

CRANFIELD UNIVERSITY

STUART JAMES GILBY

NOVEL POLYMERIC MATERIALS FOR
ELECTROCHEMICAL CELLS

DEFENCE COLLEGE OF MANAGEMENT AND TECHNOLOGY

SUBMITTED FOR THE AWARD OF PhD

CRANFIELD UNIVERSITY

DEFENCE COLLEGE OF MANAGEMENT AND TECHNOLOGY

DEPARTMENT OF MATERIALS AND APPLIED SCIENCE (DMAS)

PhD THESIS

Academic Year 2006-2007

Stuart James Gilby

Novel Polymeric Materials for Electrochemical Cells

Supervisor: Mr K V Lovell

June 2007

© Cranfield University, 2007. All rights reserved. No part of this publication may be reproduced without the written permission of the copyright holder.

Abstract

Solid polymer electrolytes have many useful properties, such as low permeability to reactants, high ionic conductivity, which make them ideal candidates for many cells, such as fuel cells, electrolyzers, and ultracapacitors.

The majority of the research on electrolytes for methanol fuel cells has been based on proton exchange polymers typified by the perfluorosulphonic acid membranes, such as Nafion®. However, alternative electrolytes based on hydroxyl ion exchange polymers have been shown to possess significant advantages, e.g. cheaper catalysis, and reduced cell corrosion.

This project had the principal aim of investigating other chemical systems, which may provide ionic conductivity as well as other necessary properties. In particular the use of liquid monomers, such as 2-methyl-2-oxazoline and 4-vinyl pyridine, that can be cast into a membrane or directly into the cell.

In the initial phase of this work, novel preparations of castable anionic exchange materials were polymerised by gamma radiation, thermal and microwave heating. Single-mode microwave heating proved viable and the production of a large cavity was undertaken.

Characterisation of the materials using laboratory tests, such as equilibrium water content, ionic conductivity and methanol permeation found several materials with good ionic conductivities when compared to a commercial anionic exchange membrane. A simplistic model of monomer composition for an ideal material has been derived and

tested, but shown not to take into effect the interaction of hydrophilic and hydrophobic materials.

Crosslinking reactions have been used to reduce methanol permeation of materials containing 2-methyl-2-oxazoline to below that of anionic and cationic commercially available membranes, allowing them to be used *in situ* with high methanol concentrations in the fuel cell, providing higher power densities than commercial materials in an alkaline fuel cell environment.

Materials have also been tested as membranes for a water electrolyser with some success.

Acknowledgements

My project has been funded under the ESPRC Doctoral Training Award, and by ITM Power plc with a CASE award.

I wish to thank my supervisor Keith Lovell for his help throughout the 3 years. His knowledge of fuel cell technology and solid polymer electrolytes is unsurpassed.

I would also like to thank all those at ITM Power plc, Sheffield, for their invaluable help in this project and the use of their equipment.

My thanks to Dr Susan Waring, Dr Jackie Horsfall and Dr Esam Kronfli for all their help in the laboratory and discussion of ideas; no matter how stupid they might have seemed at the time, and also my gratitude is also extended to all the staff at Cranfield University for help with analysis of my materials; Anjum Agha, Alex Contini, Phil Gill, Jenny Lovell and Ali MacCuish.

My gratitude goes to Professor Steve Haswell of the University of Hull for allowing me to use his single-mode microwave cavity, and also to Dr Ivor Morrow of the Department of Aerospace, Power and Sensors, Cranfield University for his help on designing and testing a single-mode microwave cavity.

Many thanks also go to my friends for their support throughout my time at Shrivenham, Aimee Lister, Miles Tawell, Paul Bourke, Matt Andrews and Richard Hall who have read my work, encouraged my thinking and gone to the shops for chocolate when needed.

A big thanks to my parents, who supported me throughout all of my studies.

Lastly my biggest thank you goes to my family. My wife Abi, who helped me achieve my goal when no PhD was in sight, and during the hectic 3 years of my studies has continued to support me and even managed to somehow give me a wonderful son and find time to read my thesis. Isaac, you have given me a pick up when ever I have needed it with your great little smile, watching you grow is a pleasure.

Contents

Abstract	i
Acknowledgements	iii
Contents	iv
List of Figures	vii
List of Tables	xi
Abbreviations	xii
Formulae and Constants	xv
Glossary	xvi
Introduction	1
Chapter 1 . Literature Review-Electrochemical Cells	4
1.1 Introduction	4
1.2 Electrolysers	4
1.3 Fuel Cells	8
1.4 Fuels	15
1.5 Chapter Summary	23
Chapter 2 . Literature Review-Membranes	26
2.1 Introduction	26
2.2 Types of Membrane	27
2.3 Ion Exchange Membrane Preparation by Polymerisation	31
2.4 Current SPE Membrane Technology	36
2.5 Membranes for the DMFC	40
2.6 Summary	42
Chapter 3 . Microwaves	44
3.1 Introduction	44
3.2 Microwave Spectrum	44
3.3 Comparison of Thermal and Microwave Heating	46
3.4 Microwave Enhanced Chemistry	51
3.5 Multi-Mode or Single-Mode?	51
3.6 Single-Mode Cavity Design	53
3.7 Summary	55
Chapter 4 . Materials	57

4.1	Introduction.....	57
4.2	Hydrophilic Monomers.....	57
4.3	Hydrophobic Monomers.....	62
4.4	Ionic Exchange Materials.....	62
4.5	Crosslinking Agents.....	64
4.6	Thermal Curing Agents.....	66
4.7	Blended Copolymers.....	66
4.8	Summary.....	67
Chapter 5 . Experimental		68
5.1	Polymerisation Techniques.....	68
5.2	Production of Single-Mode Microwave Cavity.....	75
5.3	Cutting and Polishing of Discs.....	76
5.4	Characterisation Techniques.....	76
5.5	Fuel Cell Testing.....	81
5.6	Water Electrolysis Testing.....	83
5.7	Soxhlet Extraction.....	85
Chapter 6 . Results and Discussion.....		89
6.1	Polymerisation.....	89
6.2	Materials Properties and Characterisation.....	103
6.3	Effect of Monomer Concentration.....	106
6.4	Optimisation of Materials.....	119
6.5	Effect of Crosslinking Agent.....	121
6.6	Effect of Crosslinking Radiation.....	129
6.7	Analysis of Extracted Liquors.....	132
6.8	Long Term Methanol Permeation Testing.....	136
6.9	Membrane Production for Fuel Cell Testing.....	137
6.10	Fuel Cell Testing.....	138
6.11	Electrolyser Testing.....	158
6.12	6.12 A Comment on Errors.....	162
6.13	6.13 Results Summary.....	163
Chapter 7 . Conclusions.....		166
7.1	Introduction.....	166
7.2	Polymerisation.....	166
7.3	Effect of Monomers and Crosslinkers.....	167

7.4	Analysis.....	169
7.5	Membrane Production.....	169
7.6	Fuel Cell Testing.....	169
7.7	Electrolyser Testing	170
7.8	Overall Conclusion	170
Chapter 8	. Future Work.....	172
8.1	Introduction.....	172
8.2	Polymerisation	172
8.3	Radiation Crosslinking.....	172
8.4	Ideal Material Model.....	173
8.5	Long Term Fuel Cell Testing.....	173
8.6	Optimisation of MEA Preparations	173
8.7	Effect of Fuel Flow Rate on Power Density	174
8.8	Catalysis of Ethanol	175
8.9	Alkaline Water Electrolysis	175
	References.....	176
	Appendix A-E.....	183

List of Figures

Figure 1.2: A simple fuel cell	9
Figure 1.3: Efficiency of “energy on demand” system, from a primary green energy source	18
Figure 2.1: Radical polymerisation.....	32
Figure 2.2: AIBN thermal initiator	33
Figure 2.3: AIBN free radical initiation.....	33
Figure 2.4: VAZO® initiator	34
Figure 2.5: Potassium persulphate initiator	34
Figure 2.6: General formula for Nafion®	37
Figure 4.1: General formula of oxazoline, where R is a methyl, ethyl or phenyl group	38
Figure 4.2: Reaction schematic for ionic polymerisation of oxazolines.....	59
Figure 4.3: 4-vinyl pyridine monomer	59
Figure 4.4: Neutral polyaniline	61
Figure 4.5: Aniline monomer in base state	61
Figure 4.6: N-Vinyl-2-pyrrolidone	62
Figure 4.7: Acrylonitrile	62
Figure 4.8: (<i>ar</i> -Vinylbenzyl)trimethyl ammonium chloride.....	63
Figure 4.9: (a) 2-(dimethylamino)ethyl acrylate, (b) 2-(dimethylamino)ethyl methacrylate. The different groups are shown in red	64
Figure 4.10 Allyl methacrylate	65
Figure 4.11: 2,4,6-Triallyloxy-1,3,5-triazine	65
Figure 4.12: 1,3,5-Triallyl-1,3,5-triazine-2,4,6-(1H, 3H, 5H)-trione	66
Figure 5.1: Cobalt-60 gamma radiation facility.....	68
Figure 5.2: Domestic multi-mode microwave	69
Figure 5.3: Equipment for purging solution with nitrogen to remove oxygen	71
Figure 5.4: Polymerisation of rods in gamma radiation source	71
Figure 5.5: Solution soaked separator prior to thermal polymerisation.....	73
Figure 5.6: Brass plates used for thermal polymerisation of membranes.....	74
Figure 5.7 Conductivity measurement cell diagram, top view.	78
Figure 5.8: Conductivity measurement cell	78
Figure 5.9: Typical Nyquist Plot.....	79
Figure 5.10: Methanol permeation cell.....	80

Figure 5.11: Methanol permeation cell, showing rod for extracting sample	81
Figure 5.12: Diagram of fuel cell, top expanded view	82
Figure 5.13: Photograph of Fuel Cell	83
Figure 5.14: Water electrolysis cell diagram, top expanded view	84
Figure 5.15: Water electrolysis cell and gas storage tanks	84
Figure 5.16: Soxhlet Apparatus	86
Figure 6.1: Possible free radical polymerisation of PhOX, showing possible steric hinderance of final product in red	92
Figure 6.2 Possible free radical polymerisation between MeOX and AN, where R is a free radical formed by gamma radiation.	93
Figure 6.3: Average absorbed power of Proline 700 W multi-mode microwave	97
Figure 6.4: Effects of variation in concentration of AN in a VPy system	107
Figure 6.5: Effects of variation in concentration of AN in a MeOX system	108
Figure 6.6: Effects of variation in concentration of NVP in a MeOX system	109
Figure 6.7: Effects of variation in concentration of VPy in a VPy system	111
Figure 6.8: Effects of variation in concentration of MeOX in a MeOX system	112
Figure 6.9: Effects of variation in concentration of BV in a VPy system	113
Figure 6.10: Effects of variation in concentration of BV in a MeOX system	113
Figure 6.11: Methanol permeation (DK) with increasing BV concentration	114
Figure 6.12: Effects of variation in concentration of AMX in a VPy system	116
Figure 6.13: Effects of variation in concentration of AMX in a MeOX system	116
Figure 6.14: Copolymer Water content with moles of AMX crosslinking sites	118
Figure 6.15: effects of crosslinking agent on VPy system	123
Figure 6.16: Methanol permeation for VPy system with different crosslinking agents	124
Figure 6.17: Effect of crosslinker on MeOX system	125
Figure 6.18: Water content against moles of active sites with various crosslinkers..	126
Figure 6.19: Methanol permeation for MeOX system with different crosslinking agents	127
Figure 6.20: Effect of crosslinking radiation on 06SJG038	130
Figure 6.21: Effect of crosslinking radiation on 06SJG038 methanol permeation....	131
Figure 6.22: Effect of radiation on samples containing MeOX	132
Figure 6.24: Comparison of polarisation curves for 06SJG038O at various temperatures	141

Figure 6.25: Comparison of polarisation curves for 06SJG038O at various temperatures with 10 M MeOH/1 M NaOH.....	142
Figure 6.26: Comparison of polarisation curves for 06SJG038O at approx 24 °C and 80°C with various molarities of methanol fuel	142
Figure 6.27: 06SJG038O MEA after cell testing.....	143
Figure 6.28: Comparison of polarisation curves for 06SJG038P for various temperatures	144
Figure 6.29: 06SJG038P MEA after fuel cell testing. Tear visible in top left hand corner.	145
Figure 6.30: Top-anode, Bottom-cathode after contact with 6M MeOH/6 M NaOH solution.....	145
Figure 6.31: Polarisation curve of 06SJG041J	146
Figure 6.32: Comparison of polarisation curves at various temperatures for 06SJG041K (note reduced axis compared with similar figures, for clarity of presentation).	147
Figure 6.33: Temperature versus max power density for material 06SJG041K with 4M MeOH/1M NaOH	147
Figure 6.35: Comparison of polarisation curves for 06SJG041M at various temperatures with 10 M MeOH/ 1 M NaOH.....	149
Figure 6.36: Comparison of power curves for 04SJG041M at various temperatures with 2 different fuel concentrations	150
Figure 6.37: Comparison of polarisation curves for ADP-100 at various temperatures	151
Figure 6.38: Comparison of polarisation curves for Nafion® 117 at various temperatures	152
Figure 6.39: Sample showing break-up of membrane due to physical stress after hydration	156
Figure 6.40: Current-voltage characteristic of electrolyser with material 06SJG044	158
Figure 6.41: Voltage with time for material 06SJG044.....	159
Figure 6.42: Current-voltage characteristic for electrolyser material 06SJG044 after equilibrating	160
Figure 6.43: Current-voltage characteristic for material 06SJG044 with 0.1 M NaOH	161

Appendix B

Figure B.1: Single-mode cavity body.....	184
Figure B.2: Single-mode cavity end plate.....	185

Figure B.3: Addition of magnetron to single-mode cavity.....	186
Figure B.4: Finished single-mode cavity with magnetron	187

Appendix C

Figure C.1: Calibration curve for methanol permeation measurements.....	188
Figure C.2: Change in methanol concentration with time.....	189

Appendix D

Figure D.1: Typical HPLC chromatogram showing N-vinyl pyrrolidone standard ..	190
Figure D.2: HPLC chromatogram of liquors from sample 06SJG044.....	190
Figure D.3: Typical UV profile showing acrylonitrile Standard.....	191
Figure D.4: UV profile of sample with material similar to UV profile of AN	191
Figure D.5: FT-IR spectra, showing N-vinyl pyrrolidone standard	192
Figure D.6: Typical GC-MS chromatogram, showing sample 06SJG038K.....	192

Appendix E

Figure E.1: Top view of polishing jig, and side view of rod.....	193
Figure E.2: Cut away side view of polishing jig loaded with sample.....	193

List of Tables

Table 1.1: Classes of fuel cell ^[13]	12
Table 1.2: General electrode reactions for types of fuel cell	12
Table 1.3: Advantages and disadvantages of different types of fuel cell	16
Table 3.1: Frequency bands for radio frequency range ^[59]	45
Table 6.1: Radiation curing of samples	90
Table 6.2: Thermal curing of samples	95
Table 6.3: Microwave curing of samples.....	98
Table 6.4: Properties of materials polymerised by gamma radiation	104
Table 6.5: Ideal polyelectrolyte systems	120
Table 6.6: Characterisation of optimised samples	120
Table 6.7: Material composition for crosslinking studies of VPy system	122
Table 6.8: Material composition for crosslinking studies of MeOX system	125
Table 6.9: FT-IR analysis for 06SJG038J.....	134
Table 6.10: FT-IR analysis for 06SJG038K and 06SJG038L	134
Table 6.11: GC-MS analysis of peaks for sample 06SJG038J (0 kGy).....	135
Table 6.12: GC-MS analysis of peaks for sample 06SJG038K (30.5 kGy)	135
Table 6.13: GC-MS analysis of peaks for sample 06SJG038L (50.1 kGy).....	135
It was expected that open circuit voltages (OCV) would not be close to the theoretical maximum of ~1.2 V, due to non-optimised construction of the MEA and the subsequent affect on catalysis. OCV's were expected to be in the range 0.7-1.0 V (as reported in the literature). As regards energy density it was expected that, because the materials were of high anionic conductivity and low methanol permeation, high concentrations of methanol could be used, and energy densities in the region of 10 mW cm ⁻² would be achieved.....	139
Table 6.14: Samples tested under alcohol fuel cell conditions	140
Table 6.15: Fuel cell test results.....	154

