provides also greater confidence in the present method and the experimental results.

There are scarcely any studies in which experimental values of effective diffusivities are reported for binary mixtures through porous cermet materials relevant to the construction of anode supported SOFCs. In a recent investigation by Divisek et al. [22] experimentally determined effective diffusion coefficients were provided for typical binary mixtures. Although the data of that study had been corrected to 800°C, the values of the measured effective diffusivities were inexplicably high. Even then, the effective diffusivity for the gas pair of CO-CO₂ was found to be at least an order of magnitude higher than the average value reported here (Table 5.15). Note that the reported ratios of porosity to tortuosity used in the study were very close to the range of ratios derived for this work and will be discussed in the next section. Therefore comparisons cannot be drawn with the present results of this work.

5.6.5 Prediction of Binary Diffusion Coefficients of Gases: Prediction from Theory and Empirical Correlations

It is important to compare the experimentally measured effective diffusivities with values obtained by the theoretical equation and estimation procedures so that the degree of agreement and the accuracy of the results can be evaluated. Moreover, the values obtained by the theoretical equation along with the measured ones allow an estimate of the tortuosity of the porous ceramic supports. The characterisation techniques and tests analysed in the first part of this chapter were used to determine the physical properties of the ceramic materials such as the pore size, the mean pore diameter and the porosity. The determination of the tortuosity completes the investigation of the microstructure of the porous supports. Therefore the main estimation methods are briefly introduced here, followed by the extraction of tortuosity and the comparison in the next sections.

The theory describing diffusion in binary gas mixtures at low to moderate pressures has been well developed. As seen previously, in section 5.2.3.1, the theory results from solving the Boltzmann equation and the results are credited both to Chapman and Enskog. The results of this theory are based on the analyses of molecular motion on dilute gases and these analyses depend on the assumption that molecular interactions involve collisions between only two molecules at a time.

Chapman and Enskog independently derived the following equation [17] for the binary diffusion coefficient,

$$D_{AB} = \frac{3}{16} \sqrt{2\pi kT \left(\frac{1}{M_A} + \frac{1}{M_B} \right)} \frac{1}{n\pi\sigma_{AB}^2 \Omega_{D,AB}} f_{D,AB} \quad (5.30)$$

where all the quantities have the same meaning as those ones appear in Equations (5.17) and (5.18) of section 5.2.2.1. If $f_{D,AB}$ takes the value of unity and n expressed by the ideal gas law, Equation (5.30) takes the form of Equation (5.18) and it is given once again here:

$$D_{AB} = 0.0018583 \sqrt{T^3 \left(\frac{1}{M_A} + \frac{1}{M_B} \right)} \frac{1}{p \sigma_{AB}^2 \Omega_{D,AB}} \quad (5.31)$$

These equations are derived for dilute gases consisting of nonpolar, spherical, monoatomic molecules. However, Equations (5.30) and (5.31) give very accurate results over a broad range of temperatures and provide approximate values of the binary diffusion coefficient.

Apart from Equation (5.31) derived from the theory, several empirical correlations of estimating the diffusion coefficients in low-pressure binary gas systems have been proposed by a number of researchers. These formulas retain the general form of the Equation (5.31), with empirical constants based on experimental data. Fuller, Schettler and Giddings [23], proposed an effective empirical relationship:

$$D_{AB} = \frac{0.001 T^{1.75}}{p \left[\left(\sum V_i \right)_A^{1/3} + \left(\sum V_i \right)_B^{1/3} \right]^2} \sqrt{\frac{1}{M_A} + \frac{1}{M_B}} \quad (5.32)$$

where T is the absolute temperature in Kelvin, p is the pressure in atmospheres and V_i are the values of the atomic diffusion volumes of parts of the molecules, tabulated in corresponding tables [17,24,25].

Othmer and Chen [26], Wilke and Lee [27] among many researchers developed empirical formulas and equations based on the classical kinetic theory. Chen and Othmer [28] employed the following empirical equation:

$$D_{AB} = \frac{0.015 T^{1.81} \left(1/M_A + 1/M_B \right)^{1/2}}{P \left(T_{cA} T_{cB} \right)^{0.1405} \left(V_{cA}^{0.4} + V_{cB}^{0.4} \right)^2} \quad (5.33)$$

where T_{cA} , T_{cB} , V_{cA} , and V_{cB} are the critical temperatures and the critical volumes of the two gases, and M_A , M_B are the molecular weights of gases A and B.

5.6.5.1 *Estimation of Tortuosity*

As previously seen the experimentally measured effective binary diffusion coefficients refer to the diffusion of gases through the porous ceramic supports and therefore the impact of the porous microstructure on the gaseous diffusion has to be taken into account. The approach typically adopted is to consider porous media as consisting of a certain percentage of open pores namely the porosity. They also have a degree of interconnection resulting in paths through the solid, which are some percentage longer than a direct path. This relative length of the diffusional path across the thickness of the porous support defines the tortuosity [29].

Unlike porosity the tortuosity cannot be measured directly, but by combining the experimental data and a diffusion model can be estimated approximately. Among the proposed types of diffusion models two are mostly preferred. The parallel path pore model is the first type of these models. Rothfeld [30] and Scott [31] developed a modified parallel path model using effectiveness factors and the transition region capillary equation. Their model version assumes that the porous material can be substituted by a bundle of straight cylindrical capillaries with identical radius (average pore radius). Johnson and Stewart [32] modified this and integrated over the pore size range. Their model is based on a similar idea that a porous structure can be visualised as a bundle of parallel cylindrical pores but of different radii. The second type of diffusion model describes the porous media as a packed bed of equal spherical particles [33]. Both types require the pore size or particle size as well as the porosity and tortuosity of the porous material.

These two models can be regarded as special cases of a more general model. This is known as the dusty gas model [34]. For instance, the equation that describes the diffusion flux for a binary gaseous mixture in the Rothfeld and Scott's model is identical with the diffusion equation of the dusty gas model. It is important to note that the dusty gas refers to the theory or the mathematical formulations of the transport equations, which describe the transport of gases in porous media and not to the structured model of the porous media (e.g. parallel pore or packed spheres).

In the dusty gas it is possible to obtain a solution of the diffusion and viscous flows while the porous structure is somehow isolated. The geometric characteristics are

included into the transport coefficients as constants (e.g. ε/τ). In other words this assumes that the transport coefficients, can be modified empirically to account for geometrical aspects. Thus the effective diffusion coefficient can be given by,

$$D_{AB}^{eff} = \frac{\varepsilon}{\tau} D_{AB}^{free} \quad (5.34)$$

where ε is the porosity of the porous medium, τ is the tortuosity, D_{AB}^{eff} is the measured effective diffusivity and D_{AB}^{free} is the “free” molecular diffusivity.

From Equation (5.34) estimates of tortuosity can be calculated when the other parameters are known. The average values of the effective diffusion coefficients for the binary mixtures are taken from Table 5.5 to Table 5.8 and Table 5.11 to Table 5.15, whereas the free molecular diffusion coefficient for the gaseous mixtures can be calculated by Equation (5.31). The average porosities of the porous supports determined by different tests in the first part were 21.56% and 15.24% for the CSZ and MMA respectively. The results obtained from Equation (5.34) are shown in Table 5.16.

Porous support	Gas pairs	D_{AB}^{eff} (m ² /sec) x10 ⁻⁶	D_{AB}^{free} (a) (m ² /sec) x10 ⁻⁴	Tortuosity
CSZ	H ₂ -N ₂	5.30	0.73	2.97
	CH ₄ -N ₂	1.23	0.22	3.86
	CO-N ₂	1.16	0.20	3.71
	CO ₂ -N ₂	1.12	0.15	2.89
	CH ₄ -CO	1.38	0.22	3.44
	CO ₂ -CO	1.10	0.15	2.94
MMA	H ₂ -N ₂	2.96	0.73	3.76
	CH ₄ -N ₂	0.66	0.22	5.08
	CO-N ₂	0.61	0.20	5.00
	CO ₂ -N ₂	0.62	0.15	3.69
	CH ₄ -CO	0.75	0.21	4.27
	CO ₂ -CO	0.60	0.15	3.81

Table 5.16: Estimated tortuosity for a range of gas pairs.

(a) Calculated by theoretical Equation (5.31)

In Table 5.16, a range of tortuosities estimated at ambient pressure and temperature for different binary systems can be found. This range allows us to fit the experimental data and make reasonable predictions as to the diffusion behaviour for other binary gas mixtures in these porous supports. For the CSZ support the tortuosity varies from 2.89 to 3.86, whereas for the MMA support the estimates cover a range of higher values from 3.69 to 5.08. Because the tortuosity is a characteristic physical property of the porous ceramic support, it should be virtually constant under varying conditions. This may be partly a consequence of uncertainties in the experimental data.

Another significant factor in the estimation of tortuosity is the pore size distribution. It has been shown [35] that for a bidisperse pore size distribution an increasing proportion of micro size pores results in an increase in the tortuosity. However for both the porous supports here the pore size distribution is not bimodal, while most of

the pores lie in the range from 0.5 to 3.0 μm namely the macropore region. This leads to the relatively low values of the tortuosity estimated for the CSZ support but tortuosity values as high as 5.08 have been found for the case of the MMA support.

It is evident from the results in Table 5.16 that there is a repeated pattern with regard to the extracted values of tortuosity for both samples and that there is a definite gas effect on the extraction of tortuosity. For example the gas pair of hydrogen-nitrogen presents smaller tortuosity than that of methane. The reason for this difference in tortuosities may lie on the fact that methane, a big molecule, cannot penetrate that deep into the porous structure while hydrogen does.

In the Table 5.17, the average vales of the tortuosities and porosities along with the bulk densities of the two porous supports, determined by the analysis in the first part, are shown.

Porous support	Bulk density (Kgr/m ³) x10 ³	Tortuosity	Porosity
CSZ	3.74	3.30	21.56%
MMA	2.75	4.27	15.24%

Table 5.17: The bulk density and the average tortuosity for the CSZ and MMA support.

From Table 5.17, it is shown that the MMA support with smaller bulk density has greater tortuosity than the CSZ support with the bigger bulk density. In studies on diffusion in porous solids of the same compressed alumina powder, the tortuosity has been reported to increase markedly with increasing the bulk density of the material. The latter was achieved by using a higher compression on the powder in making the porous solids. This leads to the decrease of the average pore radius and the macroporosity. The pore size distributions of the above materials have demonstrated this finding by showing that as the bulk density increases, micropores dominate while very few macropores remain.

But in this work the materials are different and no bidisperse distribution was shown by the analysis. The range of high tortuosities for the MMA support could be

explained by the MMA microstructure itself. The micrographs for the MMA support showed grains of rough and angular shape as opposed to more symmetrical particles of the CSZ sample. The irregular shape and size of the grains may have caused pores of varying cross sections and further constrictions, which in turn have resulted in higher tortuosity.

5.6.5.2 Comparison of Estimation Methods for Binary Gas Diffusion Coefficients

An attempt is made in this section to establish the relative accuracy of two estimation methods for predicting the diffusivities of gases. These are the empirical relationship, Equation (5.32), proposed by Fuller, Schettler and Giddings and the empirical equation by Chen and Othmer, Equation (5.33).

Using the effective diffusivities for the different binary mixtures as well as the porosities and the average values of tortuosities determined in the previous section and shown in Tables 5.16 and 5.17, the 'free' molecular diffusivities can be computed by Equation (5.34). These extracted values serve as the experimental data upon which comparison of results from the two empirical correlations is based.

Gas pairs	D_{AB}^{free} (m ² /sec) x 10 ⁻⁴	FSG(a) Average error %	Chen Othmer Average error %
H ₂ -N ₂	0.82	-3.18	20.31
CH ₄ -N ₂	0.19	-5.02	24.25
CO-N ₂	0.18	-4.60	-1.49
CO ₂ -N ₂	0.17	0.59	-1.15
CH ₄ -CO	0.21	-5.33	27.25
CO ₂ -CO	0.17	4.91	7.90

Table 5.18: Comparison of the results obtained from two estimation methods with the experimental data taken from this work.

(a) FSG = Fuller, Schettler and Giddings empirical relationship

Table 5.18 contains the values of the experimental diffusivities as those extracted using Equation (5.34). The other two columns contain the percentage error introduced by the two equations used to predict the experimental diffusion coefficients. All results refer to 298K temperature and 1 atm pressure.

Fuller, Schettler and Giddings empirical correlation is seen to perform substantially better than the Chen and Othmer equation. Only in one case is the error introduced by Chen and Othmer equation smaller than that of Fuller, Schettler and Giddings method. This estimation method with an average error of 3.94% shows the best agreement between calculated and experimental values.

Since the discussion of the results in this chapter involves only ordinary (bulk) diffusion, it is important to justify that Knudsen diffusion can be eliminated. The comparison between the mean free path of the gases and the pore size is the factor that determines whether ordinary diffusion or Knudsen diffusion is the dominant mode of gas transport within the pores. The mean free paths of individual gases can be calculated from the kinetic theory of gases (Hirschfelder et al [15]):

$$\lambda = \frac{kT}{\sqrt{2}\pi d^2 P} \quad (5.35)$$

where λ and d are the mean free path and the molecular diameter of the gas respectively, and they are both expressed in nanometers. Values of the molecular diameters (at $T=25^\circ\text{C}$, $P=1\text{ atm}$) along with the calculated values of mean free path are listed below:

Gas	H ₂	N ₂	H ₂ O	CO ₂	CH ₄	CO
σ (nm)	2.915	3.749	2.641	3.996	3.796	3.590
λ (nm)	1.076	0.651	1.311	0.573	0.635	0.709

Table 5.19: Molecular diameters of the gases and the calculated values of the mean free path, at $T=25^\circ\text{C}$, $P=1\text{ atm}$.

Mercury porosimetry results have shown that the most probable pore diameter for both porous materials is $2.0\text{-}2.1\text{ }\mu\text{m}$. A comparison of the above results shows that the mean free path for all gases are less than the pore diameter (at least three orders of magnitude) and therefore diffusion should be within the molecular diffusion range. Even in high operating temperatures, those relevant to SOFC operation, the Knudsen diffusion can be neglected since the mean free paths are still quite smaller than the pore diameter of the individual gases.

5.7 Conclusions

In order to investigate and describe the morphology and the porous structure of two porous substrates and measure their basic geometrical properties, a number of characterisation techniques have been applied, such as scanning electron microscopy, mercury porosimetry, image analysis, as well as water and ethanol uptake measurements.

Scanning electron microscopy is suitable for the observation of the microstructure and the qualitative assessment of the structure and texture of the porous materials. By image analysis, it was possible to estimate the total porosity and the mean pore diameter or radius. Mercury porosimetry is considered to be the only method that can quantitatively determine the open porosity and the volume of open pores (or “channels”).

These parameters may then be correlated with gas transport coefficients obtained by diffusion measurements and presented here. This will provide the basis for the understanding of the interplay between the microstructure of the porous materials and gas diffusion.

The effective diffusivities for a number of binary gaseous mixtures have been obtained and their composition dependence has been examined. The kinetic theory of gases has been employed to explain any variations in the range of the effective diffusivities. No effect of the concentration of the gas under analysis was found within the accepted experimental uncertainty. In general the measured diffusion coefficients of the gases through the CSZ support are greater than those in the MMA support.

No effect of different support sample has been identified. Using different porous samples from the same substrate has shown that the values of the effective diffusivities are in very close agreement with those values measured through the initial samples.

Estimates of the tortuosity for the two porous supports have been obtained by using the appropriate diffusion model and the experimental data. A range of tortuosities

ranging from 2.89 to 3.86 has been found for the CSZ support, while for the MMA the range is from 3.69 to 5.08. It is obvious that the values of the tortuosities for the MMA support are higher than those ones for the CSZ. The non-constancy of the tortuosity can be partly attributed to the uncertainties in the experimental data.

With the effective diffusivities and the average values of porosity and tortuosity an estimate of the molecular diffusivity for the different binary mixtures was obtained. Comparison of these extracted experimental values with those calculated by two semiempirical correlations has provided the relative accuracy of the estimation methods.

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Chapter 6

Anode Support Performance Modelling

6.1 Introduction

In this chapter an anode support performance model, which takes into account gas diffusion within the porous support, is presented.

Firstly, an account of the basic models for gas transport in porous media is given. Their theoretical foundation is discussed and the mathematical formulation of the transport equations, that is expressions of the diffusive fluxes through the porous medium, is introduced.

Then the dusty gas model approach is presented. The dusty gas is viewed as the theory which describes the transport of gases through porous media. Its general principles and the mathematical equations for the different transport mechanisms are presented. The combined transport equation is derived for the case of a binary gaseous mixture. Simplification of the general form of the combined transport equation, through a number of approximations, is shown to lead to the ordinary diffusion equation. In this form the dusty gas model is adopted to describe the gas diffusion through the porous supports. The model development is completed by the appropriate boundary conditions.

The steady and the unsteady state ordinary diffusion/Fick's equations are solved for a binary gas mixture through both types of the porous supports. The physical properties of the materials are incorporated into the model and their impact on the anode support performance is shown. Thus losses arising from the diffusion process are quantified by calculating the concentration polarisation of the anode and improved microstructures for the porous supports are recommended.

6.2 Models of Porous Media for Gas Diffusion

In the previous chapter experimental diffusion data were obtained by using the steady state countercurrent diffusion technique of Wicke-Kallenbach. In this method the values of the diffusion coefficients and the diffusion fluxes were calculated from a mass balance for the diffusion cell. Therefore the investigation of diffusion of

binary gaseous mixtures in the porous supports did not depend on any porous model. The use of a porous model as a means of visualising and describing the porous structure was made necessary only when the certain physical parameters of the porous structure (i.e. tortuosity) had to be determined.

The models of porous media do not only provide a means for the representation of the porous structure but also permit the mathematical description. There is a number of theoretical and semiempirical models of porous media proposed for the mechanism of gaseous diffusion in porous materials and solids and most of these models provide a method for the computation of the diffusion fluxes. A reliable model would also predict diffusion coefficients from known physical properties of the gases and the porous materials. In the majority of the studies reported in the literature simple structures have been used with only one pair of gases. The most widely used and studied binary mixtures consisted of gases such as nitrogen, hydrogen, helium and argon.

A comparison of the most widely employed models of porous media has been reported in a number of studies [1,2]. A brief review of some of them is presented in the following sections.

6.2.1 Parallel Path Pore Models

As already mentioned in the previous chapter, in the parallel path pore model the porous structure can be represented by an array of straight, cylindrical pores of different radii. The model developed by Johnson and Stewart [3] is based on this idea. The diffusion in pores of different sizes occurs in parallel, whereas the pore orientation is assumed randomly distributed in space. For isobaric, binary diffusion the differential flux expression in the transition region is obtained by integrating the single pores flux over all pore sizes,

$$N_A = - \int_0^\infty \left[\frac{D_{ABK}(r)/\tau}{(1 - \alpha \delta_A(r) y_A)} \right] \left(\frac{dc_A}{dz} \right) f(r) dr \quad (6.1)$$

where $D_{ABK}(r)$ (diffusivity for the transition region in a straight circular pore of radius r) and $\delta_A(r)$ are defined as:

$$D_{ABK}^{-1} = D_{AB}^{-1} + D_{KA}^{-1} \quad (6.2)$$

$$\delta_A^{-1} = 1 + \left(\frac{D_{AB}}{D_{KA}} \right) \quad (6.3)$$

$$\alpha = 1 + \left(\frac{N_B}{N_A} \right) \quad (6.4)$$

D_{AB} and D_{KA} are the bulk binary diffusion coefficient and the Knudsen diffusion coefficient in straight circular capillary tube respectively. Also the function $f(r)$ is the pore volume distributions function of the porous material. This model can be used to predict the diffusive flux (given that the tortuosity τ is known) or to calculate the tortuosity from experimentally determined fluxes.

Rothfeld and Scott's model [4,5] is a modified version of the above model. It assumes that the porous medium can be substituted by a bundle of straight cylindrical capillaries. Here the difference is that the radii of the pores are the same (average pore radius $\bar{r}$). In the transition region the diffusive flux of component A in a binary gaseous mixture is given by

$$N_A = -D'_{ABK} \left(\frac{dc_A}{dz} \right) + \delta_A y_A N \quad (6.5)$$

where the effective diffusion coefficient D'_{ABK} is related to the coefficient $D_{ABK}(\bar{r})$ by

$$D'_{ABK} = \frac{\varepsilon}{\tau} D_{ABK}(\bar{r}) \quad (6.6)$$

This model can be used to predict the effective diffusion coefficients or the diffusive fluxes on the basis of experimental diffusion measurements made with another gaseous system but on the same porous sample. If the tortuosity can be obtained independently, experimental measurements are not necessary. It is necessary though

to know the average pore radius $\bar{r}$. However, there is not a satisfactory procedure for the estimation of the average pore radius from the pore volume distribution curve. This is a drawback of Rothfeld and Scott's model which makes its application less straightforward.

Wakao and Smith [6,7] proposed the random pore model for bidisperse porous materials. In this model the pore structure is not actually represented by an array of straight, cylindrical pores but the pores are rather divided into two types, the macropores and the micropores. It is further assumed that the diffusion occurs through the micropores, the macropores and through parts of micro and macropores connected in series. The probability that the micro and macropores line up is assumed proportional to the square of the porosity. No tortuosities are assumed and the model uses only the pore size distribution data to predict the diffusion rate. Application of the random pore model is described in a number of studies [8,9] in which experimental data for diffusion in bidisperse porous pellets of alumina have been compared with those predicted by the random pore model.

It can be seen that the various models require different amounts of information with regard to the properties of the system. Therefore in the equations which provide the diffusion fluxes different constants appear. In most of the cases these constants characterise the porous medium itself and they do not have a physical meaning. Thus they can be seen as adjustable parameters. The comparison and applicability of the various models is mainly based on the constancy of these parameters for different pairs of gases as well as for different concentration conditions and on the critical evaluation of their numerical value.

Therefore it becomes clear that it is always necessary to carry out a determination of the porous structure parameters as well as an experimental study of the diffusion fluxes.

6.2.2 The Packed Spheres Model

For this type of model the porous medium is considered to consist of loosely packed particles so that gas molecules can move between them. The physical parameters of the medium such as porosity and tortuosity can be defined here too but the derivation

of mathematical equations for them is not that simple. The model is apparently suitable for the dusty gas model, with the particles of the solid medium clearly acting like dust in the gas.

6.3 The Dusty Gas Model

The various types of models analysed in the previous section can be seen as idealisations of the structure of the porous media. These models can be considered as special cases of a more general model which is known as dusty gas model (DGM) [10]. The dusty gas model is a complete theory that has been developed to describe the transport of gases through porous media.

It is very important to recognise that this term refers to the set of the mathematical equations that describe the gas transport and not to the choice of porous media model (e.g. parallel pore or packed spheres). It can be applied to any of the previous porous media models, since its results are of considerable generality and are not model specific.

It is so called because it views the porous medium and the gas as a mixture where the porous medium is pictured as giant evenly distributed dust particles at rest (motionless). How this distribution actually looks makes no difference since the structure of the medium is absorbed into the values of the transport coefficients or into constants of proportionality.

In the dusty gas model, the structural problem is a separate one and can be made as simple or as complicated as necessary. The question of the geometry of the structure arises only when the general differential equations for the transport of all the species in the mixture need to be integrated. This means that boundary conditions need to be specified. In fact this is one of the main advantages of the dusty gas approach. The structural problem is avoided until the end when it can be treated independently.