Abbreviations

γ -radiation	Gamma Radiation
Ω	Ohms (electrical resistance)
%	Percent
~	Approximately
μL	Microlitre
μm	Micrometre
^{60}Co	Cobalt-60
$^{\circ}\text{C}$	Degrees Celsius
$^{\circ}\text{F}$	Degrees Fahrenheit
A	Amps
AFC	Alkaline Fuel Cell
AEM	Anionic Exchange Membrane
AI	Aniline
AIBN	Azo-bis-isobutyronitrile
AMX	Allyl methacrylate
AMPSA	2-Acrylamido-2-methyl-1-propanesulfonic acid
AN	Acrylonitrile
BE	2-(Dimethyl amino) ethyl acrylate
BV	(ar-Vinylbenzyl) trimethyl- ammonium chloride
C	Specific Heat Capacity (J g K^{-1})
CEM	Cationic Exchange Membrane
CHP	Combined Heat and Power
cm	Centimetre
CNT	Carbon NanoTubes
DK	Diffusion Coefficient ($\text{cm}^2 \text{s}^{-1}$)
DMFC	Direct Methanol Fuel Cell
emf	Electro Motive Force
ETFE	Ethylene tetrafluoroethylene
EtOH	Ethanol
eV	Electron Volts
F	Farad
FEP	Fluorinated ethylenepropylene
FT-IR	Fourier Transform Infra Red Spectroscopy
g	Gram
G	Gibbs Free Energy (kJ)
GC-MS	Gas Chromatography – Mass Spectrometry
GHz	Gigahertz
Gy	Gray
h	Hour
HEMA	2-Hydroxy ethyl methacrylate
HPLC	High Pressure Liquid Chromatography
J	Joules
K	Kelvin
kg	Kilogram
kGy	Kilogray
kHz	Kilohertz
kJ	Kilojoules
kW	Kilowatt

KWh	Kilowatt Hour
L	Litre
M	Molar
m	Metre
mA	Milliamp
mbar	Millibar
MCFC	Molten Carbonate Fuel Cell
MEA	Membrane Electrode Assembly
MeOH	Methanol
MeOX	2-Methyl-2-oxazoline
mg	Milligram
MHz	Megahertz
min	Minute
mL	Millilitre
mm	Millimetre
mol	Moles
mS	Millisiemen
mV	Millivolt
mW	Milliwatt
NASA	National Aeronautics and Space Administration
nm	Not Measured
NMR	Nuclear Magnetic Resonance
NVP	N-Vinyl-2-pyrrolidone
OCV	Open Circuit Voltage
PAFC	Phosphoric Acid Fuel Cell
p.d.	Power Density
PEDOT	Poly(3,4-ethylenedioxythiophene)
PEM	Proton Exchange Membrane
PEMFC	Proton Exchange Membrane Fuel Cell
pH	Potential of Hydrogen
PhOX	2-Phenyl-2-Oxazoline
ppm	Parts per million
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride
RI _m	Refractive Index of Measured Sample
RI _w	Refractive Index of Water
S	Siemens
s	Seconds
SPE	Solid Polymer Electrolyte
SOFC	Solid Oxide Fuel Cell
TBq	Terabequerel
TEABF ₄	Tetraethylammonium tetrafluoroborate
TT	2,4,6-Triallyl-1,3,5-triazine
TTT	1,3,5-Triallyl-1,3,5-triazine-2,4,6-(1H, 3H, 5H)-trione
\$US	American Dollar
UV	Ultraviolet
V	Volt
VPy	4-Vinyl pyridine
VAZO ®	Azo-bis(cyclohexane carbonitrile)
W	Watts

Wh	Watt Hours
wrt.	With Respect To
wt	Weight
w/w	Weight for Weight

Formulae and Constants

AlCl_3	Aluminium chloride
BF_3	Boron trifluoride
$\text{CH}_2\text{CH}_2\text{OH}$	Ethanol
$(\text{CH}_2\text{OH})_2$	Ethylene glycol
CH_3OH	Methanol
$\text{CH}_4\text{NOH} \cdot x\text{H}_2\text{O}$	Tetra methyl ammonium hydroxide hydrate
CO	Carbon monoxide
CO_2	Carbon dioxide
CO_3^{2-}	Carbonate Ion
e^-	Electron
E°	emf
H^+	Proton
H_2	Hydrogen
HCl	Hydrochloric acid
HF	Hydrogen Fluoride
H_2PO_4	Phosphoric acid
H_2O	Water
H_2SO_4	Sulphuric acid
K_2CO_3	Potassium carbonate
$\text{K}_2\text{S}_2\text{O}_8$	Potassium persulphate
KOH	Potassium hydroxide
LiAlH_4	Lithium aluminium hydride
N_2	Nitrogen
NaBH_4	Sodium borohydride
NaOH	Sodium hydroxide
N_2H_4	Hydrazine
$(\text{NH}_4)_2\text{S}_2\text{O}_8$	Ammonium persulphate
O_2	Oxygen
O^{2-}	Oxygen Ion
OH^-	Hydroxyl Ion
Pt	Platinum
Ru	Ruthenium
RuO_2	Ruthenium oxide
SnCl_4	Tin tetrachloride
TiO_2	Titanium oxide

Glossary

Anionic Exchange Membrane

Membrane containing positively charged groups, which allow selective permeation of negative ions (anions).

Anode

The negative electrode, where fuel is delivered and electrons produced.

Cathode

The positive electrode, where the oxidant is delivered

Cationic Exchange Membrane

Membrane containing negatively charged groups, which allow selective permeation of positive ions (cations).

Hydrophilic

Having a strong affinity for water.

Hydrophobic

Having little or no affinity for water.

Membrane Electrode Assembly (MEA)

Structure containing a membrane with catalyst cloth on either side.

Solid Polymer Electrolyte (SPE)

Polymeric material of a solid nature used in an electrochemical cell.

Introduction

It is widely accepted that the energy needs of the world are increasing and that it will not be possible to continue to service the demand from fossil fuels (oil, coal and gas) as has largely been the case up to now. Furthermore, it is also accepted that the continuing high use of fossil fuels is leading to a massive increase in the quantity of greenhouse gases being released into the atmosphere, resulting in damaging levels of global warming.

Thus, alternative sources of energy, particularly electrical energy, are being sought. These include solar, wind, geothermal, wave and tidal, the use of renewable biomass, and fuel cells. Strictly, of course, these are energy conversion methods, rather than energy generation, and not all are able to work continuously. Thus methods of energy storage will also be needed, such as batteries, ultracapacitors, and the efficient production and storage of hydrogen. Hydrogen is seen as particularly appropriate since the products of its combustion are water and energy.

For fuel cells to produce zero emission they must be fuelled with hydrogen. But the majority of hydrogen production today utilises fossil fuel cracking, and thus produces large quantities of carbon dioxide. However hydrogen can be produced without the carbon dioxide waste, by water electrolysis. If this is fuelled by a green energy source, such as wind or wave power, a truly green energy grid could be realised.

The concept of a fuel cell has been known for over 150 years^[1], and it has been widely considered as a replacement for the internal combustion engine for automotive power, which also produces large quantities of greenhouse gases. Success in this area will assist

many countries in their endeavour to reduce greenhouse gas emissions in accordance with their commitments under the Kyoto Protocol^[2].

This project focuses on fuel cells as an energy conversion device and the electrolyser as a means of producing a suitable fuel, hydrogen, by the electrolysis of water. Both are electrochemical cells and consist of two electrodes and an electrolyte, and it is the electrolyte that dominates the cells performance and chemical reactions taking place within the cell.

There are a number of types of fuel cell, which use different electrolytes, for example ceramics, molten carbonates and polymers. The principal aim of this project is to develop new polymer electrolyte materials for these electrochemical cells to overcome some of the deficiencies of the present materials. The polymer in a proton exchange membrane fuel cell is often referred to as a Solid Polymer Electrolyte (SPE) and it is required to possess special properties, such as exceptional stability, low permeability to reactants, and high ionic conductivity. Similar properties are required of the separators used in electrolysers and it is an aim of the project to evaluate new materials for this application as well as in fuel cells.

The majority of the research on SPE's has been based on proton exchange polymers such as perfluorosulphonic acid membranes, typified by Nafion®. Nafion® is prepared using toxic chemicals, thus the preparation of electrochemical cells using Nafion® membranes is expensive. However, alternative electrolytes based on anionic (hydroxyl ion) exchange polymers have been shown to possess potentially significant advantages, e.g. cheaper catalysis, and reduced cell corrosion.

These anionic exchange polymers may utilise a different fuel to hydrogen, and methanol is currently one of the leading candidates.

The aims of this project are therefore to develop novel anionic exchange polymeric systems, with specific emphasis on materials for alkaline methanol fuel cells. The principal methods for producing the new SPEs will be the use of liquid monomer systems to produce thin film membranes with high anionic conductivity as well as the other necessary properties of low reactant permeability, high thermal and chemical stability.

An objective will also be to consider the possibility of directly casting the liquid monomer systems into a fuel or electrolyser cell geometry. These monomers, along with additional functional groups, may then be polymerised by gamma radiation, thermal or microwave methods. This approach accords with one of the major aims of ITM Power plc who are partially funding this project via the CASE award scheme.

Chapter 1 . Literature Review-Electrochemical Cells

1.1 Introduction

An electrochemical cell consists of two electrodes and an electrolyte. The cell can be configured to generate an electric current, (i.e. a battery or fuel cell) or an electric current passed through it to produce a chemical reaction (i.e. an electrolyser or electroplating cell). Alternatively a cell with a different configuration may be used to store energy to be used at a later time (i.e. capacitor).

It is possible that each type of electrochemical cell can use similar materials for the electrodes and electrolytes; therefore novel materials developed for one type of electrochemical cell may have properties that are valuable in other cells.

This project focuses on two different types of electrochemical cell: fuel cells and electrolyzers. This chapter contains a review of the literature with regard to these cells to provide a background for the subject area.

1.2 Electrolyzers

In the 1820s it was noted that if an electric current flowed through water, two gases were produced. It was not until 1833 that Michael Faraday used the term electrolysis and explained the phenomenon. Electrolysis is used in many processes today, such as the chlor-alkali process, where brine is split into chlorine and sodium hydroxide (caustic soda) or where water is split into hydrogen and oxygen (See figure 1.1).

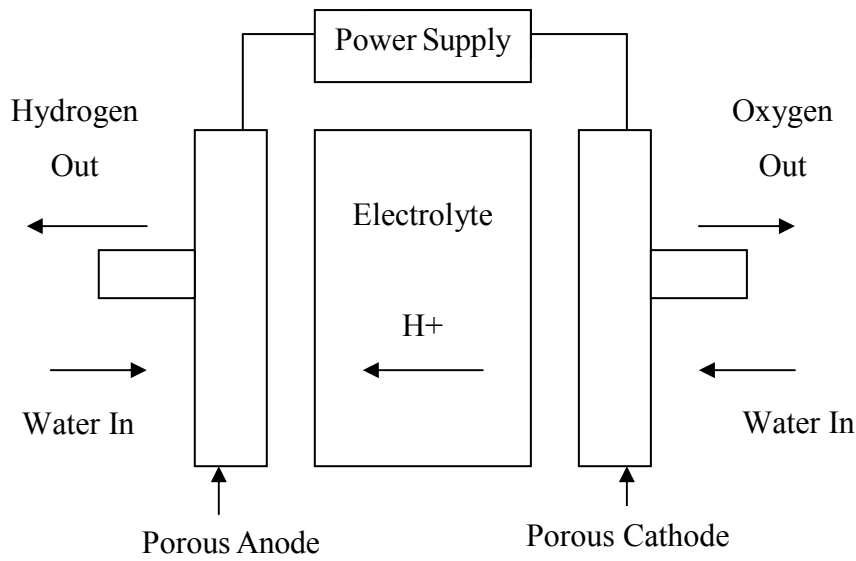
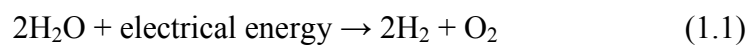


Figure 1.1: Water electrolyser (Expanded)

1.2.1 Water Electrolysis

The electrolysis of water can produce clean hydrogen by utilizing electricity from renewable energy without carbon dioxide (CO₂) emission to the atmosphere^[3] (see equation 1.1.).



Water is a poor ionic conductor and for this reason a conductive additive, such as sodium hydroxide (NaOH) can be added to the water or used as a solid-state electrolyte. Both alkaline and acidic electrolytes can be used in water electrolysis^[4].

The cost of hydrogen produced by industrial electrolyzers is high, partially due to the high-energy requirement of 4.5-5 kWh m⁻³ of hydrogen^[5]. However, hydrogen from water electrolysis is still of great importance, due to its high efficiency of 80-90 %^[6], and

electricity produced in excess of demand can be used to produce hydrogen using a water electrolyser, and thereafter stored. Electricity demand in excess of production can then be met by converting the stored hydrogen to electricity through a fuel cell^[7]. This could be especially applicable to renewable energy sources such as wind power and solar power, which are not constant or always present. Although the overall efficiency of a water electrolyser/fuel cell system may be relatively low ($\sim 48\%$ ^[8]), it offers a truly green energy route, which may become more viable and important in the future.

In 2003 there were less than 20 manufacturers of industrial water electrolyser's worldwide^[9]. They can be broadly divided into two categories; the alkaline-type water electrolyser and the proton exchange membrane (PEM) type water electrolyser^[7].

1.2.1.1 Alkaline Electrolysers

Most commercial electrolysers use an alkaline electrolyte, mainly due to lower investment costs and minor corrosion problems^[4]. 30 wt % potassium hydroxide (KOH) solution is used as the electrolyte because of its good conductivity. The cell operates below 100 °C to reduce corrosion problems^[4], in the range of 60-80 °C, and in the production of hydrogen operates in the pressure range of 1-30 bar^[10].

1.2.1.2 Proton Exchange Membrane (PEM) Electrolysers

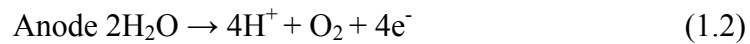
General Electric first proposed the use of a PEM for electrolysers^[9]. The advantages of PEM over alkali electrolysers include a non-caustic environment resulting in greater safety and reliability, a high differential pressure sustainable in some systems, the ability to run at high current densities and high efficiencies^[11]. The PEM within the electrolyser also acts as a barrier, separating the oxygen and hydrogen produced. Thus it needs to be

free of defects and structurally strong enough to prevent the two gases from mixing. The PEM-type water electrolyser can operate over a wide range of temperatures, pressures and current densities compared with alkaline-type water electrolyzers, though up to 1995 little work had been published on PEM technology for water electrolysis^[11].

Divisek and Emonts suggested that only a perfluorinated polymer can be used as the separator in a PEM electrolyser and its replacement by other polymers is unlikely^[12]. They suggest that non-perfluorinated polymers lack stability in an electrolysis environment. Yet work by ITM Power plc on hydrocarbon solid polymer electrolytes for electrolysis have shown stability for over 500 hours.

1.2.2 Anode Versus Cathode Feed Water Electrolysis

The general reaction for PEM electrolyzers where water is fed to the anode is given in equation 1.2 and 1.3.



When the water is supplied only at the anode side, it dissociates so that the protons migrate to the cathode under the effect of the electric field and neutral oxygen gas is formed. The oxygen gas has to be separated from the feed water before it can be used or stored. The product hydrogen should be ‘dry’ and could be used in combustion without purification. The pH of the un-electrolysed water does not change^[13].

When water is circulated only through the cathode cavity, water passes through the membrane by diffusion to the anode. Some of the water is dissociated at the anode into

protons and oxygen. The protons become hydrated by the remainder of the water and migrate back through the membrane to the cathode to form hydrogen. As a result the oxygen product gas is free of liquid water. The hydrogen produced is hydrated and may be used in hydrogen fuel cells.

Water can also be circulated through both the cathode and anode compartments of the electrolyser. Here the oxygen and hydrogen produced are both hydrated. Millet *et al* distributed water on both the anode and cathode side of the cell^[11], and during the electrolysis extra amounts of water were transferred from the anode side to the cathode by electro-osmosis. They believed this to be in the region of 3.5 molecules per proton. They suggested applying a differential pressure to the two compartments to balance this transfer. Significant water flows from one compartment to the other were also observed with small differential pressures, as low as 20 mbar. They found that, at high pressure, control of the differential pressure across the cells was required.

Millet *et al*^[11] also found that non-homogenous current distribution at the electrode-solid electrolyte interface resulted in the formation of hot spots, which could eventually lead to the melting and production of holes in the membrane.

1.3 Fuel Cells

A fuel cell (see figure 1.2) uses an oxidation-reduction reaction to create electricity, where the fuel is oxidized at the anode into positive ions and electrons. The electrons are directed around an external connecting circuit and the ions are transported towards the cathode through the electrolyte and recombined with the electrons at the cathode.

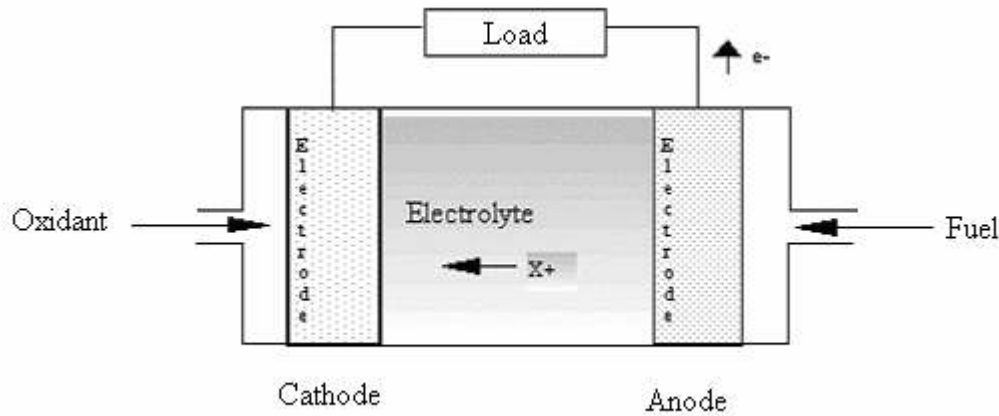


Figure 1.2: A simple fuel cell

1.3.1 History of Fuel Cells

Fuel cells are one of the oldest electrical energy conversion technologies known^[14]. In 1839 British lawyer/inventor Sir William Robert Grove discovered an oxidation-reduction reaction whilst working on the electrolysis of water and showed the feasibility of a fuel cell, using hydrogen and oxygen as fuels with an aqueous sulphuric acid electrolyte^[1]. He created a bank of 50 cells and which he called a ‘gaseous voltaic battery’, but was unable to generate a large current, probably due to the materials available at the time, which were limited in their properties.

Ludwig Mond and Charles Langer improved on this early fuel cell using a platinum black catalyst, though the reactivity decreased with time^[15]. They corroborated Grove’s work in 1889, and first used the term “fuel cell”. In 1913 Siegl supported the platinum catalyst on carbon particles and reduced the amount of catalyst needed, thereby reducing the cost of the cell^[15]. Thereafter the development of fuel cells lacked drive for the next four decades, as primary energy sources, such as batteries, were abundant and inexpensive^[14].

The major exception was the work of Francis T. Bacon, who in 1932 constructed a fuel cell using an alkaline electrolyte. He used inexpensive nickel electrodes and increased the operating temperature of the cell. By 1952 he had produced a 5kW cell, which he used to power a forklift truck.

However it was not until the 1960's that the National Aeronautics and Space Administration (NASA) undertook serious research into fuel cells for space flights. The fuel cell was seen as a lightweight power supply that also provided the added bonus of potable water for the astronauts. General Electric produced the first Proton Exchange Membrane Fuel Cell (PEMFC) as part of the Gemini space programme using a divinylbenzene styrene sulphonic acid membrane. However this type of membrane was found to be physically unstable over long periods (over 500 hours)^[14], and improving this became the driving force for the solid polymer electrolyte (SPE) research until the present day.

1.3.2 Fuel Cell Energy

If a fuel cell uses hydrogen as a fuel, the overall chemical reaction is the same as a combustion reaction but, instead of heat, it is electrical energy that is mainly produced.

If there are no energy losses within the cell, then all of the Gibbs free energy (G) (See equation 1.4) will be converted into electrical energy. The Gibbs free energy is defined as “the free energy change that accompanies the formation of one mole of a compound in its standard state from its constituent elements in their standard states”^[16]. This can be defined in an equation:

$$\Delta G = \sum G_{\text{products}} - \sum G_{\text{reactants}} \quad (1.4)$$

For a hydrogen fuel cell the Gibbs free energy equals $237.2 \text{ kJ mol}^{-1}$ and is the free energy for the formation of liquid water at 25°C ^[8].

1.3.3 Fuel Cell Classifications

Fuel cells can be divided into classes in several ways. Kordesch splits fuel cells into 3 classes: direct, indirect and regenerative^[17]. Direct fuel cells are ones where the fuel is directly oxidised and the products of the reaction are discarded. Indirect fuel cells use a reformer or biochemical enzymes to produce fuel (usually hydrogen) from another chemical (fuel carrier). Regenerative fuel cells rejuvenate the spent reactants of the fuel cell reaction for re-use.

Fuel cells may also be categorised by operating temperature, low temperature ($25\text{-}100^\circ\text{C}$), intermediate temperature ($100\text{-}500^\circ\text{C}$), high temperature ($500\text{-}1000^\circ\text{C}$), and very high temperature (over 1000°C). Fuel cells can also be described by the fuel or even fuel state, (gas, liquid or solid) or their operating pressure. Most commonly, however, fuel cells today are categorised by their electrolyte.

In classifying fuel cells by their electrolyte type (Table 1.1), the following abbreviations are commonly used: Alkaline Fuel Cell (AFC), Phosphoric Acid Fuel Cell (PAFC), Molten Carbonate Fuel Cell (MCFC), Solid Oxide Fuel Cell (SOFC) and Proton Exchange Membrane Fuel Cell (PEMFC). When hydrogen is the fuel the cells have similar electrode reactions (Table 1.2). The exception to classifying by the electrolyte is the Direct Methanol Fuel Cell (DMFC), which is classified by its fuel. The following descriptions of the different types of fuel cell are in relation to their electrolyte only.

Other differences, such as cell engineering, which affect the fuel cell performance, are outside the scope of this study.

Table 1.1: Classes of fuel cell^[13]

Type	Mobile Ion	Operating T (°C)	Details
Alkaline (AFC)	OH^-	50-200	Used in space vehicles
PEMFC	H^+	50-100	Vehicles & mobile applications
Phosphoric acid (PAFC)	H^+	~220	200kW combined heat/power (CHP)
Molten Carbonate (MCFC)	CO_3^{2-}	~650	Suitable for large scale CHP
Solid Oxide (SOFC)	O^{2-}	500-1000	All sizes of CHP
DMFC	H^+	60-120	Mobile Phones, Laptops

Table 1.2: General electrode reactions for types of fuel cell

Fuel Cell	Anode reaction	Cathode reaction
AFC	$\text{H}_2 + 2(\text{OH}^-) \rightarrow 2\text{H}_2\text{O} + 2\text{e}^-$	$\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2(\text{OH}^-)$
PEMFC	$\text{H}_2 \rightarrow \text{H}^+ + 2\text{e}^-$	$\frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$
PAFC	$\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$	$\frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$
MCFC	$\text{H}_2 + \text{CO}_3^{2-} \rightarrow \text{H}_2\text{O} + \text{CO}_2 + 2\text{e}^-$	$\frac{1}{2}\text{O}_2 + \text{CO}_2 + 2\text{e}^- \rightarrow \text{CO}_3^{2-}$
SOFC	$\text{H}_2 + \text{O}^{2-} \rightarrow \text{H}_2\text{O} + 2\text{e}^-$	$\frac{1}{2}\text{O}_2 + 2\text{e}^- \rightarrow \text{O}^{2-}$
DMFC	$\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^-$	$\frac{3}{2}\text{O}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow 3\text{H}_2\text{O}$

Alkaline Fuel Cell

The alkaline fuel cell (AFC) is a non-divided cell, requiring no membrane. The AFC was developed around 1902 using potassium hydroxide electrolyte (KOH) solution, (typically 35-50 wt %) at low temperatures, around 100 °C^[8]. Oxidation kinetics are much faster in an alkaline electrolyte than in acid, making the AFC attractive^[14]. AFC's exhibit the highest electrical efficiencies of all fuel cells, but operate only with very pure gases^[14].

The oxidant supply for AFC's must be carbon dioxide (CO₂) free, as any CO₂ in the oxidant will combine with the KOH to produce potassium carbonate (K₂CO₃). This has

the potential to block catalyst sites and increase the overall electrical resistance within the cell, therefore reducing fuel cell performance. However one of the major advantages of AFC's is that a wide range of catalysts can be used, such as nickel, silver, metal oxides and noble metals. AFC's were used on Apollo and Shuttle orbiter craft and also produced drinkable water for the astronauts^[8].

Phosphoric Acid Fuel Cells

Phosphoric acid fuel cells (PAFC) are also non-divided fuel cells requiring no membrane. PAFC's were the first fuel cell to be commercially produced in quantity and have enjoyed widespread terrestrial use. They are commonly used in stationary power plants^[14] and use concentrated phosphoric acid as the electrolyte operating in the region of 160-220 °C. This is because the phosphoric acid is a poor ionic conductor at lower temperatures.

Molten Carbonate Fuel Cell

Molten carbonate fuel cells (MCFC) are a divided cell using a ceramic electrolyte membrane. MCFC's employ an electrolyte made from alkali carbonates in a ceramic matrix of lithium aluminium oxides. They operate in the region of 600-700 °C, since at these high temperatures the alkali carbonates form a highly conductive molten salt. The carbonate ions provide the ionic conductance. Due to the high temperatures utilised there is little or no need for catalysis, as electrode kinetics for oxidation and reduction are sufficiently fast to permit the direct use of hydrocarbon fuels.

Solid Oxide Fuel Cells

Solid oxide fuel cells (SOFC) are another type of divided cell using a solid electrolyte barrier. SOFC's utilise a nonporous ceramic metal oxide such as yttrium oxide stabilised

zirconium oxide. The cell operates at ~ 650-1000 °C where ionic conductance by oxygen ions can take place. Operating at this high temperature means that they do not need catalysts; however the ceramics are presently very fragile and expensive to produce.

Proton Exchange Fuel Cells

Proton exchange membrane fuel cells (PEMFC) are a further type of divided cell, using a polymeric membrane as the electrolyte. The first reported ion exchange polymers were made by D'Alelio in 1945^[18] and the idea of an ion exchange membrane as the electrolyte in a fuel cell was originally described by Grubb in 1957^[18]. It has been stated that the PEMFC epitomises the essential simplicity of the fuel cell^[8].

General Electric developed the first production PEMFC in the 1960's using a polystyrene divinyl-benzene sulphonic acid membrane^[19] and NASA further developed it for use on the early manned missions to space. The PEMFC's used on the first manned spacecraft only had a lifetime of approximately 500 hours, due largely to the chemical instability of the membrane^[14].

The use of Proton Exchange Membranes (PEM) is said to confer 3 major benefits^[19] to the fuel cell;

- 1) A small electrolyte volume so that only small amounts of hydrogen and oxygen are in solution in the electrolyte, meaning there is a lower chance of an explosive mixture of hydrogen and oxygen forming.
- 2) The nature of the electrolyte allows quick start up and rapid shut down of the system, as the electrolyte does not have to be circulated or reach high operating temperatures.

- 3) High current densities can be sustained compared to other systems, due to the high conductivity of the membranes.

The major disadvantage is that if they become dehydrated their conductivity decreases, because although the PEM contains the ionic exchange groups bound to the membrane, the mobile ion only has significant mobility in the presence of water^[20].

Direct Methanol Fuel Cell

The DMFC is a special form of low temperature fuel cell based on PEM technology and therefore operates similarly to the PEMFC. The electrolyte used in the DMFC is a proton conducting solid polymer membrane and the methanol fuel is fed directly into the fuel cell, without reforming into hydrogen. However, the membrane must also prevent methanol crossover from the anode to the cathode compartment, which otherwise will produce a parasitic loss within the cell.

1.4 Fuels

Fuel cells have been considered and tried with many fuels and oxidisers other than hydrogen and oxygen. Fuels in two states, gas and liquid, have been evaluated and various solid materials have also been used for hydrogen provision, such as sodium borohydride (NaBH_4) and lithium aluminium hydride (LiAlH_4), although these materials are classified as fuel carriers. Each type of fuel has its own advantages and disadvantages, and requires different membranes and catalysts to use them efficiently. The advantages and disadvantages of each type of fuel cell are summarised in Table 1.3.

Table 1.3: Advantages and disadvantages of different types of fuel cell

Fuel Cell	Advantages	Disadvantages
Alkaline Fuel Cell (AFC)	Wide range of catalysis available Membrane not always required	CO ₂ contamination will form K ₂ CO ₃ with KOH Fuel/oxidant supply needs to be CO ₂ free Selective catalyst required if no membrane present
Phosphoric Acid Fuel Cell (PAFC)	No membrane required Reject heat can be used to heat water or air	High cost catalysis Must run above 160 °C for phosphoric acid to be conductive
Molten Carbonate Fuel Cell (MCFC)	Little need for catalysis due to high temperature Reject heat can be used to raise steam to drive a steam turbine	CO ₂ required at cathode to form carbonate ion Low sulphur tolerance compared to PAFC
Solid Oxide Fuel Cell (SOFC)	No catalysts Electrolyte cast into flexible shapes	Solid oxide electrolyte has high electrical resistivity
Proton Exchange Membrane Fuel Cell (PEMFC)	Solid electrolyte avoids leakage problems Low temperature operation allows rapid start up and shut down High current densities Differential fuel and oxidant pressure possible	Platinum catalysts are sensitive to CO Requires high catalyst loadings High membrane cost at present
Direct Methanol Fuel Cell (DMFC)	Liquid fuel, with high energy density Solid electrolyte avoids leakage problems	Kinetics slow in acidic media

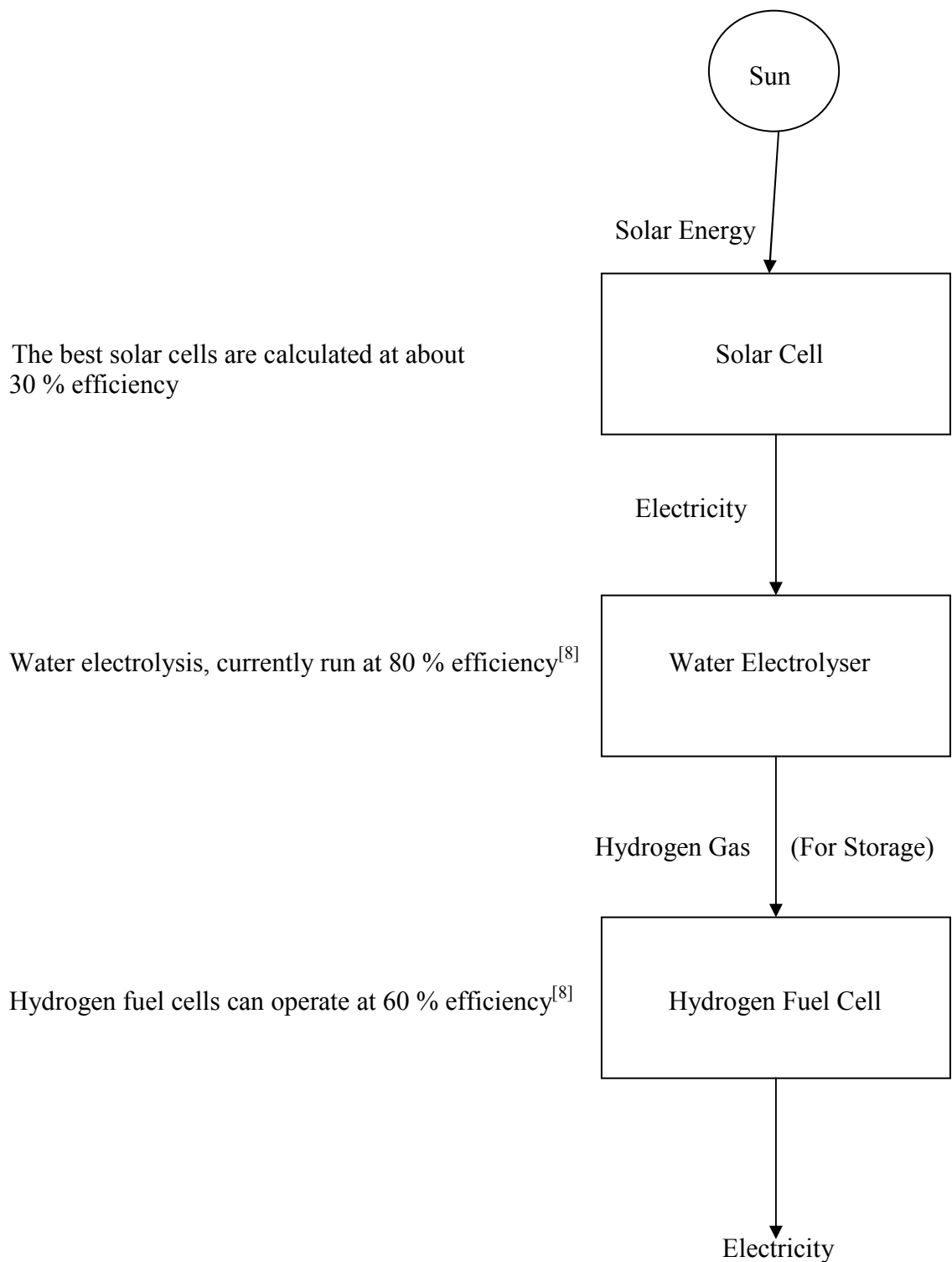
1.4.1 Hydrogen

Fuel cells are synonymous with hydrogen. It was the first fuel to be considered for fuel cells and produces only water as waste. It is therefore justifiably considered a non-polluting energy source. However, at present the majority of hydrogen is commercially made from cracking fossil fuels, which also produces carbon dioxide. This can be seen as non-environmentally friendly, and arguably negates the green image of fuel cells.