The derivation of transport equations for the gas is based on molecular kinetic theory arguments. However the important aspects of the dusty gas model can be presented in a simple way without having to discuss all the mathematical complexities of the kinetic theory of gases. In the following subsections these essential aspects of the

dusty gas are presented through the elementary equations that describe the various mechanisms of gas transport.

6.3.1 Modes of Gas Transport

Before giving the general transport equations the different transport modes by which gas can be transferred need to be introduced.

1) *Free-molecule or Knudsen flow*, in which the gas density is so low that collisions between molecules can be ignored compared to collisions of molecules with the walls of the porous medium. In other words the mean free path of the molecules is smaller or the same order of magnitude as the diameter of the pores.

2) *Viscous or Convective flow*, in which the gas acts as a continuum fluid with the pressure gradient being the driving force, and molecule-molecule collisions dominate over gas-wall collisions. This is sometimes called bulk flow.

3) *Ordinary or Continuum Diffusion*, in which the different species of a mixture move relative to each other under the influence of concentration gradients (concentration diffusion), temperature gradients (thermal diffusion) or external forces (forced diffusion). In this case gas-gas collisions also dominate over gas-wall collisions.

4) *Surface Flow or Diffusion*, in which molecules move along a solid surface in an absorbed layer. This mechanism is assumed to be independent and it is usually omitted from the basic analysis as it is of less significance.

6.3.1.1 Knudsen Flow

As previously mentioned, if the gas density is low, or the pores of the medium are quite small, or both, the molecules collide with the pore wall much more frequently than with each other.

In general, if there is a gas with a molecular density of n molecules/cm³ at one side of a porous hole and a vacuum at the other, the free-molecule or Knudsen flux is

$$J_K = wn\bar{v} \quad (6.7)$$

where J_K has units *molecules/cm²s*, w is a dimensionless probability factor, and $\bar{v}$ is the mean molecular speed,

$$\bar{v} = \left(\frac{8RT}{\pi M} \right)^{1/2} \text{ or } \bar{v} = \left(\frac{8k_B T}{\pi M} \right)^{1/2} \quad (6.8)$$

with k_B being the Boltzmann's constant, For a long straight circular tube of radius r and length L ($L \gg r$), from whose surface the molecules rebound diffusely, the value of w is $(2r/3L)$. If there is a gas mixture instead of a single gas, each species acts independently, and the total flow is a sum of terms

$$J_K = \sum w_i n_i \bar{v}_i \quad (6.9)$$

where i denotes the particular gas species.

For a gas on both sides of the porous hole, the net flux is proportional to the difference in gas number densities at the two sides. We can write it in a differential form and define a Knudsen diffusion coefficient D_{iK} having units *cm²/s*,

$$J_{iK} = -D_{iK} \nabla n_i \quad (6.10)$$

for species i . The minus sign shows that the gas moves “down” the gradient when D_{iK} is positive. Comparing the above equations for the fluxes, it is evident that the D_{iK} is proportional to the mean molecular speed $\bar{v}$. It is customary to make this proportionality explicit by defining a Knudsen flow parameter or permeability coefficient K_o by

$$D_{iK} = \frac{4}{3} K_o \bar{v}_i \quad (6.11)$$

The value of K_o depends only on geometry of the porous and the gas-surface scattering law. For a long, straight, circular tube of radius r with diffuse scattering, the value of K_o is $r/2$. It is much easier to measure K_o experimentally than to calculate it from the geometry (which is rarely known with any accuracy). It is also obvious from Equation (6.11) that D_{iK} independent of pressure and increases with temperature as $T^{1/2}$.

For two different gases at the same pressure at the two sides of the porous,

$$\frac{-J_{1K}}{J_{2K}} = \frac{D_{1K}}{D_{2K}} = \frac{\bar{v}_1}{\bar{v}_2} = \left(\frac{M_2}{M_1} \right)^{1/2} \quad (6.12)$$

provided that K_o is the same for both gases. This is Graham's law of effusion.

6.3.1.2 Viscous or Convective Flow

In the viscous or convective flow, the gas flow is induced by a pressure gradient. The inertial terms are omitted from the equation of motion of the fluid (gravity in the general Navier–Stokes equation) and turbulence is not included in the present study. Therefore, only the so-called “creeping flow” is treated.

The viscous flux for gases is described by Poiseuille's law (same as liquids). The basic idea is simple: if the gas is not accelerating the net force ($\sum F$) on any element of it must be zero, so that the viscous-drag force balance the force due to the pressure difference across the element:

$$J_{visc} = \text{flow} / \text{area} = \frac{-nB_o}{\mu} \nabla p \quad (6.13)$$

where J_{visc} is the viscous flux in *molecules/cm² s*, n is the total number density, B_o is the viscous flow parameter characteristic of the geometry with units of *cm²*, μ is the viscosity of the gas in *g/cm s* and p is the pressure. The boundary conditions for continuum flow is that the gas velocity is zero at the walls (no-slip condition). Any slip flow at the walls is incorporated into the Knudsen flow. The compressibility

enters through the equation of state $n=p/k_B T$, making the coefficient of ∇p in Equation (6.13) dependent upon position through its dependence on p .

For long, straight, circular capillary of radius r , the value of B_o is $r^2/8$ and integration of Equation (6.13) leads to Poiseuille's law. For a porous medium or a bed of packed particles it is easier to determine the value of B_o experimentally than to calculate it from the geometry, just like the case for K_o .

For mixtures, the viscous flux of species i is proportional to its mole fraction x_i in the mixture, since the flow is nonseparative (bulk flow has no tendency to separate a mixture into its components),

$$J_{i visc} = x_i J_{visc} \quad (6.14)$$

6.3.1.3 Ordinary or Continuum Diffusion

The ordinary diffusion mechanism is the most difficult of the three main mechanisms of gas transport to define satisfactorily. In order to make the problem simple at this point, temperature gradients and external forces are ignored. Also a diffusion coefficient can be defined for a mixture in which the net flux is zero, and in which there is no pressure gradient so that there is no viscous flow and no pressure diffusion. In this case, there are only the diffusive fluxes J_{1D} and J_{2D} for the binary mixture,

$$J_{1D} = -D_{12} \nabla n_1 \quad (6.15)$$

$$J_{2D} = -D_{21} \nabla n_2 \quad (6.16)$$

where the ordinary diffusion coefficients D_{12} and D_{21} are in cm^2/s . It is easy to see that $D_{12} = D_{21}$, because $J_{1D} + J_{2D} = J_D = 0$ for no net flux and $\nabla n_1 + \nabla n_2 = \nabla(n_1 + n_2) = \nabla n = 0$ for no pressure gradient (pressure is maintained constant).

Setting up an experiment to produce such a situation is very difficult, because a small pressure different is necessary to keep $J_D = 0$. This can be described physically

by considering two different gases contained in two vessels at the same temperature and pressure and which are connected by a small tube (or a porous plate). The faster light molecules tend to get through the tube more quickly than the slower, heavy ones. As a result of this the pressure rises on the side of the heavy gas until the viscous flow induced back through the tube (viscous flow caused by this temporal small pressure difference) is just sufficient to make the net flux zero again. The resulting steady-state pressure difference is very small if the tube has a large diameter, but can be large for small capillaries or fine porous media.

To keep the pressure uniform in the two vessels (in other words no pressure difference across the tube or the porous plate), a second tube with a sliding, frictionless piston can be added to the previous arrangement. In order to keep the pressures equal the piston must be moved and this movement gives rise to a net mass flux between the vessels. Therefore the net flux of gas is obviously not zero any more. This new situation can be described by the same diffusion coefficients D_{12} and D_{21} defined previously, provided that an extra term for the net flux contribution of each species is included in the diffusive fluxes expressed by Equations (6.15) and (6.16),

$$J_{1D} = -D_{12}\nabla n_1 + x_1 J_D \quad (6.17)$$

$$J_{2D} = -D_{21}\nabla n_2 + x_2 J_D \quad (6.18)$$

where $J_{1D} + J_{2D} = J_D$ and $x_i = n_i/n$ is the mole fraction. All the fluxes are diffusive in this case because there is no pressure gradient. It is easy to see that $D_{12} = D_{21}$ by adding these two equations and noting that $\nabla n = 0$. Equations (6.17) and (6.18) can be thought of as defining the diffusion coefficients in a coordinate system moving with a velocity that corresponds to the average velocity, $u = J_D/n$.

Equations (6.17) and (6.18) define pure diffusive transport in the continuum region. The most important point is that the pressure is uniform, so that the viscous flow is zero. To determine the flux when the pressure is nonuniform, the viscous flux due to the pressure gradient has to be determined first, and combined with the diffusive flux. These two fluxes are simply additive to a high degree of approximation.

Because of this additivity, diffusion at uniform pressure can be regarded as a more fundamental process than equal countercurrent diffusion.

The relation between the two fluxes in Equations (6.17) and (6.18) was discovered experimentally and it is the following:

$$\frac{-J_{1D}}{J_{2D}} = \left(\frac{M_2}{M_1} \right)^{1/2} \quad (6.19)$$

provided that the pressure is kept uniform. This is Graham's law of diffusion and it looks like the effusion law, but it is quite different. Its range of validity does not depend on any special relation between the mean free path and the pore size or tube diameter so it holds at all pressures, whereas effusion law holds only in the free-molecule region.

The foregoing discussion of the ordinary diffusion is based on the assumption that the geometry of the pore or the tube through which diffusion occurs is well known, which is also rarely the case for the porous media. However it is found experimentally that diffusion in a porous medium can be modelled by the transport equations of the same form as Equations (6.17) and (6.18), provided D_{12} is replaced by an effective diffusion coefficient D_{12}^{eff} . This accounts for the geometry the medium. It has been previously shown (chapter 5) that the relation between the two diffusion coefficients has the form of

$$D_{12}^{eff} = \left(\frac{\varepsilon}{\tau} \right) D_{12} \quad (6.20)$$

where the constant ε/τ is the ratio of porosity over tortuosity as introduced in chapter 5. According to this ratio, the free space in a porous medium for diffusion is a fraction of the total apparent volume of the medium, determined by the porosity ε and each pore or hole is on average longer by some factor than a straight pore though the solid, as determined by the tortuosity τ . Usually ε/τ is determined experimentally just as are K_o and B_o .

6.3.1.4 Combined Transport Equations For Binary Mixture

At first the combinations of free-molecule and continuum diffusion are considered. The equations for these two transport mechanisms have been already derived in the previous sections and for the species 1 of a binary mixture are,

$$J_{1K} = -D_{1K} \nabla n_1 \quad (6.21)$$

$$J_{1D} = -D_{12} \nabla n_1 + x_1 J_D \quad (6.22)$$

Using the Ideal Law of gases, ($p_i = n_i kT$), these equations take the form of

$$J_{1K} = -\frac{D_{1K}}{kT} \nabla p_1 \quad (6.23)$$

$$J_{1D} = -\frac{D_{12}}{kT} \nabla p_1 + x_1 J_D \quad (6.24)$$

According to Newton's second law, if species 1 is not accelerating, then the average momentum transferred to it by collisions with the walls and with the other species must be balanced by some force. Assuming that there not external forces like gravity, this force can be attributed to the gradient of the partial pressure of the species, ∇p_i . This force consists of separate contributions, each one sufficient to balance the momentum transfer by wall collisions and by collisions with each of the other species in the mixture. Equations (6.23) and (6.24) can be re-written as,

$$-\nabla p_{1(wall)} = \frac{kT}{D_{1K}} J_{1K} \quad (6.25)$$

$$-\nabla p_{1(molecule)} = \frac{kT}{D_{12}} (J_{1D} - x_1 J_D) \quad (6.26)$$

Considering the above argument, the total partial pressure in the gas mixture is given by the sum of both contributions. Thus the individual terms ∇p_i add together and Equations (6.25) and (6.26) can be combined,

$$-\nabla p_1 = \frac{kT}{D_{1K}} J_{1K} + \frac{kT}{D_{12}} (J_{1D} - x_1 J_D) \quad (6.27)$$

with a similar equation for species 2.

It should be noted that Equation (6.27) describes the diffusion of one component of a binary mixture at uniform total pressure for the entire pressure range between the Knudsen limit and the continuum limit. Therefore this equation gives the combined diffusive flux (J_{1D}). J_{1K} and J_{1D} are really the same just as the current through two resistors in series is the same. This follows from the electrical analogue for combining the different transport mechanisms and which combines the diffusive fluxes in series.

In addition, if a gradient of total pressure exists, the resulting viscous flux must be added to the diffusive flux. According to the dusty gas approach [10] the reason for the additivity, results from the kinetic theory of gases in that there no viscous terms in the diffusion equations and no diffusion terms in the viscous-flow equations; the two are independent in the sense that there is not direct coupling terms in these equations. Viscous flux is given by Equation (6.13).

Similarly, the surface flux should be added to the diffusive flux. In fact this is more a physical assumption than the result of a more general principle. The equation for the surface flux is,

$$J_{1S} = -D_{1S} \nabla n_1 \quad (6.28)$$

Now the total flux of species 1 is given by:

$$J_1 = J_{1D} + J_{1visc} + J_{1S} = J_{1D} + x_1 J_{visc} + J_{1S} \quad (6.29)$$

with an analogous equation for species 2. And the total flux for all the species is,

$$J = J_1 + J_2 = J_D + J_{visc} + J_S \quad (6.30)$$

The viscous flux is given in terms of ∇p by Equation (6.13) and the combined diffusive flux in terms of ∇p by Equation (6.27). It is easier to combine these equations by solving for J_{1D} from Equation (6.29) and J_D from Equation (6.30) and finally substituting the results in Equation (6.27), which yields,

$$-\frac{1}{kT} \nabla p_1 = \left(\frac{1}{D_{1K}} + \frac{1}{D_{12}} \right) J_1 - \frac{x_1}{D_{12}} J - \frac{x_1}{D_{1K}} J_{visc} - \left(\frac{1}{D_{1K}} + \frac{1}{D_{12}} \right) J_{1S} + \frac{x_1}{D_{12}} J_S \quad (6.31)$$

Then substituting for J_{visc} from Equation (6.13) and for J_{1S} from Equation (6.28) and rearranging gives,

$$J_1 = -D_1 \left(1 + \frac{D_{1S}}{D_1} + x_1 \frac{(D_{1S} - D_{2S})}{D_{12}} \right) \nabla n_1 + x_1 \delta_1 J - x_1 \gamma_1 \left(\frac{nB_o}{\mu} \right) \nabla p + \frac{x_1}{kT} \frac{D_{2S}}{D_{12}} \nabla p \quad (6.32)$$

where

$$\frac{1}{D_1} = \frac{1}{D_{1K}} + \frac{1}{D_{12}} \quad (6.33)$$

$$\delta_1 = \frac{D_1}{D_{12}} = \frac{D_{1K}}{D_{1K} + D_{12}} \quad (6.34)$$

$$\gamma_1 = \frac{D_1}{D_{1K}} = \frac{D_{12}}{D_{1K} + D_{12}} = 1 - \delta_1 \quad (6.35)$$

Equation (6.32) and a similar one that holds for species 2, describe the phenomena of isothermal diffusion and flow in a binary mixture (including all the different transport mechanisms) over the whole pressure range.

6.3.1.5 Approximations for the Combined Transport Equations

The important thing about the form of Equation (6.32) is that it clearly shows different behaviours as different transport mechanisms dominate as well as the behaviour in the transition region. Apart from surface diffusion, which is usually ignored, the dominant transport mode in the different regions is found either through the pressure dependence of parameters D_1 , δ_1 and γ_1 or the comparison of the pore diameter with the mean free path.

Assuming that the pores of the porous medium are much larger than the mean free path of the gases, the Knudsen term can be neglected (D_{1K} tends to infinity with increasing the radius of the pores, see section 6.3.1.1 for derivation of D_{1K}). Therefore $D_1=D_{12}$, $\delta_1=1$ and $\gamma_1=0$. Also the terms that contain the surface diffusion coefficients are dropped since the surface diffusions is ignored. Thus taking into account all the assumptions made, Equation (6.32) becomes:

$$J_1 = -D_{12}\nabla n_1 + x_1 J \quad (6.36)$$

Equation (6.36) gives the total flux for species 1 in the continuum region and it is the same as Equation (6.17) for continuum diffusion, if the pressure gradient is zero. It is easy to see that dropping the Knudsen term leads to the drop of the viscous flow term (the one containing the gas viscosity). This is to be expected since there are no collisions with the pore wall therefore there will be no shear forces transmitted trough the gas from the walls.

The opposite case is characterised by pores significantly smaller than the mean free path. This makes the continuum diffusion insignificant (D_{12} goes to infinity as the pore radius decreases-since the pores are quite small there will be no collisions between gas molecules and therefore no pressure drop due to this type of collisions and therefore from Equation (6.26) D_{12} should tend to infinity). In this case $D_1=D_{1K}$, $\delta_1=0$ and $\gamma_1=1$ yielding,

$$J_1 = -D_{1K}\nabla n_1 - x_1 \left(\frac{nB_o}{\mu} \right) \nabla p \quad (6.37)$$

When no pressure gradient is present, Equation (6.37) reduces to the Equation (6.10) derived in section 6.3.1.1, for the definition of the Knudsen diffusion. The viscous-flow term should vanish in the free-molecule region anyway. There not pressure drop from gas molecular collisions, so any pressure drop must be from Knudsen collisions. But the viscous flow is defined for continuum flow and viscosity is a continuum parameter [11,12].

In the transition region where both ordinary and Knudsen diffusion are equally important and in the absence of pressure drop, Equation (6.32) takes the following form:

$$J_1 = -D_1 \nabla n_1 + x_1 \delta_1 J \quad (6.38)$$

Assuming that the net flux is zero the above equation gives:

$$J_1 = -D_1 \nabla n_1 = - \left[\frac{1}{D_{1K}} + \frac{1}{D_{12}} \right]^{-1} \nabla n_1 \quad (6.39)$$

In Equation (6.39) the diffusion coefficient D_1 , valid for both free-molecule and continuum diffusion, is given by the so-called Bosanquet formula [13]. This formula was originally obtained by an elementary mean free path argument, but it appears to be in agreement with more detailed calculations and experimental data. Note that for the equations presented in the previous section and in this section, the diffusion coefficient D_{12} should be replaced by the effective diffusion coefficient D_{12}^{eff} defined in Equation (6.20), since this parameter accounts for the transport in the porous structure.

6.4 Model Development for the Concentration

Polarisation

In the previous discussion on the dusty gas approach, it has been shown that for great pressures and pore sizes significantly larger than the mean free path, the main contribution to the total flux is due to the continuum or ordinary diffusion. Through these assumptions the combined transport equation results in Equation (6.36) for the species 1 in a binary gas mixture.

In a number of studies [14,15,16] this kind of approach has been adopted by many investigators in order to model the transport of reactants and products through the porous support and anode of a solid oxide fuel cell. The schematic diagram in Figure 6.1 shows the main transport processes that occur in a supported solid oxide fuel cell.

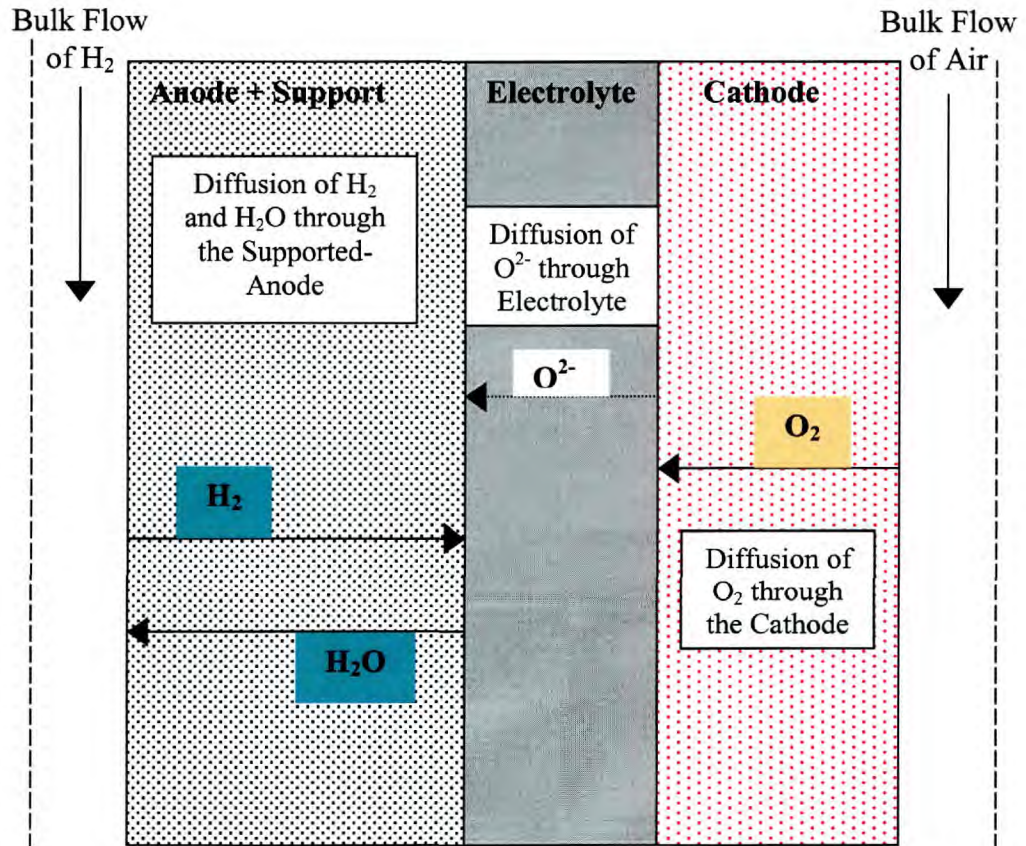


Figure 6.1: Transport processes occurring in an anode-supported SOFC.

Fuel (in this case hydrogen) and air are transported in the channels by bulk flow. Diffusion of oxygen ions takes place through the electrolyte while reactants (hydrogen and oxygen) and products (water) are transported by diffusion through the porous electrodes.

For the purpose of this study, the analysis focuses only on the diffusion process occurring in the support-anode section of the cell. Diffusion through the electrodes can be modelled by either applying the conservation of species or by adopting the appropriate transport model and applying the corresponding transport equations. In addition, in this analysis the anode is incorporated into the porous support of the cell since the thickness of a support is usually much larger than that of the anode electrode for the case of an anode-supported cell.

Concentration polarisation is related to losses arising from the change in concentration of the reactants at the surface of the electrodes, as fuel is used.

Because the reduction in concentration is the result of a failure to transport sufficient reactant to the electrode surface, these losses are also called mass transport losses. An attempt to calculate the concentration variations of hydrogen and water (as a product) is made through a simple, one-dimensional, steady-state model for the transport of species through the porous support. This eventually leads to the computation of the losses resulting from the diffusion process. Analysis of the model is carried out in the following section.

6.4.1 Steady State Diffusion Model

Using the dusty gas approach, it has been shown that for great pressures and pore sizes much larger than the mean free path, the combined transport equation reduces to a much simpler form. For the current model these approximations are actually verified, since the typical total pressure on anodic side is taken to be on the order of 1 atm , while the pore size distribution provided a mean diameter of $2\text{ }\mu\text{m}$ for both CSZ and MMA porous supports, as shown in the mercury porosimetry results of the previous chapter.