Hydrogen can be produced without the cracking of fossil fuels by the electrolysis of water. However the source of the electricity used must be from a green renewable source such as wind or wave power for it to be considered a truly green energy source. At the present time hydrogen generation by water electrolysis is expensive and if taken into account would increase the overall cost of the energy from a hydrogen fuel cell.

Unfortunately power production using hydrogen from water electrolysis has poor efficiency. With each energy transformation, there is an associated energy loss. The efficiency of each step's energy conversion can be calculated. The total efficiency of the entire system can be quite small, possibly less than 15 % (see figure 1.3).

Hydrogen is a flammable gas, and concerns over its safety and storage have been widely discussed^[21]. This has led to much research into alternative forms of storing hydrogen, such as liquefaction, immobilisation in organic matrices such as solid hydrides including sodium borohydride.



Overall efficiency of system = solar cell efficiency x water electrolyser efficiency x hydrogen fuel cell efficiency
Overall efficiency = $0.30 \times 0.80 \times 0.60 = 0.144 = 14.4\%$ efficiency.

Figure 1.3: Efficiency of “energy on demand” system, from a primary green energy source

Despite the drawbacks hydrogen is considered to be the fuel of the near future^[22] as it can be used in stationary as well as in mobile applications. Although a perfect fuel in many respects, hydrogen must overcome a number of barriers before it can be considered to be commercial e.g. storage, transport and refuelling facilities for fuel cells. The world is set up to use liquid fuels, and the change to a gaseous fuel will incur massive costs, which may potentially hinder hydrogen fuel cells commercialisation.

1.4.2 Methanol

Because it is a liquid, methanol (CH_3OH) is of great interest as a fuel for fuel cells. It has a superior specific energy density (6000 Wh kg^{-1}) in comparison with the best rechargeable batteries, lithium polymer and lithium ion polymer systems (theoretical 600 Wh kg^{-1})^[23].

This has lead some to speculate that the DMFC may well be the first portable fuel cell to become widely available^[24]. But before this is possible, obstacles such as the low catalytic activity and high cost of catalysts for methanol oxidation, and the parasitic crossover of methanol within the fuel cell, will need to be overcome.

The efficiency and power output of the DMFC is also reduced by poisoning of the anode catalyst by carbon monoxide (CO)^[25], which is produced from the methanol. The only electrocatalyst material so far shown to catalyse methanol with the required stability and efficiency are platinum based materials^[14], e.g. Platinum/Ruthenium alloys, which are expensive, thus keeping the price of the DMFC high.

A disadvantage of the DMFC is the fact that methanol is usually fed to the fuel cell diluted with water, typically at 1-2 M. This proportionally decreases the theoretical energy density. Methanol permeation decreases with increasing current density, because of increased methanol utilisation at the anode.

1.4.3 Ethanol

Ultimately fuel cell researchers will have to look for an entirely green fuel. Ethanol is one such possibility, as it has a good specific energy^[4] (8000 Wh kg⁻¹). It can be produced by biological means, where bacteria fix carbon dioxide in the air to produce ethanol in a fermentation process. Although an ethanol fuel cell produces carbon dioxide, it can be argued that ethanol is a carbon neutral fuel (see figure 1.4) as there is no net gain or loss of carbon to the atmosphere^[4]. Unfortunately, although the production of ethanol from biomass is a commercial venture, the catalysis in a fuel cell to produce electricity is still in its infancy and an inexpensive and suitable catalyst system is not available at this time.

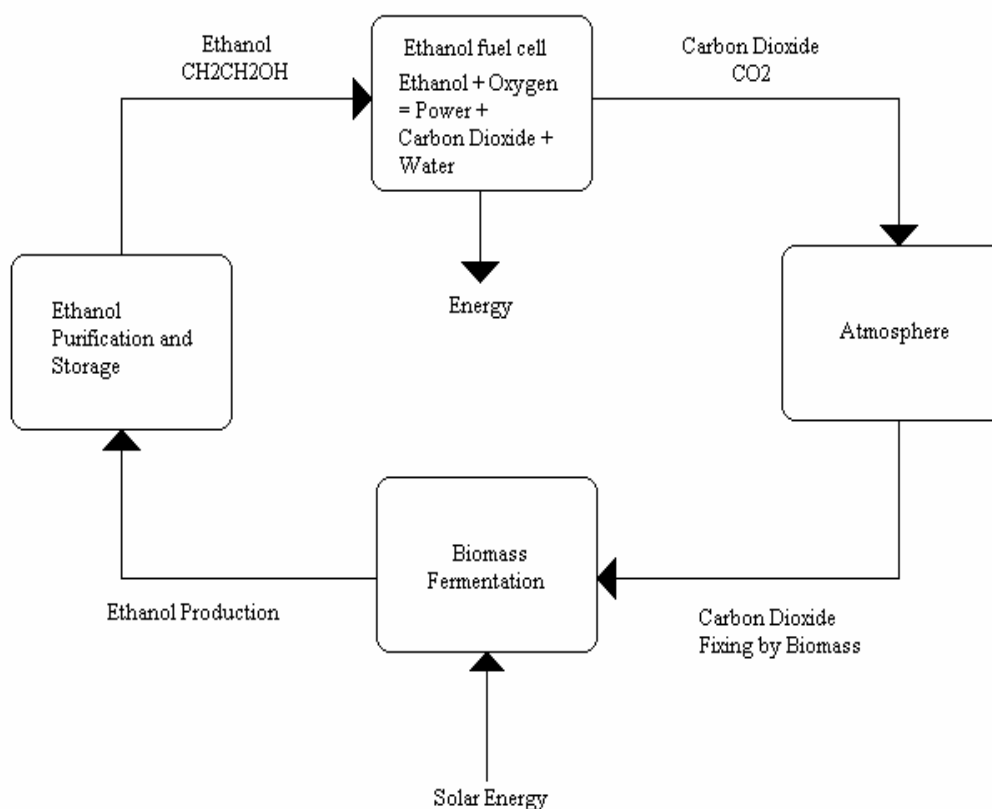
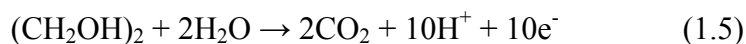


Figure 1.4: Carbon cycle for ethanol fuel cell with biomass ethanol production

1.4.4 Ethylene Glycol

It has been shown that in alkaline media ethylene glycol can be oxidized at high rates using a Raney-nickel catalyst^[26], with the hydroxyl ion carrying the charge. Such a cell would thus require an anionic exchange membrane (AEM).

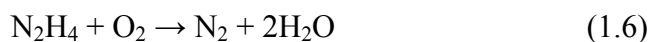
Ethylene glycol (CH₂OH)₂ is, however, reported to block the membrane and thus reduce the electrolyte conductivity^[26]. Initially it had been thought that ethylene glycol would not be suitable in an acidic environment^[27], though present studies^[26] into ethylene glycol oxidation in acidic media, using Raney nickel catalysts above 60 °C, show that ethylene glycol does produce protons^[28] via the reaction in equation 1.5.



1.4.5 Hydrazine

Hydrazine (N_2H_4) is considered as an ‘ideal’ fuel as it does not suffer from carbon dioxide poisoning effects^[25]. Using a perfluorinated membrane, high cell voltages have been shown, compared to a DMFC, especially at low current densities^[25].

In a fuel cell hydrazine is supplied to the anode and oxidised producing nitrogen and protons, the protons are then conducted through a PEM and water is produced at the cathode (see equation 1.6)



It has been shown that hydrazine permeation increases with increased current density, unlike methanol in the DMFC. This can be overcome by running the hydrazine fuel cell in an alkali medium with an AEM. Hydrazine and ammonia permeation through the AEMs is much lower than through cationic exchange membranes (CEM). Using alkaline environments and AEMs would also mean it would be possible to use cheaper catalysts such as silver or nickel.

The disadvantage of hydrazine as a fuel is its high toxicity and explosive nature^[4] and this will probably prevent its widespread use as a fuel in almost all situations.

1.4.6 Summary of Fuels

Of the liquid fuels being considered for fuel cell applications, methanol and hydrogen are the most researched (see table 1.4 for a comparison of major fuels). Methanol is a liquid at room temperature and the petroleum infra-structure could be more easily adapted for a

liquid fuel. Unfortunately, today, methanol is produced by steam reforming of fossil fuels. Furthermore methanol fuel cells also produce carbon dioxide as a by-product, though at stationary power plants this could be collected, and sold for commercial activities such as in the brewing industry.

Table 1.4: Comparison of major fuel types for fuel cells

Fuel	Approximate Energy Density	State at 25 °C	Advantages	Disadvantages	Source of Fuel
Hydrogen	40,000 Wh kg ⁻¹	Gas	Produces no CO ₂ waste	Difficult to transport and use	Fossil fuels, Water electrolysis
Methanol	6000 Wh kg ⁻¹	Liquid	Ease of transport/ refuelling	Catalysis poor, produces CO ₂ waste	Fossil fuels
Ethanol	8000 Wh kg ⁻¹	Liquid	Ease of transport/ refuelling, Production by biomass.	Catalysis poor	Fossil fuels, Biomass

1.5 Chapter Summary

Water can be split into its constituent components, oxygen and hydrogen, by the process of water electrolysis, using electricity. The hydrogen gas can be used in hydrogen fuel cells and if this process uses electricity from renewable energy, an energy storage and production without CO₂ emission to the atmosphere can be achieved. This may in time help countries in reducing their overall ‘greenhouse gases’ fuel emissions as set down in the Kyoto agreement.

Fuel cells are predominately characterised by the separating electrolyte, with the exception of those cells using alcohol fuels. PEMs can be used in fuel cells and electrolyzers, and provide the necessary advantages as physical fuel separation.

Solid polymer electrolytes (SPE) such as the PEM offer other advantages when compared to other electrolytes utilised in fuel cells. These include rapid start up, and low volumes of gas in solution. Specifically, PEMs are capable of sustaining high current densities when compared to other systems.

At the present fuel cells utilising PEMs are required to have excellent water management within the cell to prevent the membranes from drying, and ionic conductivity and performance decreasing. PEM fuel cells also utilise expensive platinum based catalysts, which will keep the price of fuel cells high. The fuelling of PEMs with gaseous hydrogen may cause problems on a large scale, hindering the commercialisation of hydrogen PEM fuel cells.

Liquid fuels, such as methanol or ethylene glycol, are therefore of interest, as it would be easier to adapt existing petroleum refuelling stations. The lead candidate for liquid fuel cells is methanol. Unfortunately methanol fuel cells also utilise platinum based catalysts which have poor oxidation activity in an acidic environment, leading to lower fuel cell performance than achieved by hydrogen fuelled cells. .

However the implementation of an alkaline environment could provide a fuel cell where more active and less expensive catalysts could be used.

This project targets the specific advantages for both electrolyzers and fuel cells that solid polymer electrolytes can provide (see chapter 2). To aid commercialisation a liquid fuel cell would be beneficial and the project focuses on liquid fuelled cells using novel anionic exchange membranes (AEM), which may reduce the overall cost of the fuel cell by providing an alkaline environment in which inexpensive catalysts can be used.

Chapter 2 will discuss solid polymer electrolytes, proton exchange membranes and alkaline exchange membranes, including commercially available materials.

Chapter 2 . Literature Review-Membranes

2.1 Introduction

As described in Chapter 1 different fuel cell types require different membrane properties, yet all membranes must be selectively permeable to ions, and stable within the cell environment. The optimum membrane will be determined by the cell type and will influence the performance of the cell.

Solid polymer electrolytes (SPE) have been under investigation in many electrochemical cell systems, due to their useful properties of physical robustness, low permeability to reactants and high ionic conductivity. The majority of this research has been based on polymer membranes for fuel cells.

The aims of this project were to develop novel anionic exchange polymeric systems using liquid monomer systems. The systems should be able to be cast into fuel cell or electrolyser geometries in thin film membranes. The properties of high anionic conductivity, low reactant permeability, high thermal and chemical stability were seen as important goals.

It was considered that the liquid monomer systems would require at least 3 compounds to produce a suitable ionically conducting polymeric material. These will include a hydrophilic monomer, to help control the water content of the polymer, a hydrophobic monomer, to provide strength in the polymer and stop the polymer dissolving completely when hydrated and an anionic exchange moiety to provide the necessary ionic exchange character.

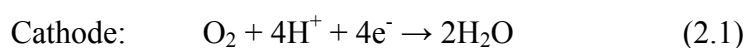
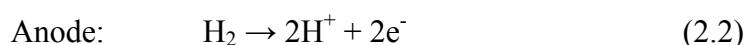
The choice of liquid monomers in the study was initially unrestricted. However, some of the typical supplied by ITM Power contained monomers which provided the necessary properties for use within an anionic exchange membrane. These materials have been used, in conjunction with other new monomers, to produce novel anionic exchange membranes.

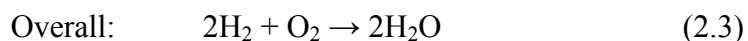
2.2 Types of Membrane

Ion permeable membranes are generally designed to selectively allow ions of a specific charge to pass, i.e. positive charges (cations) or negative charges (anions). Therefore membranes can either be Anionic Exchange Membranes (AEM), those that allow anions (negatively charged ions) to pass, or Cation Exchange Membranes (CEM), those that allow cations (positively charged ions) to pass. Today ion permeable membranes are usually manufactured from organic polymers with covalently bound ionic groups^[29] and thus have many similarities to ion exchange resins, other ionomers and polyelectrolytes.

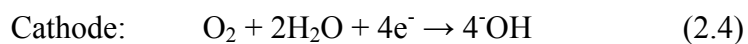
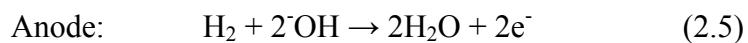
The SPE may operate as an AEM or CEM depending on its composition. The majority of the research and development for fuel cell membranes has focused on CEMs with much less work being published on AEMs. The overall cell reaction can be the same for both types of cell; the individual electrode reactions will be different in each case. (See equations 2.1 to 2.6)

For the CEM electrolyte:





For the AEM electrolyte:



In the CEM case, the majority charge carrier through the electrolyte is therefore the proton, whilst in the AEM case; the majority charge carrier is the hydroxyl ion.

As discussed earlier, all electrolyte membranes require similar properties and Graham^[30] suggests eight properties for the ideal membrane;

- 1) High ionic conductivity
- 2) Zero electronic conductivity
- 3) Low gas permeability
- 4) Dimensional stability
- 5) High mechanical strength
- 6) Low transference of water by conducting ions (electro-osmosis)
- 7) High resistance to dehydration
- 8) Chemical stability to oxidation hydrolysis.

Of Graham's properties, high ionic conductivity, low electronic conductivity, and high mechanical stability are the most important. If a membrane is not conductive to ions or is conductive to electrons, the cell performance will be compromised. The membranes must also be mechanically and chemically stable to survive cell assembly and the harsh environment of the cell.

In line with these principles, the objective of this project is to produce membranes that are chemically stable, have the appropriate mechanical properties and sufficient ionic groups to ensure that they have an acceptable conductivity and selectivity.

Early membrane work centred on styrene and divinylbenzene copolymers^[14], which had ionically conductive substituents on the phenyl rings. Usually these types of polymer had a high degree of crosslinking, due to the presence of the divinylbenzene. This gave the polymer a rigid structure and a high concentration of ionic groups homogeneously distributed through the polymer. The polymers required sulphonation to confer ionic conductivity. Styrene is reactive in the *para*- position and the sulphonation is assumed to occur at this position in such polymers.

Many of the membranes used in electrochemical technology today are based on copolymers of styrene or a vinylpyridine in which the ionic groups are introduced after polymerisation. The overall structure is highly uniform.

Since the late 1960's work has focused on copolymers of perfluorinated alkenes and substituted perfluorinated alkenes. These are linear polymers with regular side chains with terminal ionic groups. Here the strength comes from regions of hydrophobic fluorocarbon backbone of the structure. The ionic groups can collect together to form channels for the passage of the ions.

Perfluorinated ion permeable membranes were first developed by DuPont and marketed in the early 1970's as membranes for electrolyzers. They are made from polymers which have a backbone of poly(tetrafluoroethylene) with regular side chains ending in

sulphonic or carboxylate ion exchange groups. When swollen by water, these polymers undergo phase separation on a macromolecular scale, forming discrete hydrophilic and hydrophobic domains.

2.2.1 Ionic groups

Ion exchange membranes can contain two types of ion; those bound into the polymer, and the counter ions, which are free. When the membrane is immersed in a medium in which it is insoluble, the counter ions become mobile and can be exchanged for other counter ions from the medium. Ions of the same type bound to the polymer do not have free movement into and through the polymer.

Sun *et al*^[31] suggest that ionic conduction consists of a Grotthus-type mechanism, where the ion hops between the conducting groups.

Ion exchange groups can be broadly divided into four groups,

- 1) Strong cationic, such as sulphonic acids, and their salts.

Sulphonic acids have been well studied as an ionic group in hydrogen fuel cell PEM's. Sulphonated polymers can be prepared in the free acid form ($\text{-SO}_3\text{H}$), the salt ($\text{-SO}_3^-\text{Na}^+$) or the ester ($\text{-SO}_3\text{R}$)^[32].

- 2) Weak cationic, such as carboxylic acids and their salts.

The use of carboxylic acid groups in place of sulphonic acid, can lead to reduced water uptake and increased methanol permeation^[33]. This is largely due to the carboxylic acids weak proton dissociation at low pH, which in turn leads to low conductivity. However, the combination of sulphonic and carboxylic acid groups, can lead to lower conductivities than either group alone^[33].

- 3) Strong anionic, such as quaternary ammonium groups.

The quaternary ammonium-ion has a considerably higher thermal and chemical stability than other anionic exchange groups^[34].

- 4) Weak anionic, such as ammonium chloride or hydroxide.

Groups such as tetramethyl ammonium hydroxide hydrate ($\text{CH}_4\text{NOH} \cdot x\text{H}_2\text{O}$) show some ionic conductivity in the solid state^[31].

2.3 Ion Exchange Membrane Preparation by Polymerisation

Polymer ion exchange membranes are generally made by co-polymerising monomers together or by the grafting of monomers onto existing polymer substrates. The polymerisation can be ionic or radical.

2.3.1 Ionic Polymerisation

Ionic polymerisation is initiated by an ionic species, such as a Lewis acid (AlCl_3 , BF_3 , SnCl_4). A charge is transferred to the monomer, which then reacts with further monomers to produce a polymer. There is no natural termination step in this kind of polymerisation. To terminate ionic polymerisation a terminating agent is added, such as ammonia in the case of anionic polymerisation^[35].

2.3.2 Radical Polymerisation

Radical polymerisation is more widely used than ionic polymerisation and involves three stages: initiation, where the radical is produced, propagation, where the radical is transferred to a monomer and this causes a double bond to open and attach to another monomer, increasing the chain length of the polymer, and termination, where two radicals combine to stop the reaction (see figure 2.1).

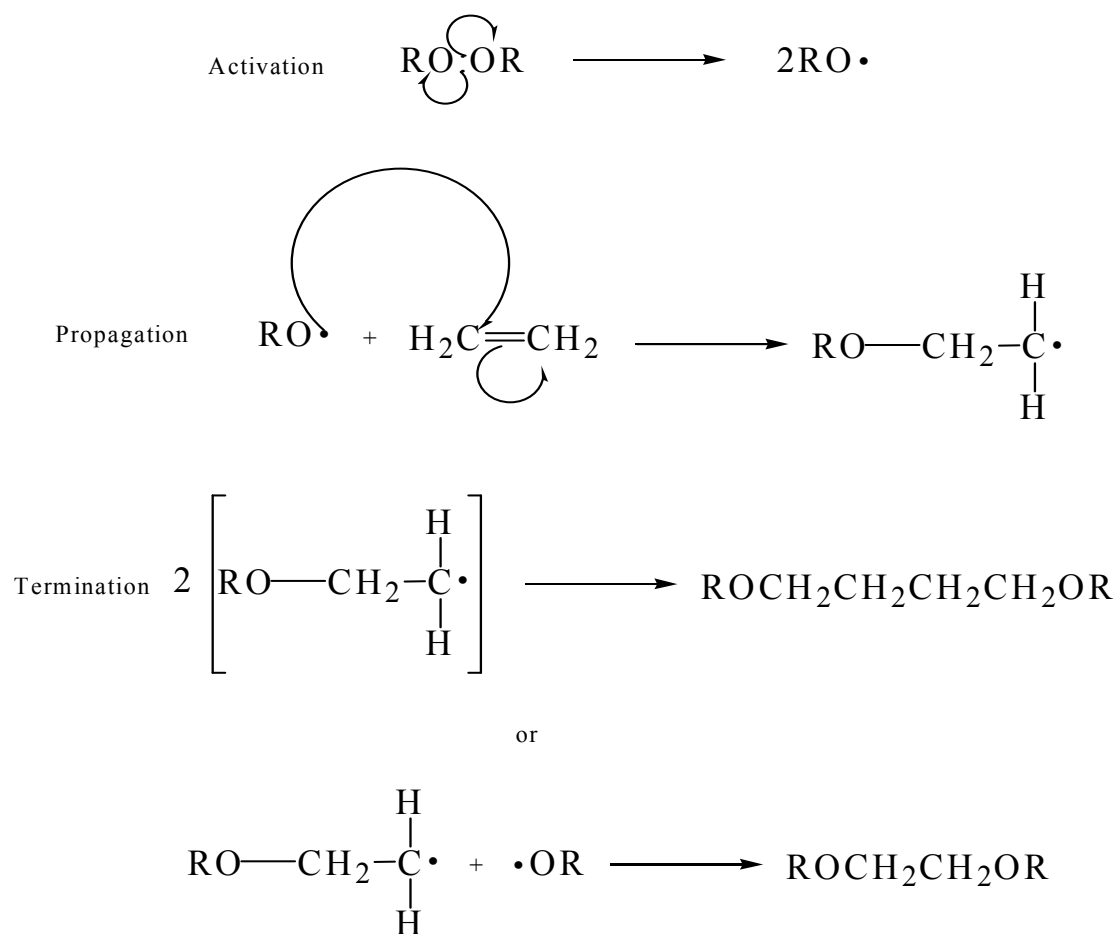


Figure 2.1: Radical polymerisation

There are a number of methods for producing radicals for radical polymerisation, and these are detailed below. Irrespective of how the radical polymerisation is initiated, the polymerisation proceeds in a similar way.

Free radicals react rapidly with oxygen to form peroxy radicals, and therefore materials being polymerised by free radical initiation are usually polymerised in a vacuum or under an inert atmosphere, such as nitrogen or carbon dioxide.

2.3.3 Gamma Radiation Polymerisation

On interaction with organic compounds, the photon energy is transferred to the bulk of the material, and is spent mainly on ionisation of the molecules^[36]. Gamma radiation (γ -radiation) is high-energy radiation, which causes ionisation in materials and possesses sufficient energy to break chemical bonds^[37].

There are three main chemical reactions that occur as a result of gamma irradiation, chain growth polymerisation, chain scission (bond breaking) and crosslinking.

A side effect of radical formation is gas evolution, which can cause voids to be formed in the polymer^[36], (acrylonitrile gives off 0.2-0.3 molecules of gas per 100 eV of radiation).

2.3.4 Thermal Polymerisation

The polymerisation of monomers using heat is frequently used in industry. The process usually requires a thermal initiator, such as azo-bis-isobutyronitrile (AIBN) (see figure 2.2), which absorbs heat to form a radical, (figure 2.3), which then initiates the polymerisation process.

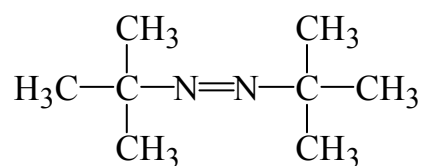


Figure 2.2: AIBN thermal initiator

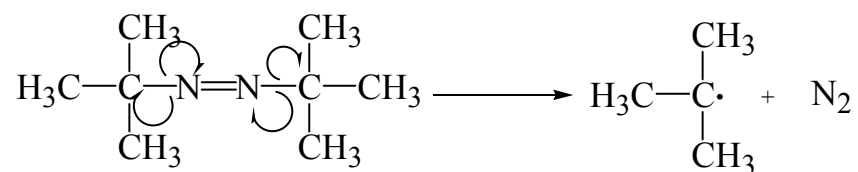


Figure 2.3: AIBN free radical initiation

As can be seen from figure 2.3 the production of radicals by AIBN, also produces gaseous nitrogen and this may cause bubbles to become trapped during curing of the polymer as discussed above.

Other initiators that produce radicals on heating include Azo-bis(cyclohexane carbonitrile) (VAZO®) (see figure 2.4) and the persulphates, such as ammonium persulphate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, and potassium persulphate, $\text{K}_2\text{S}_2\text{O}_8$ (see figure 2.5). It should be noted that the persulphates produce free radicals without producing a gaseous side product.

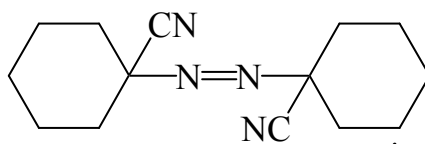


Figure 2.4: VAZO® initiator

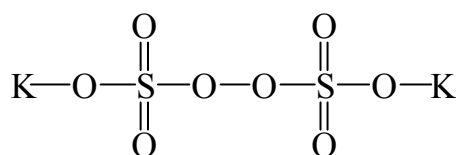


Figure 2.5: Potassium persulphate initiator

2.3.5 Ultraviolet Polymerisation

Ultraviolet radiation (UV) can also produce radicals particularly if a UV initiator, such as benzophenone, is present, which produces radicals on absorbing UV light and thus initiates the polymerisation. The major drawback to this approach is that, as the depth of polymer cure increases, the penetration of the UV radiation decreases, and the polymerisation may be anisotropic as a result.

2.3.6 Microwave Polymerisation

Microwave polymerisation has been shown to offer greater yields, shorter reaction times, a reduction of by-products and no thermal decomposition of products^[38]. There are reports that polymerisation by this method produces harder polymers, which would suggest more crosslinking within the matrices, or a higher degree of polymerisation^[39].

It has also been suggested that microwave curing is not simply another way of transferring heat; Porto *et al*^[38] suggest that “the mechanism of energy transfer using a microwave field is considerably different from the well-established modes (radiation, conduction, convection) of heat transfer.” Though they do not say how microwave radiation is different to other methods of heat transfer. Other workers report that solvents can be heated above their normal boiling temperature without boiling, when heated in a microwave^[40] and the chemistry able to take place within this ‘superheated’ region may give rise to unexpected results when compared to reactions in solvents at sub-boiling temperatures^[41]. It may be that the ‘superheated’ chemistry leads to higher yields, shorter reaction times, reduction of by-products and no thermal decomposition of product, in turn leading to harder polymers.

Although it is possible that microwave heating may not be considerably different to normal thermal methods, it is the speed at which these reactions take place that is of interest in this project. Production of membranes in shorter time scales would aid in reduction of costs and a curing method such as microwave would represent a distinct advantage over curing by γ -radiation, which clearly has safety and cost implications. This is discussed more fully in chapter 3.

2.4 Current SPE Membrane Technology

The worldwide market for membranes for electrochemical cells is large, with many different types of membrane available, depending on the type and use of the cell.

All new membranes in development must achieve the essential properties for SPE technology such as high conductivity, thermally stability, chemically stability, and thin and durable but at a lower cost than the current benchmark SPE's such as Nafion®, Selemion® and Aciplex® if they are to achieve market acceptance.

The majority of the existing membranes are of the cation exchange variety and with anionic exchange membranes fewer in number but as discussed earlier, able to find advantage in a number of fuel cell systems. The principal commercial membranes are briefly discussed below:

2.4.1 Nafion®

Developed by E. I. DuPont de Nemours in 1967, Nafion® is still widely used today to produce chlorine and caustic soda from the electrolysis of brine. It was only later that it was adapted as a SPE for fuel cell applications.

Nafion® is a non-reinforced perfluorosulphonic acid polymer. The membrane is a perfluoroalkyl chain (polytetrafluoroethylene) with a perfluorovinyl ether side chain, which contains a sulphonic acid group (see Figure 2.6). It combines the extreme hydrophobicity and chemical stability of the of perfluorinated polymer backbone with the extreme hydrophilicity of the terminal sulphonic acid. However it is difficult to

synthesize, being manufactured from fluorine containing compounds, and at present the membrane is costly (US\$ 800 m²)^{[42],[43]}.

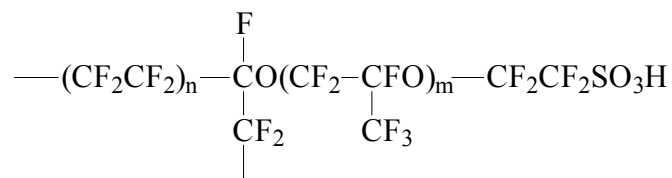


Figure 2.6: General formula for Nafion®

The ionic transport in Nafion® has been described as a ‘hopping process’^[44], such as the Grotthus mechanism, from one cluster of sulphonic acid groups to the next. The model assumes that nanometre scale channels connect the clusters.

Nafion® membranes have been shown to have outstanding stability and lasting up to 60,000 h at 80 °C in hydrogen fuel cells. However, in the DMFC, Nafion® has been shown to have a high methanol permeation rate.

2.4.2 Select® and Primea®

In 1994 W. L. Gore and Associates began to develop methods of incorporating proton-conducting ionomer into an expanded polytetrafluoroethylene (PTFE) membrane, and produced ionomer/ePTFE composites. Known as Select® membranes, Primea® Membrane Electrode Assemblies (MEA)^[45] are made from them.

The PTFE substrate makes the membrane mechanically stable, and it can be made as thin as 5 µm, which gives better (~10 times) proton conductivity compared to Nafion®.

2.4.3 Ballard BAM 3G®

In 1987 Ballard developed a membrane that gave power densities approximately four times higher than Nafion®^[14]. Ongoing development led to a third generation of these membranes which are based on sulphonated or phosphonated polyaromatics (α,β,β -trifluorostyrene). The sulphonated membranes show excellent performance in PEMFC with oxygen and air as oxidants, where as the phosphonated membranes show good performance only with oxygen. These membranes are complicated to produce and are believed to contain both sulphonate and phosphonate moieties^[14]. To date there are no reports of Ballard commercialising this membrane.

2.4.4 ITM Power plc CISTACK®

British fuel cell company ITM Power plc is developing a range of membranes using novel approaches. ITM uses a combination of liquid monomers and other soluble additives to create ionic exchange membranes, in what is described elsewhere as a blending technique. The liquid solutions can be cured by various polymerisation methods, such as thermal, radiation and UV. The resulting materials can be cationic or anionic exchange membranes, depending on the type of ionic exchange moiety added to the system before curing.

The blending technique is a promising approach due to its potential for combining the attractive features of each component while at the same time reducing deficient characteristics^[46].

The advantages of the ITM 'blended' system includes the ability to form membranes in any shape as the liquid solution can be polymerised in a shaped mould. ITM uses the

advantage to create a fuel cell stack in a ‘one-shot’ process (the CISTACK®). ITM also claims that their proprietary cationic exchange membrane is cheaper than Nafion®117. ITM Power plc materials are commercially unavailable at the time of writing.

2.4.5 Other Membranes

Many other membranes have been reported. These materials include:

- Sulphonated styrene on non-fluorinated films, such as poly(ethylene) and partially fluorinated films such as Ethylenetetrafluoroethylene (ETFE) and Polyvinylidene fluoride (PVDF)^{[47],[48]}. Grafting onto fully fluorinated films has also been attempted, using poly (tetrafluoroethene-co-hexafluoropropylene) or fluorinated ethylenepropylene (FEP)^{[42],[49]}.
- Aciplex membranes (Asahi Chemicals), which are perfluorinated or styrene/divinylbenzene copolymer membranes, similar to Nafion®. They can also produce anion exchange membranes of undisclosed composition.
- Flemion membranes (Asahi Glass), again a perfluorinated membrane with carboxylate^[50] or sulphonate fixed ionic groups, and Selemion membranes, poly(styrene) membranes in anion or cation exchange form for electrodialysis.
- Anion and cation exchange membranes, manufactured from poly(etherketones), poly(sulphones) or poly(phenylene oxide) (FuMA TECH GmbH).
- Cation and anion exchange materials by radiation grafting (Solvay), the anion exchange membrane being known as ADP-100.