Considering these simplifications, Equation (6.36) gives the total flux for the species of a binary mixture. Thus this equation can be written for hydrogen and water vapour, in one dimension, as follows:

$$J_{H_2} = -D_{H_2H_2O}^{eff} \frac{\partial n_{H_2}}{\partial z} + x_{H_2} J_{tot} \quad (6.40)$$

$$J_{H_2O} = -D_{H_2H_2O}^{eff} \frac{\partial n_{H_2O}}{\partial z} + x_{H_2O} J_{tot} \quad (6.41)$$

It is easy to see that the main contribution to the total flux is due to the continuum or ordinary diffusion.

The effective binary diffusivity in the above equations can be computed by Equation (6.20). The free molecular binary diffusivity for the binary mixture of hydrogen and water can be calculated by the equation derived from the theory, Equation (5.31), and introduced in the chapter 5. For more accurate results the diffusivity values can be corrected for high temperatures, those relevant to the solid oxide fuel cell

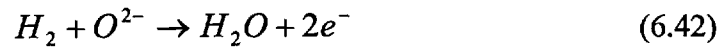
operation. As for the ratio of porosity over tortuosity, average values have been estimated and given in the previous chapter as well. Therefore the effective diffusivity values for the binary mixture of hydrogen and water along with the values of the free molecular diffusivity and porosity and tortuosity are given in Table 6.1.

Parameters	CSZ support	MMA support
$D_{H_2H_2O} (10^{-4} \text{ m}^2/\text{s})$	10.29	10.29
ε	21.56 %	15.24 %
τ	3.30	4.27
$D_{H_2H_2O}^{eff} (10^{-5} \text{ m}^2/\text{s})$	6.72	3.67

Table 6.1: Effective diffusivities values for the binary mixture of H_2 - H_2O along with parameters used for their calculation using Equation (6.20).

All the data are at 1273K and 1Atm.

Hydrogen and water vapour fluxes must be matched to the current drawn from the cell. At the anode-electrolyte interface the following electrochemical reaction occurs:



This reaction indicates that two electrons released per molecule of hydrogen reacted (water vapour produced) and therefore in steady state and for a specified current density the following equality must hold:

$$J_{H_2} = -J_{H_2O} = \frac{iN_A}{2F} \quad (6.43)$$

where F is the Faraday constant, in *Coulomb/mole*, and the negative sign shows that the flux of water vapour is in the negative direction. Substituting into Equations (6.40) and (6.41) yields,

$$J_{H_2} = -D_{H_2H_2O}^{eff} \frac{\partial n_{H_2}}{\partial z} + x_{H_2} J_{tot} = \frac{iN_A}{2F} \quad (6.44)$$

$$J_{H_2O} = -D_{H_2H_2O}^{eff} \frac{\partial n_{H_2O}}{\partial z} + x_{H_2O} J_{tot} = -\frac{iN_A}{2F} \quad (6.45)$$

Using $J_{tot} = J_{H_2} + J_{H_2O} = 0$ these equations reduce to Fick's Law. Although this condition for the total flux being zero is not quite accurate, Fick's diffusion model can be viewed as a simple approach that can give the general performance trends. Substituting n for the partial pressure p from the Ideal Law of gases, integrating with respect to z with the boundary condition for the hydrogen partial pressure $p_{H_2} = p_{H_2}^o$ at $z = 0$ (similar is the boundary condition for the water vapour) gives:

$$p_{H_2(a)} = p_{H_2}^o - \frac{RTL}{2FD_{H_2H_2O}^{eff}} i \quad (6.46)$$

$$p_{H_2O(a)} = p_{H_2O}^o + \frac{RTL}{2FD_{H_2H_2O}^{eff}} i \quad (6.47)$$

where $p_{H_2}^o$ and $p_{H_2O}^o$ are the partial pressures of hydrogen and water vapour respectively in the fuel (outside the anode) in Pa and L the thickness of the support-anode. Equations (6.46) and (6.47) give the partial pressure of hydrogen and water vapour at the anode-electrolyte interface in terms of the current density. Based on these equations the partial pressure distributions for hydrogen and water vapour in the support-anode region can be generated.

In supported cells the limiting current density, i_{la} , at which the fuel is consumed at a rate equal to its maximum supply, occurs when the partial pressure of hydrogen approaches to zero. This is given by Equation (6.46) substituting $p_{H_2}^o = 0$:

$$i_{la} = \frac{2FD_{H_2H_2O}^{eff} p_{H_2}^o}{LRT} \quad (6.48)$$

It has been shown [14,16,17] that the concentration polarisation for the anode can be calculated from the following equation:

$$\begin{aligned}\eta_{conc,a} &= -\frac{RT}{2F} \ln \left[1 - \frac{RTL}{2FD_{H_2H_2O}^{eff} p_{H_2}^o} i \right] + \frac{RT}{2F} \ln \left[1 + \frac{RTL}{2FD_{H_2H_2O}^{eff} p_{H_2O}^o} i \right] = \\ &= -\frac{RT}{2F} \ln \left[\frac{1 - (RTL/2FD_{H_2H_2O}^{eff} p_{H_2}^o) i}{1 + (RTL/2FD_{H_2H_2O}^{eff} p_{H_2O}^o) i} \right] \quad (6.49)\end{aligned}$$

This expression for the concentration polarisation of the anode may be used to calculate the losses arising from the diffusion transport of the species in the support-anode region.

For the calculations, the temperature was $T=1273\text{ K}$, and the effective diffusivities used were those given in Table 6.1 (determined at $T=1273\text{ K}$). The nominal case was considered for the partial pressures of hydrogen and water vapour in the fuel (outside the support), $p_{H_2}^o = 0.5\text{ atm}$ and $p_{H_2O}^o = 0.5\text{ atm}$ and the current density was 10000 A/m^2 .

6.4.2 Unsteady State Diffusion Model

It is interesting to know the species variations in the porous supports and especially that of hydrogen at very short times before the steady state has been reached. For this reason a dynamic model is proposed assuming no homogeneous reactions, constant diffusivity and concentration and one-dimensional transfer in x direction. The model is described by Fick's second Law,

$$\frac{\partial c}{\partial t} = D_{AB}^{eff} \frac{\partial^2 c}{\partial x^2} \quad (6.50)$$

The boundary conditions taken for this problem are,

$$\text{Initial condition:} \quad t = 0, \text{ all } x, \quad c = c_o \quad (6.51)$$

$$\text{Boundary conditions:} \quad \text{at } t > 0, \quad x = 0, \quad c = c_o \quad (6.52)$$

$$x=L, \quad -D_{AB} \frac{\partial c}{\partial x} \Big|_{x=L} = \frac{i}{2F} \quad (6.53)$$

The initial condition, Equation (6.51), presumes a uniform concentration distribution at time $t = 0$ while Equation (6.52) indicates that the concentration of the species at one side of the anode support has constant value for time $t > 0$. Equation (6.53) describes the surface condition at the other side of the support. In fact, this boundary condition expresses the rate of production by the electrochemical reaction that occurs at the surface. Substituting c indicates p from the Ideal Law of gases, Equation (6.50) can be solved for the partial pressure of the gasses.

The equation with the relevant boundary conditions presented above was solved numerically using FEMLAB[®], a MATLAB[®] based software specifically designed for chemical engineering modelling. It uses the variational Finite Element Method (FEM) with triangular meshing, and a choice of basis functions (linear, quadratic, cubic, quartic) adaptable according to the complexity of each problem.

6.5 Results and Discussion

6.5.1 Results of the Steady State Model

The results of the steady state model are first presented. Figure 6.2 shows the composition variation of hydrogen and water across the support. Consumption of hydrogen by the electrochemical reaction occurring at the anode-electrolyte interface leads to the decrease of its partial pressure and at the same time water is produced and its partial pressure increases as it diffuses through the support from the anode-electrolyte interface. The decrease in hydrogen partial pressure is greater in the MMA support since the effective diffusivity of hydrogen is smaller in MMA. It is also evident that there is a greater increase in water vapour partial pressure in the MMA than in CSZ support.

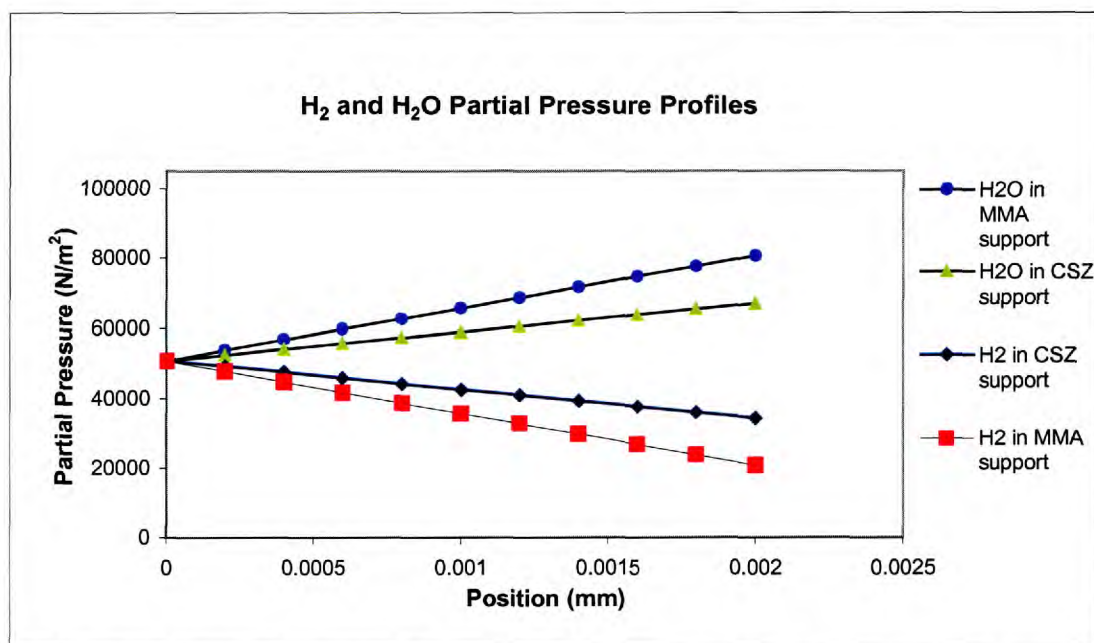


Figure 6.2: Partial pressure variation across the CSZ and MMA supports, at a current density of 10000 A/m^2 , fuel: H_2 50% + H_2O 50%.

As shown in the above figure, the partial pressure of hydrogen and water vapour are expected to vary linearly with position across most of the support and electrode thickness. But near the electrode-electrolyte interface, variation of the partial pressure is expected to be nonlinear (and rapid) despite a spatially invariant microstructure. This is because the process of charge transfer takes place over a certain thickness of a composite electrode from the electrode-electrolyte interface. In this region, the net current consists of both ionic and electronic contributions, which are both functions of position.

The anode concentration polarisation, as calculated using Equation (6.49), for a supported SOFC of 2 mm thickness support is shown in Figure 6.3. Exploring the role of the effective diffusivity, the anode concentration polarisation is estimated for both the MMA and CSZ support materials. There is a clear difference between the MMA and CSZ support. As a result of a lower effective diffusivity in the MMA, the latter exhibits higher concentration polarisation and a lower limiting current density than the CSZ support. Fuel cells must always operate at current densities below this limiting value. By extending the operating current density range the cell anode performance can be improved.