However almost all the anionic exchange membranes, such as ADP-100, have not been designed or manufactured with fuel cells in mind, rather for electrodialysis applications and consequently they have been shown not to be optimised for use in alkaline fuel cells.

2.5 Membranes for the DMFC

Fuel cells developments have to date centred heavily on Nafion® as a membrane, and this has led to the hydrogen fuel cell being considered closest to market. However some appliances, such as mobile phones and laptops, may find the use of a liquid fuel more convenient, and methanol has been considered as the most viable option to date (see section 1.2.4). The thermodynamic reversible potential at 25 °C for the overall cell reaction in the direct methanol fuel cell (DMFC) is 1.214 V, which is comparable to 1.23 V for the hydrogen-fuelled cell^[51], and thus no voltage adjustment would be expected in choosing the DMFC over the hydrogen PEMFC.

The most advanced DMFC's to date use Nafion® membranes^[52]. However, Nafion® suffers a major drawback in the DMFC, viz. high methanol permeation through the membrane, which leads to a loss of power from the cell. This permeation is dubbed 'crossover'. One way to control the methanol crossover is to reduce the concentration of the methanol fuel^[53] by dilution with water, though this proportionally reduces the power output of the cell for a given mass of fuel.

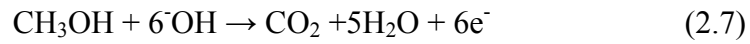
Adaptation of Nafion® for methanol fuel cells has centred on two methods^{[54],[55]}; the addition of an extra layer of material designed to block the methanol from crossing the membrane, and physical grafting of new materials onto the Nafion® film to produce a methanol barrier. However both methods suffer from the drawbacks of cost increase and conductivity decrease.

The majority of the research in DMFCs has concentrated on developing the cell in an acidic environment, mainly due to platinum based catalysts for acidic environments being

well established. These traditional catalysts have limitations in the DMFC such as poor kinetics and high cost. To overcome these disadvantages the oxidation of methanol in an alkaline environment has been proposed.

Methanol oxidation in alkaline media is improved when compared to acidic media^[56], and catalysts such as nickel and silver may be able to be used^[56]. However changing from acidic to alkaline environment in the cell necessitates changing the membranes from a cationic to anionic exchange type, because the majority charge carrier in the alkaline cell will be the hydroxyl ion (OH^-) rather than the proton (H^+) according to the reaction schemes below (see equation 2.7 to 2.9).

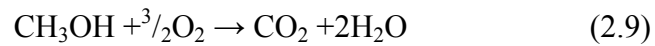
Anode reaction:



Cathode:



Overall:



It has been suggested that AEMs can lack durability in aqueous alkali solution^[57]. It is known that quaternary ammonium groups, which are used as anion exchange groups, may decompose in concentrated alkali solution, by the Hoffmann degradation reaction^[57]. The decomposition of these groups is slow in dilute alkali solution at ambient temperature, but increases with temperature and alkali concentration. Research to overcome these shortcomings is being undertaken by many groups.

Other studies have experimented with perfluorinated anionic membranes, analogous to Nafion®^[55]. They found that a perfluorinated amine is difficult to obtain because of the properties of fluorine compounds, and the elimination of hydrogen fluoride^[57] (see equation 2.10 below)



2.6 Summary

This chapter has described different types of membrane, and some useful ionic exchange groups for cationic exchange materials and anionic exchange materials.

Cationic exchange membranes such as Nafion®, though excellent for PEM cells and acidic environments, show excessive methanol crossover and poor fuel cell performance in alkaline environments. Their present cost also limits their widespread acceptability for fuel cells, though is not such a problem in electrolysis, where the high cost of membranes can be tolerated as part of the cell capital costs.

Of particular interest to this project are the blended materials from ITM. These materials have been produced for proton exchange membranes (PEM) and water electrolyzers, though blended anionic exchange membranes (AEM) have not been studied in depth.

Commercially available AEM's were not designed for fuel cells and therefore are not entirely suitable for the application. New anionic exchange membranes for alkaline methanol fuel cells are therefore needed, and such materials will need to have good stability in alkaline environments, a reduced level of permeation of methanol and cost

advantages over fluorinated polymers. There are advantages in producing membrane materials with anionic exchange functionality for use within fuel cells (specifically alcohol fuel cells) where the majority charge carrier is the hydroxyl ion. The benefits include improved methanol oxidation and the potential to utilise a cheaper catalysts such as nickel or silver.

It is the primary remit of this project to research novel monomers and chemicals for use in blended polymeric anionic exchange membranes for direct methanol fuel cells. It is also in the remit of this project to study the abilities of these anionic exchange materials in water electrolysis cells.

Chapter 3 focuses on microwave polymerisation as technique for producing solid polymer electrolytes for blended liquid monomer compositions. It discusses the mechanism of polymerisation under microwave conditions, previous work in the field and advantages and disadvantages.

Chapter 3 . Microwaves

3.1 Introduction

As seen briefly in the previous chapter there are many different ways to prepare membranes by polymerisation of monomers: Ionising radiation, ultra violet (UV), thermal and microwave radiation. Ionising radiation, such as gamma radiation and electron beam, suffer large start up costs and the legislation covering the use of these forms of radiation are complex. UV radiation, though industrially well proven, has poor penetration ability into the sample and cannot be used for curing thick layers. Thermal radiation, though widespread in use, experiences problems, which are discussed in more detail below.

There are reported advantages to microwave curing of polymer materials when compared to thermal curing. The main advantage is shorter curing times, which could aid in reducing production costs of membranes.

3.2 Microwave Spectrum

Microwaves are the name given to the region of the electromagnetic spectrum that corresponds to a wavelength of 1 cm to 1 m^[58], corresponding to a frequency of 30 GHz to 300 MHz respectively. The radio frequency ranges, containing microwaves, are divided into frequency bands (see Table 1) and the microwave spectrum runs from band 9 into band 11^[59].

Table 3.1: Frequency bands for radio frequency range^[59]

Band	Designation	Frequency Limits
4	VLF – Very Low Frequency	3-30 kHz
5	LF – Low Frequency	30-300 kHz
6	MF – Medium Frequency	300 kHz-3 MHz
7	HF - High Frequency	3-30 MHz
8	VHF – Very High Frequency	30-300 MHz
9	UHF – Ultra High Frequency	300 MHz – 3 GHz
10	SHF – Super High Frequency	3-30 GHz
11	EHF – Extremely High Frequency	30-300 GHz

Predominant applications for microwaves are radar, communications, electronic countermeasures, and microwave heating^[60]. Due to the potential for disruption to communications and radar bands, the entire microwave spectrum is not readily available for heating applications and by international convention the frequencies allocated for industrial and scientific microwave heating and drying^[61] are 915 MHz, 2.45 GHz, 5.8 GHz and 22.13 GHz.

The frequencies most used for heating are 2.45 GHz (12.2 cm) and 900 MHz (33.3 cm), of which the former is widely used in domestic microwave ovens^[61]. Microwaves at 2.45 GHz correspond with an electric field that oscillates 4.9×10^9 times per second. This oscillating field subjects dipolar species and ionic particles to a “perpetual reorientation cycle”^[62] and this strong agitation leads to a fast non-contacting heating. It is at this frequency that the vast majority of previous chemical synthesis using microwaves has been undertaken^[63].

3.3 Comparison of Thermal and Microwave Heating

With conventional thermal treatment, thermal energy is conducted to a matter through conduction, convection and radiation. Porto *et al*^[38] has suggested that “.... the mechanism of energy transfer using a microwave field is considerably different from the well-established modes (radiation, conduction, convection) of heat transfer.” Microwave heating primarily occurs through the coupling of the microwave radiation with molecular dipoles or ionic species^[64]. The energy is absorbed by the matter and transformed into molecular kinetic energy.

A molecular dipole is sensitive to external electric fields and will attempt to align itself with the field by rotation receiving the energy for this alignment from the applied field. However there is always likely to be a phase lag between the dipole and the field if the field is constantly changing. This phase difference causes energy to be lost from the dipole by molecular friction and collisions, giving rise to dielectric heating^[63]. Water is typical of a molecule that contains a dipole moment, and heat can be generated when microwave radiation is applied^[63].

If frequency of the microwaves is too high (> 1000 GHz, $\lambda < 0.3$ mm), the water molecules do not have time to react to the electromagnetic field changes and no heat is generated. If the frequencies is too low (< 1 GHz, $\lambda > 30$ cm), the molecules react to the electromagnetic field changes, but so slowly that effectively no heat is generated.

The dipole moment of water is larger than organic molecules, such as the monomers used in this study, due to the dipole difference of the oxygen:hydrogen bond compared to the carbon:hydrogen^[65]. However interaction of organic molecules and microwave energy is

achieved in microwave spectroscopy, where the absorption and emission electromagnetic radiation is observed at several discrete frequencies with any given molecule^[66]. The frequency range commonly employed for microwave spectroscopy is 4–11 GHz and this implies that the interaction of the microwave energy and specific bonds within organic molecules is likely to be achieved outside the frequency bands specified for dielectric heating (see page 44).

Therefore, in this project, with the microwave frequency fixed at 2.45 GHz, the heating of the samples is likely to occur primarily through interaction with the water molecules contained within the monomer mixtures.

Further heating occurs through ionic species present in the solution. The ions present will move through solution under the influence of an applied electric field, and this results in the expenditure of energy due to an increased collision rate, which converts the kinetic energy to heat. This heating mechanism is stronger than the dipole mechanism with regard to heat generating capacity^[63]. When combined these mechanisms can result in high heating for samples.

With thermal heating matter is heated from the outside towards the inside and a temperature gradient develops within the sample. Local overheating can cause product, substrate and reagent decomposition^[63]. With microwave heating the inner and outer parts of the matter are heated simultaneously. Therefore there is little temperature gradient and the consequent thermal stress is less. Energy input to the samples starts and stops immediately the power is turned on or off^[61], and thus a high heating rate is

obtainable. This suggests lower energy consumption for reactions when compared to thermal curing in ovens is likely^[67].

Thus the advantages of microwave heating include rapid volumetric heating, no overheating at the surface, energy-saving and lower operating costs, increased throughput, and reduced degradation^{[68],[39]}. The rapid volumetric heating may allow a reaction to overcome activation barriers more easily^[64].

Using very cheap and readily available microwave cavities, heating rates of 2-4 °C s⁻¹ may be readily achieved even for more common organic solvents^[61]. Such high heating rates are more difficult to achieve using conventional heating. Where heating at 2-4 °C s⁻¹ is achievable by conventional means it is much less controllable

3.3.1 Previous Microwave Polymerisation

Microwave initiated reactions can give better yields, shorter reaction times, reduction of by-products and no thermal decomposition of products when compared to conventional thermal initiated reactions. Many microwave assisted organic synthesis reactions have been studied, and for a review of specific synthesis the reader is directed to Lidstrom *et al*^[63] or Perreux *et al*^[40]. For a more rounded treatise of microwave assisted organic synthesis, including the basics of microwaves, Tierney *et al*^[61] provide a comprehensive review. What follows here is a brief discussion of published research in microwave-assisted polymerisations. All reactions in this section use a domestic microwave oven at 2.45 GHz, unless otherwise stated. A more in-depth review of different microwave assisted polymerisations is given by Wiesbrock *et al*^[62].

Gourdenne^[62] first investigated microwave-assisted free radical polymerisations in 1979. He demonstrated that the temperature of the reaction mixture for both microwave and thermal polymerisation gave similar profiles, although the microwave polymerisation was considerably faster.

Weisbrock *et al*^[62] achieved polymerisation of styrene using microwaves with comparable molecular weights and conversions to that found by thermal initiation. They also found that the microwave-irradiated polymerisation reached the final temperature faster than conventional heating. Porto *et al*^[38] reported that irradiation of styrene at 687 W produced 80 % conversion to polystyrene in 20 minutes, whereas heating styrene and a thermal initiator (azo-bis-isobutyronitrile, AIBN) under reflux for 10 minutes produced “no significant amount of polystyrene.” However Porto does not give any indication of the percentage conversion after 20 minutes in the thermally initiated sample, none-the-less an indication of faster polymerisation by microwaves is apparent. Chia *et al*^[69] found that at 80 °C, microwave polymerisation of styrene at 300 W showed a reaction rate enhancement of 120 %, and at 500 W this increases to 190 %, again compared with thermal initiation. Li *et al*^[70] reported the first single-mode microwave assisted nitroxide-mediated radical polymerisation of styrene in bulk, although only a small sample size, 2 mL styrene was reported. Ng *et al*^[71] polymerised methyl methacrylate using microwaves.

Zhou *et al*^[68] polymerised epoxy resins using microwaves and Boey *et al*^[72] also polymerised similar materials at powers as low as 200 W, with reaction times reduced from 48 hours to 110 minutes, when compared to a conventional oven^[73].

Of particular interest to this project is the work of Sinnwell *et al*^[74]. They showed the cationic ring opening polymerisation of 2-phenyl-2-oxazoline, using microwave heating. These reactions were undertaken in a single mode microwave, limited to a 10 mL cavity size. Weisbrock *et al*^[75] also undertook the cationic ring opening polymerisation of 2-substituted oxazolines in a single mode microwave.

It has been shown that some materials need the addition of a free radical initiator, such as AIBN or a persulphate, to initiate the reaction^[62]. The disadvantage of AIBN is the production of nitrogen gas, as a by-product as discussed earlier. The gas can be trapped within the fast developing polymer, leading to voids within the final product. But if the reaction rate is controlled it may be possible to use the nitrogen by-product to maintain an inert atmosphere. This is difficult to do in a domestic multi-mode microwave oven, but greater control is available in a single-mode microwave oven.

Unfortunately most microwave assisted organic syntheses reported have been performed in a domestic microwave oven, which causes the quality of the data in the literature to vary greatly. Many papers use ambiguous definitions in their methodology, such as ‘the use of 70 % of full power for 5 minutes’^[63]. Clearly this is not a quantitative measurement of the energy delivered to a reaction, and will be different for each microwave oven and therefore difficult to reproduce experimentally.

Although microwave polymerisations have been reported by both free radical and ionic mechanisms the majority studied have been free radical polymerisations, though both types have been achieved with enhanced reaction rates, and increased yields.

3.4 Microwave Enhanced Chemistry

Early work using microwave radiation produced polymers with different properties, when compared to thermally produced materials. Ng *et al*^[71] found that microwaves produced harder, denser polymers than comparable reactions using thermal initiation. These differences were termed “microwave effects” and Ng theorised that there was a specific activation effect due to microwave radiation, which acted in addition to the heating, causing the “microwave effects”.

Conversely Wiesbrock *et al*^[62] could not find any microwave effects in other reactions and refuted the claim that the harder, denser polymers were specifically caused by the microwave radiation. They assumed that while the reaction time was drastically reduced, the kinetics and mechanism of the reactions were not altered. Zhou *et al*^[76] noticed the disparity within the literature and undertook their own research. Their results suggested that localized superheating of the functional groups was the main mechanism of reaction rate enhancement. Wiesbrock *et al*^[62] suggest that the difference in curing is due to shorter reaction times, in which side reactions are reduced to a minimum, and consequently the purity and the polymer properties improve.

However, it is now accepted that the major part of rate enhancements observed with microwave synthesis is due to thermal effects, even though it is possible to achieve unique temperature profiles by microwave radiation^[77].

3.5 Multi-Mode or Single-Mode?

Domestic microwave ovens are clearly not designed for use in chemical experimentation, and thus have limitations. Hazardous explosions or fires are likely to accompany

chemical reactions when undertaken in a domestic microwave oven^[75]. This is particularly true for exothermic reactions and reactions with an increase in volume, such as the formation of gaseous by-products. The limitations are due to the way that domestic microwave ovens operate.

In a domestic microwave oven the walls reflect microwaves. The reflections cause a three dimensional stationary pattern of standing waves within the oven cavity, called modes^[63]. A domestic microwave oven cavity typically has three to six modes (hence a multi-mode cavity) and they create a field pattern with areas of high strength (hot-spots) and low strength (cold-spots). This leads to inhomogeneous heating so that the heating efficiency between different positions of the sample may differ greatly^[63]. To reduce this problem, in domestic microwaves a turntable moves the food through the hot and cold spots.

In addition the magnetrons used in domestic microwave ovens are optimised to give a high efficiency for a nominal 1 kg load, and are therefore less effective for smaller loads^[63].

To obtain a well-defined heating pattern for small loads, a microwave apparatus utilising a single-mode cavity is preferred. According to Lidstrom *et al*^[63] a properly designed cavity will prevent the formation of hot and cold spots within the sample, resulting in a uniform heating pattern, allowing the achievement of better reproducibility and predictability of results. Single-mode microwaves also give improved wave focusing and accurate control of the temperature throughout the reaction^[40].

Single-mode microwave reactors can allow for accurate control of temperature and pressure inside the reaction vial as discussed by Weisbrock *et al*^[78]. However, it is only very recently that polymer chemists have discovered single-mode microwave systems as new reaction devices, and Weisbrock reports little research appearing in the literature.

Single-mode microwave cavities heat the whole sample simultaneously whereas, with multi-mode, the sample must pass through modal hot spots, achieved in most microwave ovens by rotating the sample on a turntable. Therefore single-mode offers the prospect of greater control of heating of materials and allows polymerisation at lower powers than with multi-mode.

3.6 Single-Mode Cavity Design

Commercially available single-mode microwave cavities are small, which leads to small sample sizes^[78]. They are not always suitable for polymer chemistry as they have been designed and built with complex organic synthesis in mind. Operations such as bulk polymerisation are not possible on a large scale in such machines. This has led some researchers to design and build single-mode microwave cavities, specifically designed for their work.

Asmussen *et al*^[79] describes the design and production of a microwave cavity with a tuneable single-mode. The cavity is cylindrical to accept a cylinder shaped load. The sample rests on the bottom plate of the cavity or is suspended in the middle of the cavity by a cotton thread. The cavity has an internal diameter of 17.8 cm and the length of the cavity can be varied between 6-16 cm. Unfortunately at 2.45 GHz the cavity length is

limited to 6 cm. Lengthening the cavity reduced the frequency and to process larger samples the frequency is reduced to 915 MHz.

One interesting aspect of the cavity was its ability to be tuned when loaded. The frequency was applied to the loaded cavity, and the length of the cavity was varied until there were no reflected microwaves. It was found that using this cavity gave repeatable results.

With regard to this project it was decided that further experimentation with a larger single-mode microwave cavity would provide more data on suitability of single mode microwave polymerisation or the production of materials for fuel cell electrolytes.

A design study to build a large device was therefore undertaken by Dr Ivor Morrow. Preliminary mathematical model results showed a large single mode cavity was plausible (~16 cm in length). With Dr Morrow's predictions in mind a cavity was designed and built (See Appendix B for designs and photographs of cavity). This was placed inside a conventional multi-mode microwave cavity for safety. Unfortunately, although the new cavity resonated at the correct frequency (2.45 GHz) the ability of the magnetron to maintain the correct frequency was poor, leading to inhomogeneous heating during irradiation inside the cavity. The poor heating was due in part to a wide spectrum of microwaves that were emitted by the magnetron, and the commensurate inability to accurately tune the cavity to a single frequency.

To correct this it would have been necessary to insert a probe into the single-mode cavity with feedback electronics to control the magnetron frequency. The necessary re-design of

the cavity and the design and build of the control circuitry was constituted to be outside the scope of the project and the use of the single-mode microwave was discontinued after initial experimentation.

3.7 Summary

Traditional radiation sources like gamma rays, UV light, and electron beam accelerators have their limitations. Gamma radiation is very penetrative but has inherent safety problems. Electron beam accelerators suffer large start-up costs industrially^[72]. Both these types of ionising radiation are covered by complex legislation, adding further problems to using these sources for commercial polymerisation of monomers. UV light has poor penetration ability, which can cause “skinning” of solid polymer to be formed on top of a monomer. Microwave processing requires a small footprint and has improved controllability when compared to thermal curing, which makes it a more convenient process^[80].

Other workers have shown that single-mode microwave can produce polymers faster with good repeatability and high yields, reducing waste in membrane production. Single mode microwaves are not designed for bulk-polymerisation and specialist cavities have had to be designed and built. For further information on design and building of a single mode microwave cavity see section 5.

The application of microwave processing though not new has recently been seriously studied and found to be a viable alternative for the curing of polymers, with a significant increase in the rate of reaction, obtaining a so called ‘rate enhancement’^[72].

Chapter 4 discusses materials of interest for the copolymerisation into solid polymer electrolytes for fuel cells. These materials will be copolymerised under gamma radiation, thermal and microwave conditions.

Chapter 4 . Materials

4.1 Introduction

The following chapter reviews the compounds of interest in this project and which may provide a liquid ionomer system that can be polymerised by free radical polymerisation, to give a copolymer with high anionic conductivity, high physical stability and suitable water content. This chapter also outlines how they might be used as part of a multi-component polymeric system. The materials are generally liquid at room temperature, or are soluble in the other monomer constituents of the system.

These compounds are divided into 4 main areas:

- Hydrophilic monomers
- Hydrophobic monomers
- Ionic moieties
- Crosslinking agents

4.2 Hydrophilic Monomers

When polymerised hydrophilic monomers produce a hydrophilic homopolymer which are soluble in water. The copolymerisation of hydrophobic monomers and crosslinking agents creates an insoluble copolymer useful in controlling water uptake and water content of the copolymer material. Control of water uptake and water content is of major importance in membrane materials for polyelectrolytes for fuel cells (See chapter 1).

4.2.1 Oxazolines

Oxazolines can be hydrophilic or hydrophobic depending on the acyl groups (see figure 4.1). The 2-methyl and 2-ethyl derivatives are hydrophilic, whereas the 2-phenyl derivative is hydrophobic. The versatility of the 2-substituted-2-oxazolines allows the synthesis of a large range of macromolecular compounds, homopolymers, copolymers and functionalised polymers^[81]. The use of the hydrophilic monomers should give control over the water content within the copolymer, and thus its conductivity and methanol permeation.

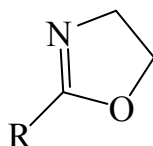


Figure 4.1: General formula of oxazoline, where R is a methyl, ethyl or phenyl group

Methyl-, ethyl- and phenyl-oxazolines are commercially available, liquids at room temperature, and therefore additionally offer the opportunity to cast a solution into a mould before polymerisation.

The heterocyclic ring in an oxazoline opens in the presence of cationic initiators,^[82] such as Lewis acids, strong acids and their esters and alkyl halides (see figure 4.2). The literature review, to date, shows no published work on the polymerisation of oxazolines using free radical initiation, such as that provided by γ -radiation. As these compounds contain a double bond, which is often a prerequisite for polymerisation with gamma radiation, it was considered possible that they may polymerise using gamma radiation to form a precursor material.

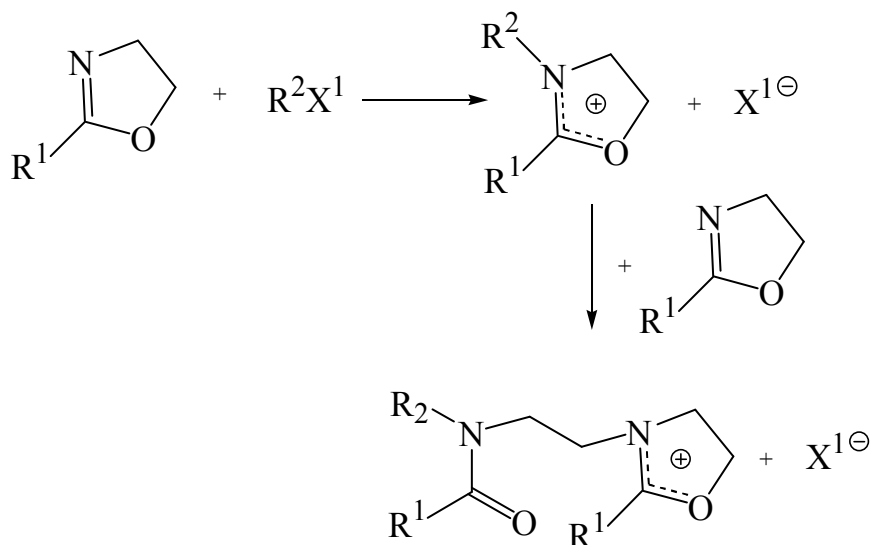


Figure 4.2: Reaction schematic for ionic polymerisation of oxazolines.

The heterocyclic ring, which contains nitrogen, may then be quaternised to lead to an anionic exchange material (see section 2.2.1).

4.2.2 4-Vinyl Pyridine

4-Vinyl Pyridine (VPy) (Figure 4.3) contains a weakly basic nitrogen atom within the pyridine unit. This permits reactions such as protonation, quaternisation or coordination of metal cations. PolyVPy can bind water to its tertiary nitrogen, which can then be quaternised. Historically, protonated or quaternised polyVPy has been found to act as a useful anion-exchange film for such anions as hexacyanoferrates, hexachloroiridates or chromates in acid media^[83].

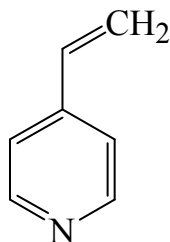


Figure 4.3: 4-vinyl pyridine monomer

The quaternisation of polyVPy produces a polymer with some unreacted pyridine residues. Xin *et al*^[84] suggest producing 1-4-vinylpyridinium salts, prior to polymerisation, so to assure fully quaternised homo- or copolymers. Fully quaternised polymers should produce a higher ion exchange capacity and improve the materials conductivity and cell performance.

Moulick *et al*^[85] have polymerised VPy thermally, and prepared polyVPy salt by acidification using hydrochloric acid (HCl). It was observed that addition of the chlorine ion increases the ionic conductivity of the polymer dramatically and the polymer polyVPy-HCl behaves as a good intrinsic ionically conducting polymer.

However pure polyVPy membranes are soft and have poor mechanical strength^[86], but when copolymerised with mechanically stable monomers, may well lead to copolymers with acceptable strength.

4.2.3 Aniline

Polyaniline (AI) (see figure 4.4) is of great interest due to its low cost, high conductivity, and environmental stability and redox properties. The salt of polyAI, is a proton conductor, while the base form of AI (natural state, as shown in figure 4.5) is not proton conductive. However Wang *et al*^[87] found that the base form of polyAI is a natural anion exchanger if OH^- is the counter ion.

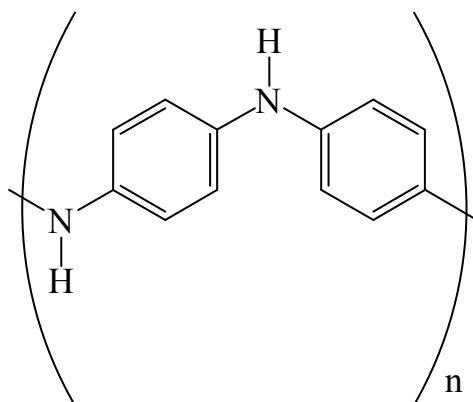


Figure 4.4: Neutral polyaniline

Further, Wang^[88] found that electrochemical impedance spectroscopy showed that polyAI coatings act as anionic membranes in rust pacification.

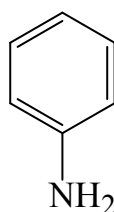


Figure 4.5: Aniline monomer in base state

4.2.4 N-Vinyl-2-Pyrrolidone

N-Vinyl-2-Pyrrolidone (NVP) (see figure 4.6) is an amphiphilic monomer^[89], which can be polymerised by γ -radiation. It contains a highly polar amide group, and hydrophobic methylene group. The homopolymer retains the monomer's amphiphilic nature, and is of low toxicity^[90]. PolyNVP is soluble in methanol^[91], and therefore is of no use as a homopolymer for direct methanol fuel cells. None-the-less, by varying the amount of this monomer within a copolymer, the water content at equilibrium can be better controlled. This maybe useful as water is a requirement for ionic conduction^[14].

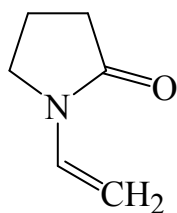


Figure 4.6: N-Vinyl-2-pyrrolidone

4.3 Hydrophobic Monomers

Hydrophobic monomers may be used to impart physical strength on copolymers containing hydrophilic materials. The addition of hydrophobic monomers to a copolymer will reduce overall water uptake and water content and in effect provide a scaffold which provides some strength to the overall copolymer.

4.3.1 Acrylonitrile

Acrylonitrile (AN) (see figure 4.7) has a high cohesive energy and imparts mechanical strength on its homopolymer and copolymers^[91]. It has been used to maintain the integrity of many hydrophilic monomer membranes^[91], such as N-vinyl pyrrolidone, hydroxyl ethyl methacrylate, and methacrylic acid.

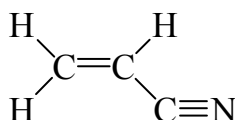


Figure 4.7: Acrylonitrile

4.4 Ionic Exchange Materials

This project is interested in anionic exchange polymeric materials, which can be used to conduct anions (negatively charge ions). They will consist of a material with a fixed positive charge, which can attract negative counter ions to be conducted, though the

interaction between the ions must not be too strong, or the counter ion will not conduct from one fixed ion to another.

4.4.1 (*ar*-Vinylbenzyl)trimethyl Ammonium Chloride

Quaternised ammonium monomers have previously been used as anionic exchange moieties^[92]. Liu *et al*^[93] copolymerised (*ar*-vinylbenzyl)trimethyl ammonium chloride (BV) (see figure 4.8) with styrene, using potassium persulphate as an initiator, to produce an anionic exchange moiety. Yeon *et al*^[94] also prepared anionic exchange materials using (*ar*-vinylbenzyl)trimethyl ammonium chloride with copolymers by γ -radiation grafting.

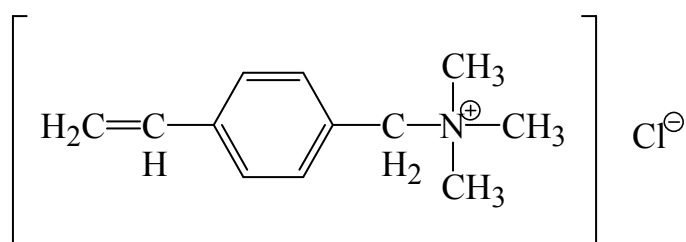


Figure 4.8: (*ar*-Vinylbenzyl)trimethyl ammonium chloride

4.4.2 2-(Dimethylamino)ethyl Acrylate

2-(Dimethylamino)ethyl methacrylate has been used as an anionic exchange moiety^[95], and has also been quaternised with reagents such as dimethyl sulphate to yield anionic exchange materials^[96].

However a literature review yields no information on the next molecule in the homologous series, 2-(dimethylamino)ethyl acrylate (BE), as an anionic exchange moiety. The difference between the methacrylate and the acrylate is the absence of a methyl group on the double bond (see figure 4.9). It might be expected that this molecule should act as an anionic exchange moiety similar to the methacrylate. It has been shown

that the acrylate can be polymerised using potassium persulphate as an initiator^[97], although no characterisation of the material's ionic exchange capacity was undertaken.

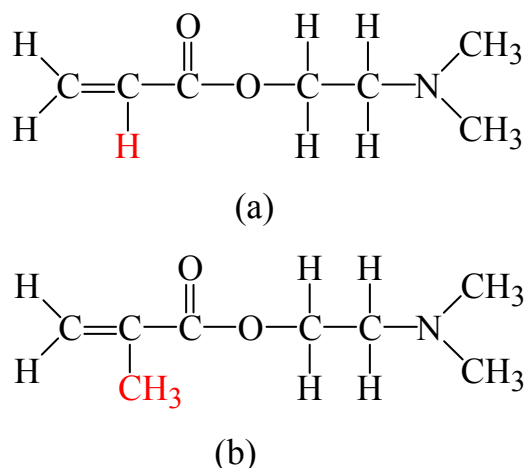


Figure 4.9: (a) 2-(dimethylamino)ethyl acrylate, (b) 2-(dimethylamino)ethyl methacrylate. The different groups are shown in red

4.5 Crosslinking Agents

Crosslinkers are molecules with two or more active sites that can undergo polymerisation. They can be used to provide insoluble crosslinked polymers which have three dimensional network structures^[98]. By increasing the amount of “crosslinks” within a system it is possible to reduce the thickness increase on the hydration of the polymer.

The methanol permeation and conductivity can also be varied by adjusting the crosslinking density of the membranes prepared^[99].

4.5.1 Allyl Methacrylate

Allyl Methacrylate (AMX) (see figure 4.10) is a regularly used as a crosslinking agent^[100]. It is a bifunctional monomer, with two double bonds with different reactivity^[101]. It increases the hydrophobicity of systems in addition to the amount of

crosslinking within a system^[102] and has been polymerised using γ -radiation, producing little or no cyclisation with copolymers^[100].