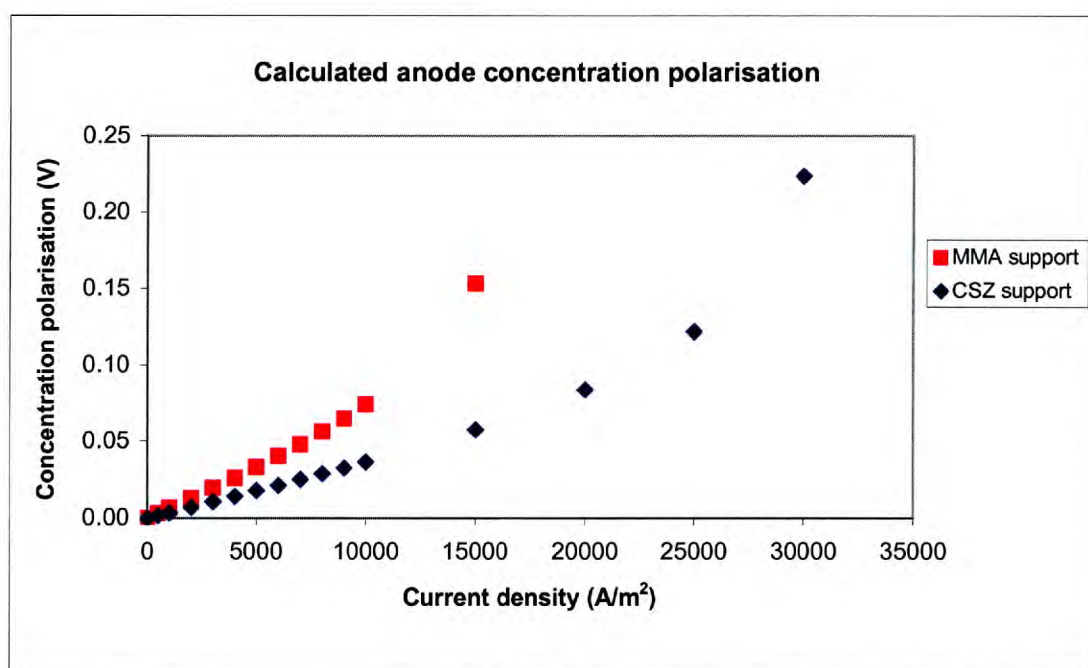


Figure 6.3: Anode concentration polarisation for the two supports of 2 mm thickness, calculated using Equation (6.49), fuel: H₂ 50% + H₂O 50%.

To investigate the effect of the support thickness on the anode performance, the concentration polarisation is calculated for different support thicknesses. This is shown in Figures 6.4 and 6.5.

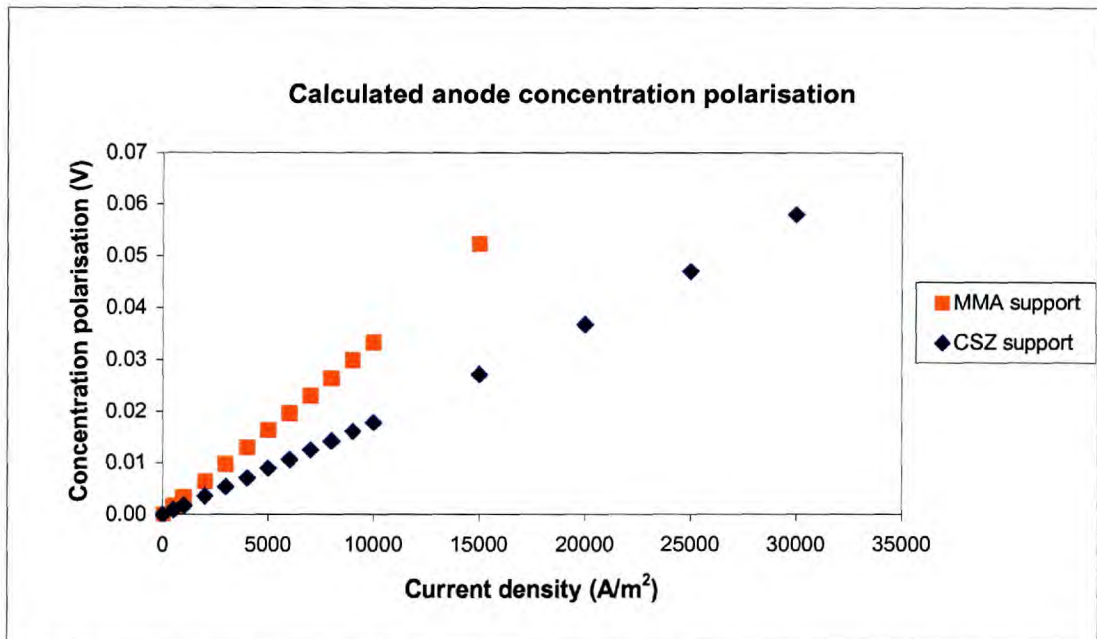


Figure 6.4: Anode concentration polarisation for the two supports of 1 mm thickness, fuel: H₂ 50% + H₂O 50%.

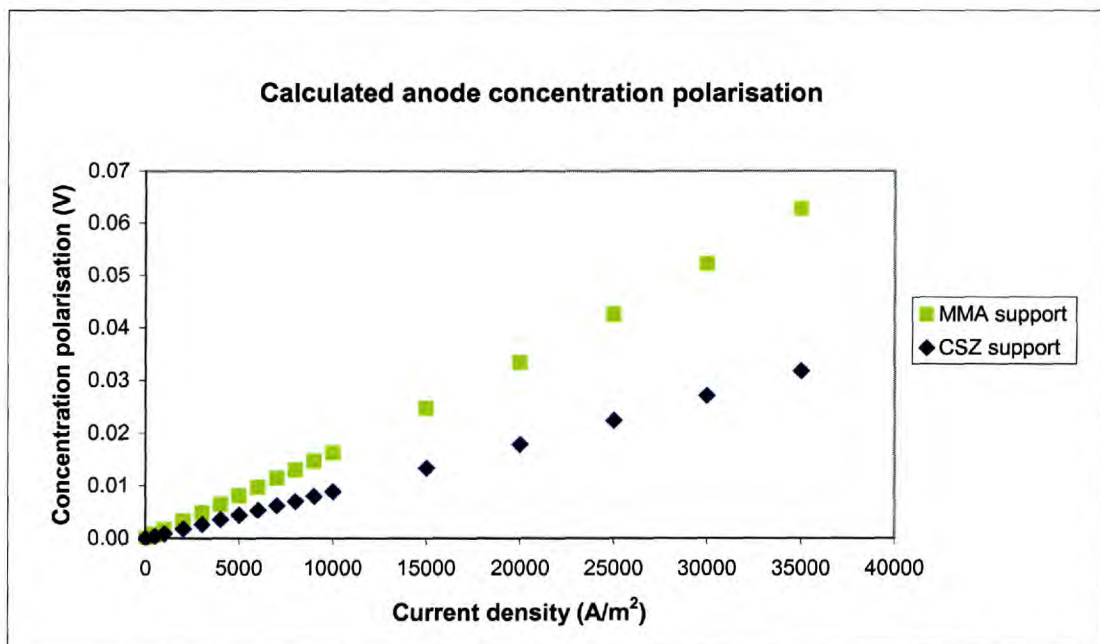


Figure 6.5: Anode concentration polarisation for the two supports of 0.5 mm thickness, fuel: H₂ 50% + H₂O 50%.

It is obvious that reducing the thickness of the two supports results in a decrease in concentration polarisation and an improved operating current density range. From all the three support thicknesses, the support of 2 mm thickness presents the greater concentration polarisation with a low limiting current density. This indicates the necessity to further improve the design specifications of this particular support. An

obvious choice would be to reduce the thickness down to 0.5 mm. However, cell design requirements related with the robustness and the mechanical support of the cell have to be taken into consideration. A support of 1 mm thickness could be attainable.

The above results were obtained for a fuel composition of 50% H_2 and 50% H_2O . Figure 6.6 shows partial pressure profiles across the two supports for a fuel consisting of 20% H_2 and 80% H_2O , representing the depleted fuel case.

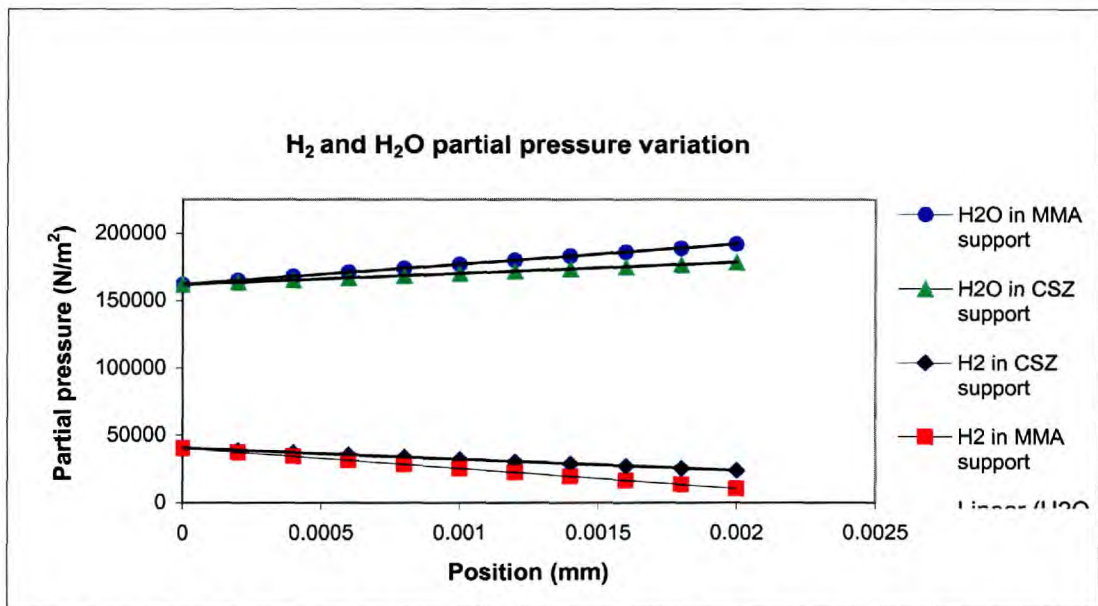


Figure 6.6: H_2 and H_2O partial pressure profiles across the CSZ and MMA supports, fuel: 20% H_2 + 80% H_2O .

The difference in partial pressure between the MMA and the CSZ is very small and it is of the same magnitude as that observed in Figure 6.2 for the nominal case. The concentration polarisation for this case was also estimated and is illustrated in Figure 6.7.

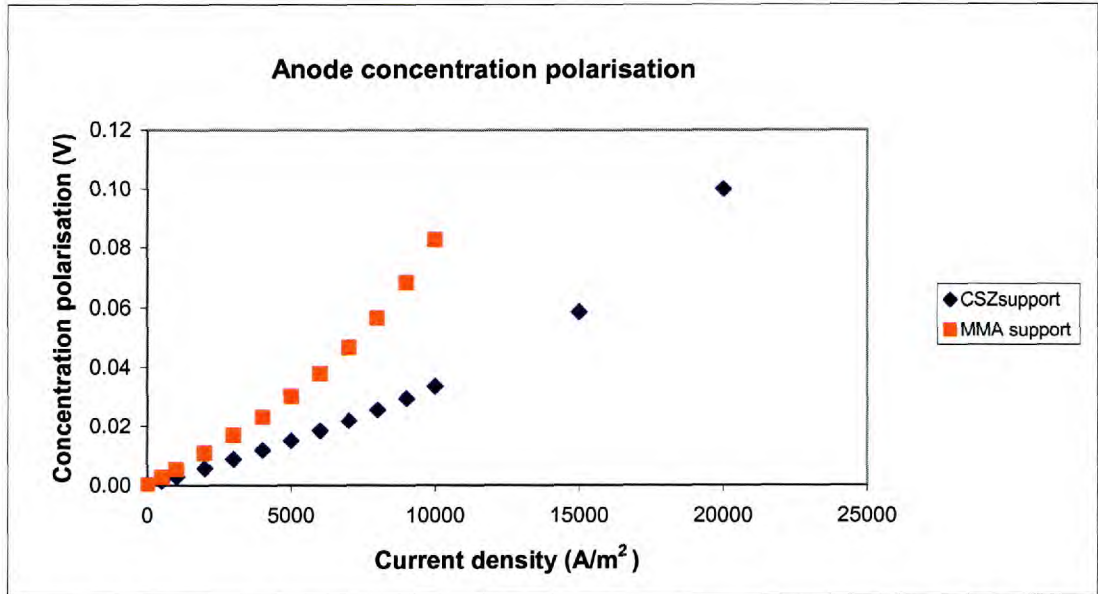


Figure 6.7: Anode concentration polarisation for the two supports of 2 mm thickness, fuel composition of 20% H₂ + 80% H₂O.

In comparison with the corresponding anode concentration polarisation for the nominal case, shown in Figure 6.3, there is a small difference. The anode concentration polarisation for both the supports appears to be lower in the depleted fuel case than in the nominal case, up to a certain value of current density. After this value, and for a small range of current densities, the reverse occurs.

6.5.2 Results of the Unsteady State Model

In this section the results of the transient diffusion model are presented. In Figures 6.8 and 6.9 the hydrogen partial pressures profiles in the two supports are shown, under transient conditions. The values used for the model calculations were similar to those used in the steady state model, the temperature was $T=1273\text{ K}$, the effective diffusivities were taken from Table 6.1 (determined at $T=1273\text{ K}$), while the partial pressures of hydrogen and water vapour in the fuel (outside the support) were set at 1 atm and the current density was 10000 A/m^2 .

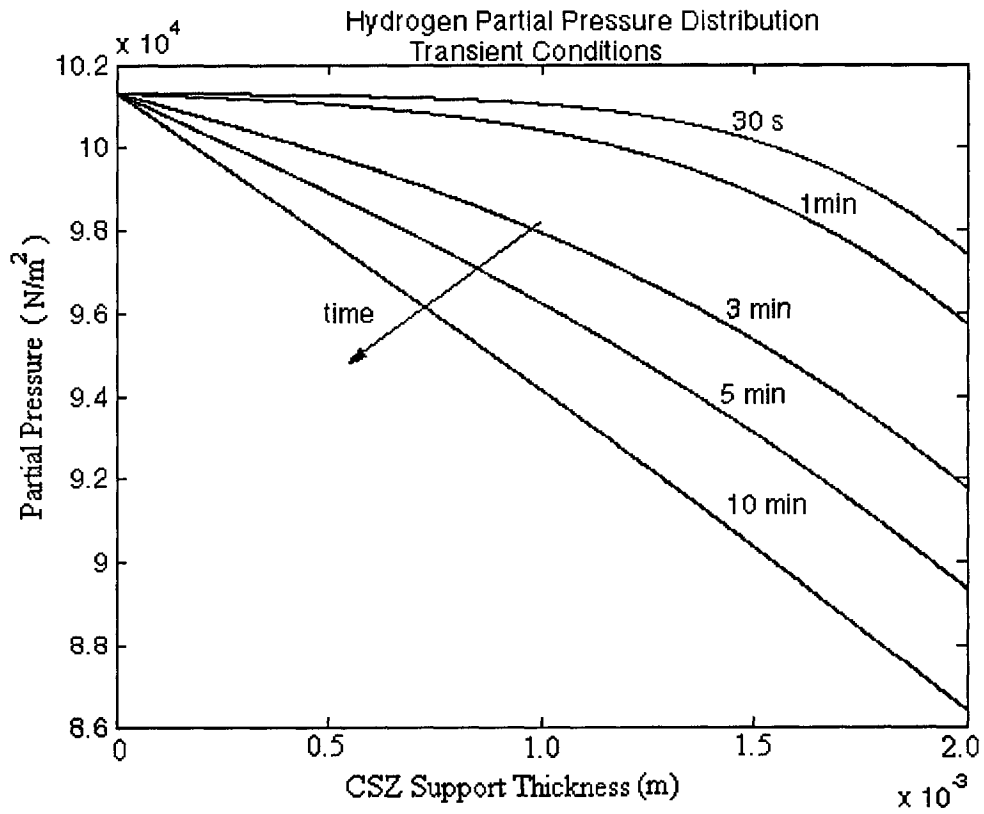


Figure 6.8: Hydrogen partial pressure profiles across the CSZ support, with increasing time.

The partial pressure of hydrogen set at a constant value at the surface of the support starts to drop as it is consumed at the anode-electrolyte interface. With increasing time the pressure variation approaches the linear profile obtained in the steady state conditions.

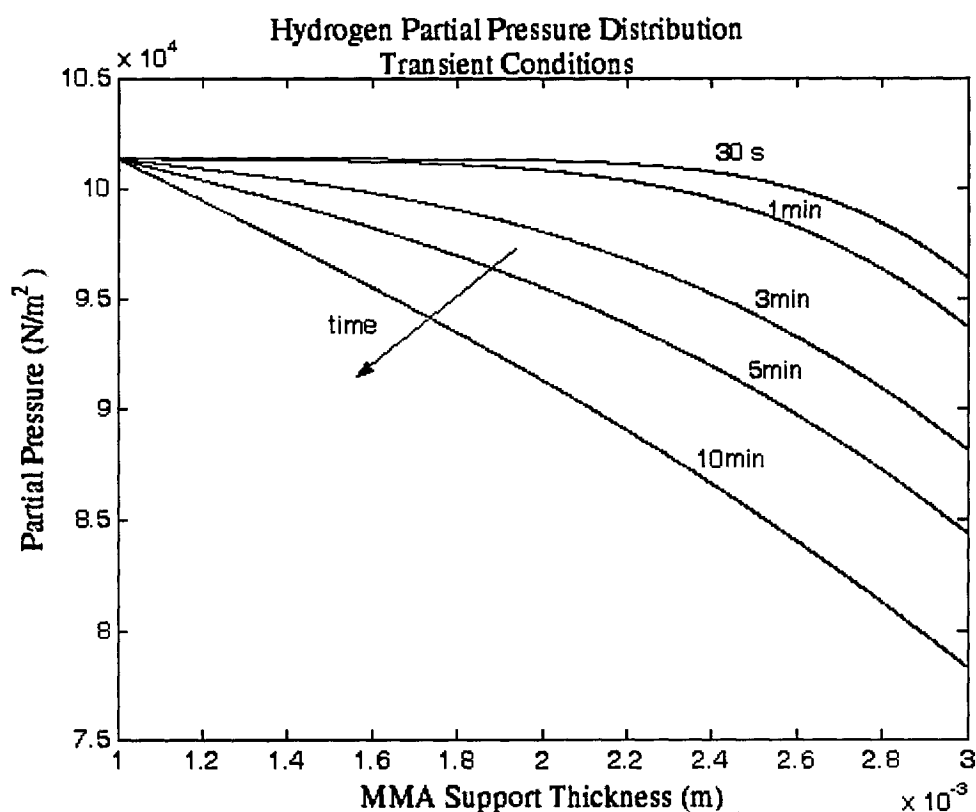


Figure 6.9: Hydrogen partial pressure profiles across the MMA support, with increasing time.

It is evident that the profiles present steeper gradients in the MMA support and the pressure drops are higher here than in the CSZ support for the same times. Since the current drawn is the same at both cases, this can be attributed to the higher value of effective diffusivity in the CSZ than in the MMA support. Hydrogen diffuses through the CSZ, satisfies the electrochemical reaction at the anode-electrolyte, and it is replenished quickly. Therefore the demand for reactants is smaller and that in turn results in smaller pressure gradients across the support.

The sensitivity of the partial pressure due to the change of the effective diffusivity is shown in Figures 6.10 and 6.11. The effective diffusivities for the mixture of H₂-H₂O were determined by using the values of molecular diffusivities shown in Table 6.1 and the range of tortuosities estimated and given in chapter 5. The time of 10 min was selected and the effect of changing the effective diffusivity on the partial pressure was determined.

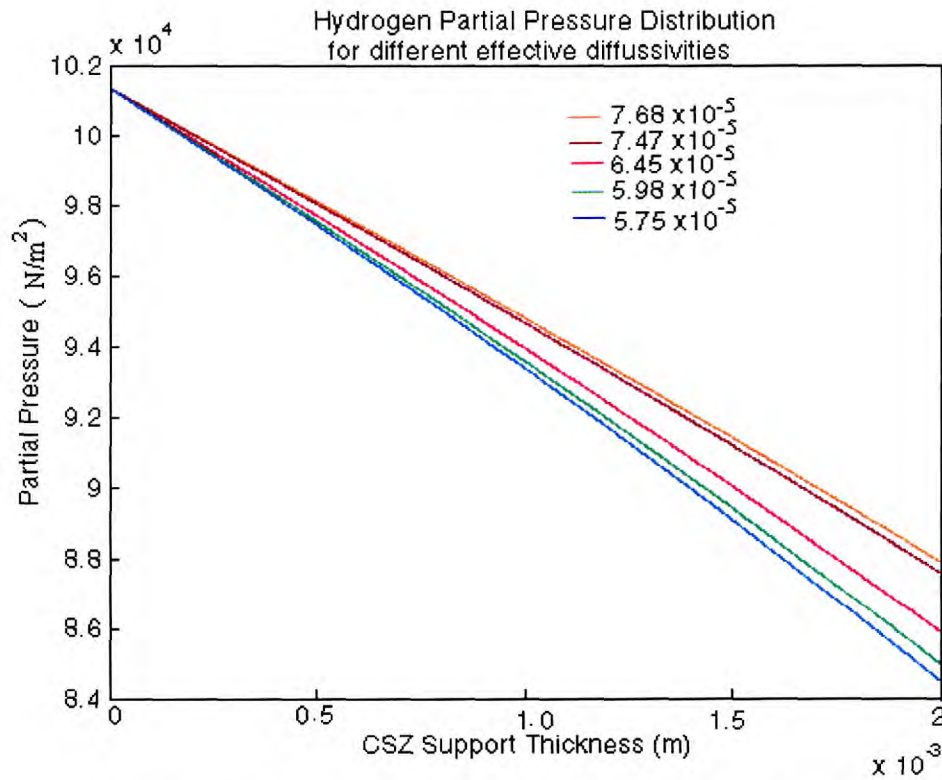


Figure 6.10: Hydrogen partial pressures profiles in the CSZ support for a range of effective diffusivities.

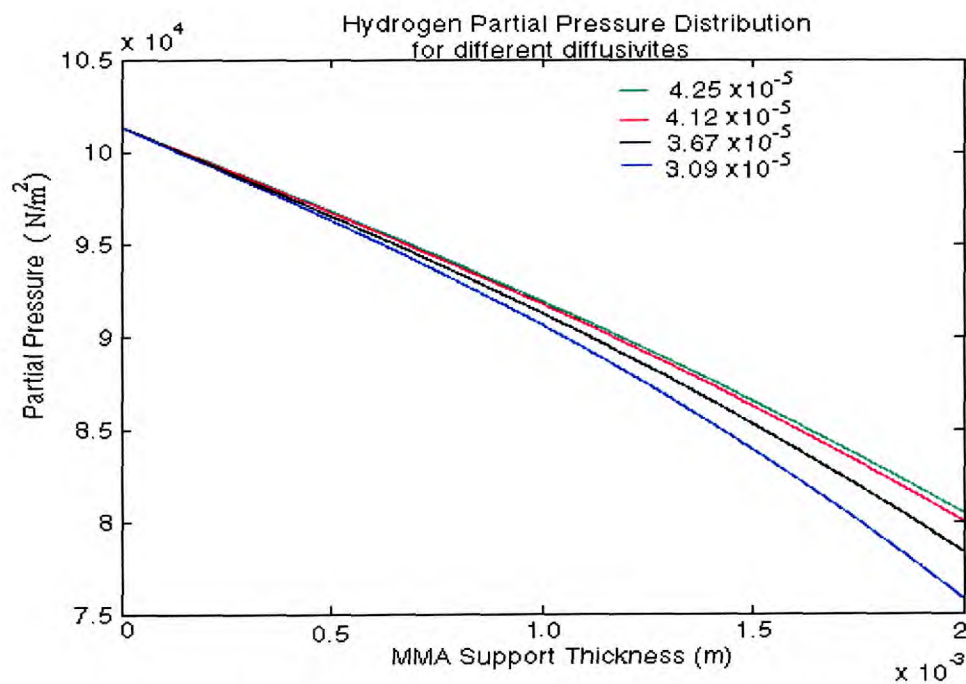


Figure 6.11: Hydrogen partial pressure profiles in the MMA support for a range of effective diffusivities.

It can be seen that the higher the effective diffusivity the smaller the pressures drop for the same time. Again this follows from the explanation given above. Comparison of the profiles between the two supports results in the conclusion that in general the pressure gradient across the MMA is larger than that across the CSZ support.

No special information is revealed from these models for the limiting current density. However, if enough time is allowed then the partial pressure can be seen to drop to zero, an indication that the limiting current density is reached. Also for the given conditions if high current is drawn, a condition that is described mathematically by the second surface boundary condition, it will again result in pressure profiles that intersect the x-axis resulting in negative values.

The pressure profiles for the water vapour are shown in Figures 6.12 and 6.13.

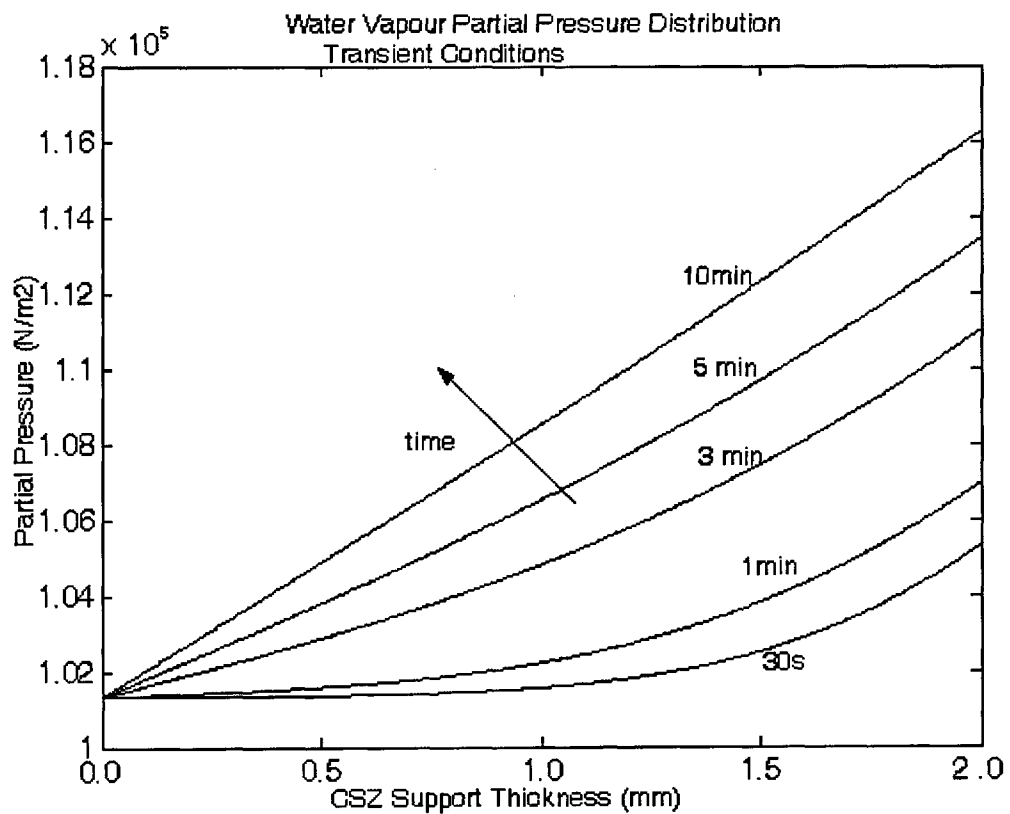


Figure 6.12: Water vapour partial pressure profiles across the CSZ support as time progresses.

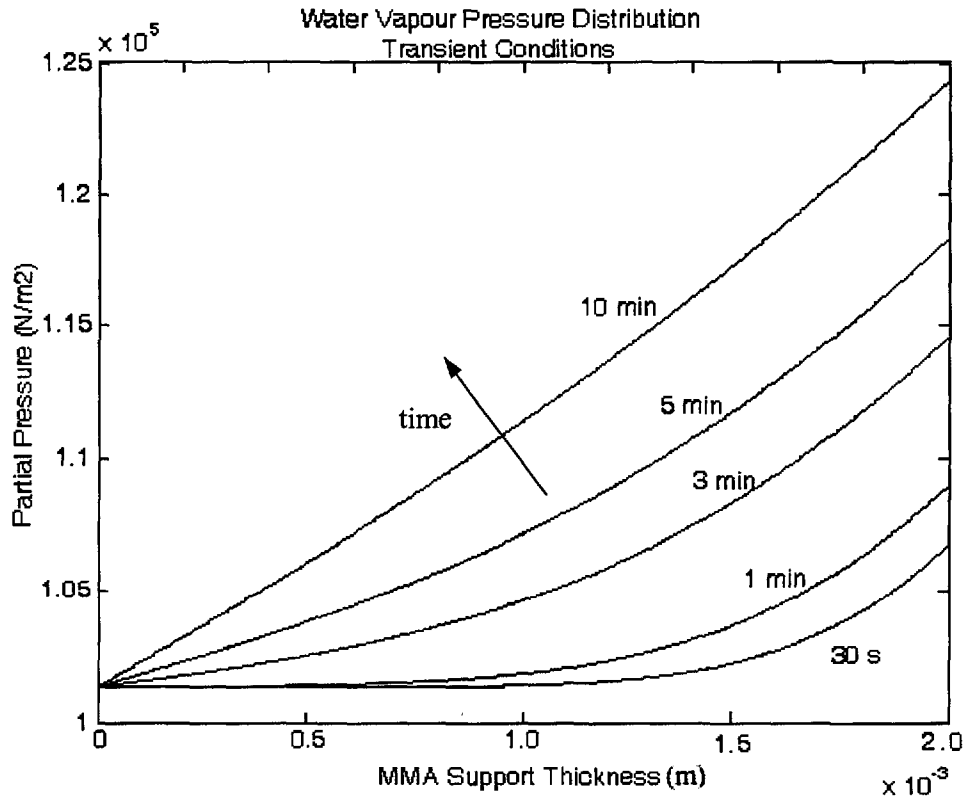


Figure 6.13: Water vapour partial pressure profiles across the MMA support, with increasing time.

In comparison to hydrogen profiles, the water vapour profiles present a symmetrical image. The patterns observed in the steady state models are also recognised here. The profiles show that there is a greater increase of water vapour pressure in the MMA than in the CSZ support. This is a feature that has also been observed in the steady state profiles for hydrogen as shown in Figure 6.2. It is important to note that as time advances the transients are dying away and the profiles reach steady state as this predicted from the steady state model.

6.6 Conclusions

The dusty gas model has been adopted to describe the transport of gas phase species within the porous support of a supported solid oxide fuel cell. Considering a model of ordinary diffusion for the binary mixture of H_2 - H_2O , the species composition variation within the porous support have been obtained for a steady state and a dynamic case as well. The variation of concentration polarisation with current density has been calculated for a range of different support thicknesses. Results have

demonstrated the need to improve the characteristics of the 2 *mm* thickness support which has shown the greatest concentration polarisation and the lowest limiting current density. To extend the operating current density range and therefore improve the cell anode performance a support of 1 *mm* thickness is recommended. As low effective diffusion coefficients cause high polarisations, these could be minimised by increasing support and electrode porosity in regions away from the electrolyte-electrode phase. This would result in higher effective diffusivities.

The anode concentration polarisation results have given insight into technological applications of supported solid oxide fuel cells. For example for supported cells operated at the current density of 10000 A/m^2 , the calculated anode concentration polarisation, for a cell with support thickness of 2 *mm*, lies in the range of 0.03-0.10 volts and for a cell of 1 *mm* support thickness in a range of 0.015-0.035 volts. This information is very important when applied to the fabrication of supported solid oxide fuel cells. A range of different materials with recommended design specifications may be used in order to obtain optimal operation for the cell at typical current densities.

6.7 References

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Chapter 7

Conclusions and Future Work

7.1 Conclusions

The effect of binary gas diffusion in porous ceramic supports on the solid oxide fuel cell anode performance was studied.

The steady-state diffusion cell experimental technique was developed to enable the measurements of effective gas diffusion coefficients. The experimental procedure involved the use and the development of a gas chromatography measurement system and the creation of specific, analytical methods that allowed the accurate quantitative determination of gaseous species entering and leaving the diffusion cell.

An alternative theoretical treatment of the diffusion data was proposed to allow the calculation of the effective diffusivities of different binary gas mixtures. This method of interpreting diffusion data obtained from the diffusion cell technique has not been reported in relevant studies so far. Also a number of parameters of the experimental design, rarely discussed, were identified and their effect on the measurements was investigated.

The porous microstructure of the ceramic supports was examined and the structural properties were determined by employing several characterisation techniques. The study of the supports structure was of prime importance since support specifications, such as the porosity, pore size and thickness can influence the proper operation of the cell anode.

Experimentally determined effective diffusivities of gas pairs were obtained from a series of diffusion measurements using the experimental techniques set up initially. Not only is this transport coefficient important from itself, but also allowed the extraction of the tortuosity, another characteristic property of the porous medium

Using these parameters obtained by the various experimental techniques, a modelling approach was adopted that allowed losses resulting from diffusion in the porous support to be predicted.

7.2 Future Work

As a follow up to the steady state diffusion experiments in the porous ceramic materials, dynamic measurements can be carried out. Dynamic techniques would be used for such measurements to give effective diffusivities that account for the micropores of a porous medium and allow the comparison of new diffusivities to those measured in this project.

Extension of the theoretical and modelling work could include a model that takes into account multicomponent diffusion in the porous supports. An obvious choice would be to include the methane reforming reaction into the model and allow a direct correlation to be made between the electrochemical performance and the reforming characteristics during fuel cell operation.

Publications and Presentations

- 1) Christos Kalyvas, Nigel Brandon and Robert Collins, "On equimass and equimolar binary diffusion", *International Journal of Heat and Mass Transfer*, (to be submitted).
- 2) Christos Kalyvas, Nigel Brandon and Robert Collins, "The effect of gas-phase diffusion on concentration polarisation in the anode supported solid oxide fuel cells", *Fuel Cell Science and Technology 2004*, Munich, Germany, 6-7 October 2004, (submitted).
- 3) Christos Kalyvas and Nigel Brandon, "Effective diffusivity measurements of binary gaseous mixtures with relevance to solid oxide fuel cell anode operation. A new proposed method for the interpretation of the diffusion data", *16th International Congress of Chemical and Process Engineering*, Prague, Czech Republic, 22-26 August 2004. (submitted).
- 4) Christos Kalyvas, Nigel Brandon and Robert Collins, "Measurements of Binary Diffusion Coefficients in Porous Ceramic Supports", *Chemical Engineering Science*, (submitted).
- 5) Christos Kalyvas, Nigel Brandon and Robert Collins, "The impact of Diffusion in Porous Supports on Solid Oxide Fuel Cell Anode Performance", in *Proceedings of 5th European Solid Oxide Fuel Cell Forum*, vol 1, pp539, edited by J. Huijsmans, 2002, Lucerne, Switzerland.

Poster Presentations

- "The Impact of Diffusion in Porous Supports on Solid Oxide Fuel Cell Anode Performance", 5th European Fuel Cell Forum, Lucerne, Switzerland, 1-5/7/2002
- "The Impact of Diffusion in Supported Solid Oxide Fuel Cells", 7th Grove Fuel Cell Symposium, London, UK, 11-13/9/2001
- "Measurements of N₂-H₂ Diffusion Coefficients through Porous Supports", The Hydrogen Road Show, Institute of Civil Engineers, London, 15/3/2001.