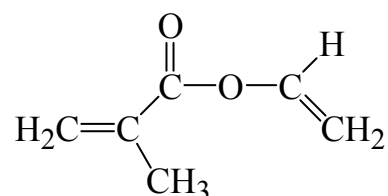


Figure 4.10 Allyl methacrylate

4.5.2 2,4,6-Triallyloxy-1,3,5-triazine (TT)

2,4,6-Triallyl-1,3,5-triazine contains 3 double bonds which could be used for crosslinking polymers (see figure 4.11). The increased number of double bonds may lead to an increase in the number of crosslinks formed during polymerisation, therefore leading to tighter three dimensional networks and a harder polymer, with reduced thickness increase.

It is also conceivable that the nitrogen atoms in the ring structure may be quaternisable, although there may be large amounts of steric hindrance from the side chains. A quaternised material, were it is possible, should increase the ionic conductivity of the copolymer.

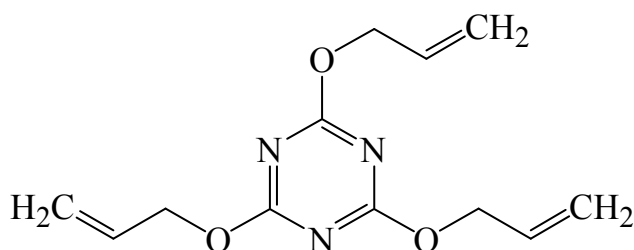


Figure 4.11: 2,4,6-Triallyloxy-1,3,5-triazine

4.5.3 1,3,5-Triallyl-1,3,5-triazine-2,4,6-(1H, 3H, 5H)-trione (TTT)

1,3,5-Triallyl-1,3,5-triazine-2,4,6-(1H, 3H, 5H)-trione also contains 3 double bonds which could be used for crosslinking polymers (See figure 4.12), and may also lead to an increased number of crosslinks formed during polymerisation, leading to a tighter three dimensional network, harder polymer and high dimensional stability.

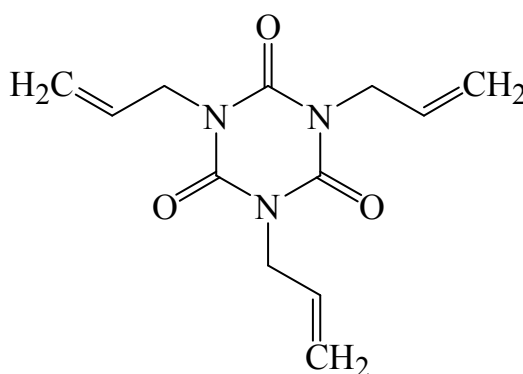


Figure 4.12: 1,3,5-Triallyl-1,3,5-triazine-2,4,6-(1H, 3H, 5H)-trione

4.6 Thermal Curing Agents

The use and reactivity of thermal curing agents is discussed in the section 2.3.4 on thermal polymerisation.

4.7 Blended Copolymers

Qiao *et al*^[99] found that a binary blended system using two monomeric materials exhibited poor mechanical properties when hydrated. The hypothesis for this project is that any system will need at least 3 compounds to produce a viable ionically conducting polymeric material. These will include a hydrophilic monomer, to help control the water content of the polymer, a hydrophobic monomer, to provide strength in the polymer and stop the polymer dissolving completely when hydrated and an anionic exchange moiety to provide the ionic exchange character desired.

4.8 Summary

This chapter has looked at a range of monomers and reagents with different hydrophobic, hydrophilic, ionic functional properties. The aim of this project is to examine ways to polymerise these compounds in combinations to produce copolymers. The copolymers will contain components which provide the essential properties of physical strength, control of water content and anionic conductivity.

Chapter 5 . Experimental

Three methods of polymerisation were employed in this project for the preparation of new materials, γ -radiation, thermal, and microwave (both multi-mode and single mode). The experimental procedures for each are described below.

5.1 Polymerisation Techniques

The γ -radiation source at Cranfield University, Shrivenham consists of twenty rods of Cobalt-60 (^{60}Co) encapsulated in steel tubes, placed in an open cylindrical arrangement. A picture of the gamma radiation source is shown in figure 5.1. The source is retractable, and is housed in a lead and steel flask, in a shielded position. Typical source activity is $60 \pm 5\%$ TBq, giving a maximum dose rate of $5.3 \text{ kGy} \pm 5\%$ per hour (9/9/05).



Figure 5.1: Cobalt-60 gamma radiation facility

Thermal Polymerisation was undertaken in a Gallenkamp OVL-570-010J oven. The microwave oven used for multi-mode testing was a Proline Power Wave 100, with a 700

W output as shown in Figure 5.2. Single-mode microwave testing was undertaken using a self built microwave cavity and more details on this are given in Appendix B.



Figure 5.2: Domestic multi-mode microwave

Gamma radiation can be used to polymerise many monomeric systems materials and can also be used to crosslink a number of polymeric systems. However start up costs for commercial gamma facilities are large due to the legislative and shielding requirements necessary. Thermal polymerisation using ovens is, by comparison, cheap to commercialise, but the polymerisation process can take time, which adds expense to production. Microwave polymerisation can be faster than both gamma radiation and thermal polymerisation, but exacting specifications for the cavity and magnetron are needed to provide uniform and reproducible power outputs, and thus materials. This remains an engineering challenge at this time.

Polyethylene tubes were supplied by I H Polymeric Ltd., with a dimension of 22 mm outer diameter, 14 mm internal diameter, and 150 mm in length, heat-sealed at one end. Rubber Septa seals were purchased from Aldrich®, catalogue number Z100765, and the balance was a Gibertini EU1000, supplied by Cherwell Laboratories, Bicester.

Sample polymers were made in two forms, rods and membranes. Materials were initially polymerised in rod form for initial characterisation, such as water content on hydration, thickness increase on hydration, conductivity and methanol permeation. Materials with good characteristics were then produced in membrane form for further testing under fuel cell conditions.

5.1.1 Mixing of Samples

Monomers were weighed into polyethylene bottles and stirred by magnetic stirrer to produce a homogeneous solution. The solution was then sealed and stored at 4 °C to reduced the possibility of spontaneous thermal polymerisation and reduce the evaporation of the monomeric solution until required.

5.1.2 Polymerisation of Rods by Radiation

The sample was transferred from the sealed bottles to the polyethylene tubes by pipette, sealed with Septa seals, and the solution purged with nitrogen for at least 5 minutes, to remove oxygen (see figure 5.3). The tubes were then placed upright in the radiation source, at varying dose rates and total doses (as shown in figure 5.4)

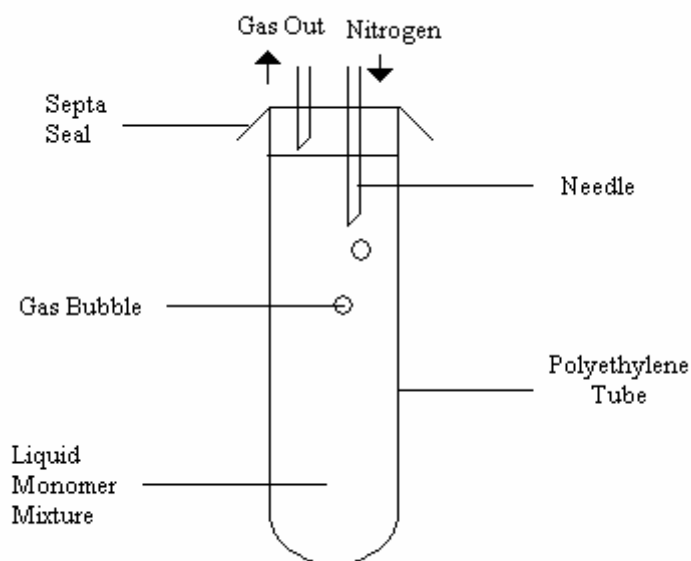


Figure 5.3: Equipment for purging solution with nitrogen to remove oxygen



Figure 5.4: Polymerisation of rods in gamma radiation source

After irradiation the polymerised rods, typically 10-15 mm in diameter and 100-150 mm in length, were removed from the polyethylene tubes and were placed in labelled seal-bags prior to sample cutting and characterisation.

5.1.3 Radiation Membrane Polymerisation

Membranes were produced with and without a separator, which was included to improve the membranes mechanical strength. Two types of separator were used, a non-woven hydrophobic nylon cloth (~0.10 mm nominal thickness) and a nylon felt cloth (~50 mm nominal thickness).

Membranes were prepared by soaking the separator material in 25 mL of the sample solution, and placing into a mould. The moulds were then placed upright in the radiation source, at varying dose rates and total doses. After irradiation the polymerised membranes, typically 50 mm² in area, were removed from the moulds and placed in labelled seal-again bags prior to characterisation.

5.1.4 Thermal Rod Polymerisation

Transfer of sample solution to the polyethylene tubes was again undertaken by pipette. The tubes were then sealed and the solution purged with nitrogen for 5 minutes before being placed upright in the oven for the defined period of time, at a defined temperature. The samples were left to cool to room temperature before being removed from the tube and stored as before.

5.1.5 Thermal Membrane Polymerisation

Thermal initiator was added to the cold solution with stirring, a short period (20-30 min) before placing the sample in the oven. To form the membrane 25 mL of solution was soaked into a separator and placed in a polyethylene bag. Air was removed from the bag which was then sealed using a heat sealer (as shown in figure 5.5).



Figure 5.5: Solution soaked separator prior to thermal polymerisation

The polyethylene bag was then placed between two brass plates, (designed and supplied by ITM Power) and squeezed to produce a flat membrane. Since the plate design was large enough to produce sufficient membrane at the required thickness, for both analysis and fuel cell testing, the ITM design was used without further modification. The plates were held together with 4 bolts as shown in figure 5.6. The sample and brass plates were then placed upright in an oven at the preset curing temperature for a set duration.



Figure 5.6: Brass plates used for thermal polymerisation of membranes

5.1.6 Crosslinking by Gamma Radiation

A number of samples were also subjected to crosslinking by gamma radiation in order to curtail their swelling in water and thus minimise the increase in thickness on hydration. Cured samples were placed in a gamma radiation source for a prescribed time to achieve the required total dose.

5.1.7 Multi-Mode Microwave Rod/Petri Dish Polymerisation

Monomers with and without thermal initiators were weighed and mixed in the polyethylene tubes or glass petri dishes. The tubes or dishes were then placed in the centre of the rotating plate in the multi-mode microwave oven. The samples were irradiated for times up to 10 minutes, at different microwave powers, (e.g. levels 6, 8, 10). In multimode microwave operation the different power levels are achieved by pulsing the magnetron for different on/off times. Between each period of radiation, a period of 5 minutes was allowed for the solution to cool and thus reduce the amount of

solution lost to evaporation. The final cured samples were left to cool to room temperature and sealed in airtight bags for future characterisation.

5.1.8 Single-Mode Microwave Polymerisation

Single-mode microwave studies were first attempted with a CEM Discovery Model single-mode microwave cavity courtesy of the University of Hull, cavity size was 5 mL. Monomers with thermal initiator were mixed in polyethylene bottles.

5 mL of monomeric mixture was placed inside a reaction vial and sealed. The vial was placed in the cavity and a temperature sensor placed over the vial cap. The CEM cavity was run at various powers and times. The programme set-up used for the oven control is given in Appendix A.

5.2 Production of Single-Mode Microwave Cavity

To avoid the continual use of the Hull CEM single-mode oven a single-mode microwave cavity with a length of 16 cm and a cavity radius of 6.75 cm was designed specifically for this project (See Appendix B). The single mode cavity behaviour was predicted by Dr Ivor Morrow (Cranfield University, Shrivenham) using a variation of Matlab. The cavity was produced by Cranfield University workshops, from an aluminium billet and was fitted with a 750 W magnetron. The cavity and magnetron were installed inside the case of a domestic multi-mode microwave oven whose electronic controls were used to ensure the safe operation of the single-mode microwave. This avoided the necessity to undertake exhaustive safety checks normally associated with custom built microwave devices.

The microwave power distribution within the cavity was measured before use with help from Dr Morrow and correlation between the predicted and actual behaviour was noted.

5.3 Cutting and Polishing of Discs

Following polymerisation and removal from the polyethylene tubes, the sample rods were cut into discs for characterisation. All discs were cut with a Proxon MBS 240E band saw from Rejon Tools, and then progressively polished in a specially made jig (see appendix E) with Norton T489 glass paper; grades P240, P600 and P1000 in a figure of eight motion, until all saw marks were removed. The finished disc was typically 10-15 mm in diameter and 0.5-20 mm thick as measured using a Mitutoyo series 293 digimatic outside micrometer

5.4 Characterisation Techniques

The techniques used to characterise the materials were thickness increase on hydration and percentage water content, ionic conductivity and methanol permeation.

5.4.1 Thickness Increase and Water Content

The discs were weighed, and the diameter and thickness recorded. They were then hydrated in deionised water for at least 18 h at 25 °C. Excess water was quickly removed by paper towel and the discs re-measured.

Water content (%) was calculated as

$$[(W_h - W_i)/W_h] \times 100 \quad (5.1)$$

Where W_h is the mass after hydration and W_i is the initial mass. Thickness increase (%) was calculated as

$$[(T_h - T_i)/T_i] \times 100 \quad (5.2)$$

Where T_h is the thickness after hydration and T_i is the initial thickness.

5.4.2 Conductivity Measurements

Conductivity measurements were undertaken with three different instruments, a Hewlett Packard 4274A, Solatron 1252A and a Agilent 4284A. For these instruments the discs were prepared using the same method. The discs were hydrated for 16 hours in deionised water at 25 °C and excess water was removed by paper towel. The same cell was used for both instruments (See figure 5.7 and 5.8) and the values quoted are a mean of 5 separate measurements. The cell temperature was kept constant at 25 °C by a water jacket. The sample was placed between the electrodes and tightened to a force of 24 kN m⁻². A container with 10 mL of deionised water was placed at the bottom of the cell and a lid placed on top to control the cell humidity.

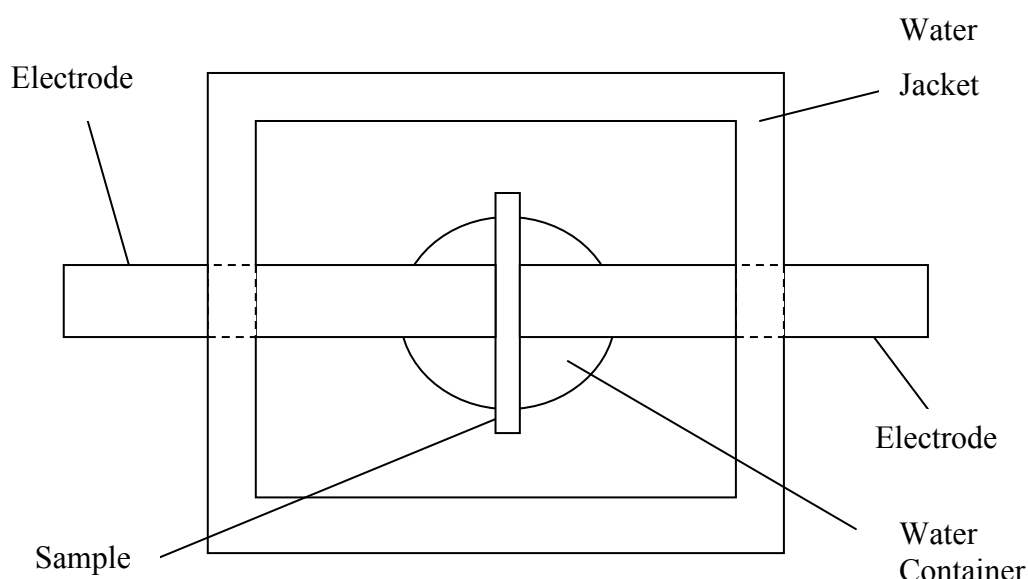


Figure 5.7 Conductivity measurement cell diagram, top view.

Figure 5.8: Conductivity measurement cell

5.4.2.1 Hewlett Packard 4274A LCR Meter

The cell was connected to the LCR meter with crocodile clips attached to the cell electrodes. The frequency was set manually at 1 kHz and impedance (Z) and phase angle (θ) readings recorded. This was repeated at frequencies of 2, 4, 10, 20, 40 and 100 kHz.

A Nyquist plot ($Z\sin\theta$ vs $Z\cos\theta$) was constructed (as depicted in Figure 5.9) in an Excel spreadsheet and the conductivity was determined from the following equation;

$$C = \frac{T}{\Omega a} \quad (5.3)$$

Where C is conductivity (S cm^{-1}), Ω is the resistance of the sample (secondary intercept on abscissa from Nyquist plot), T is membrane thickness (cm), and a is electrode area (cm^2).

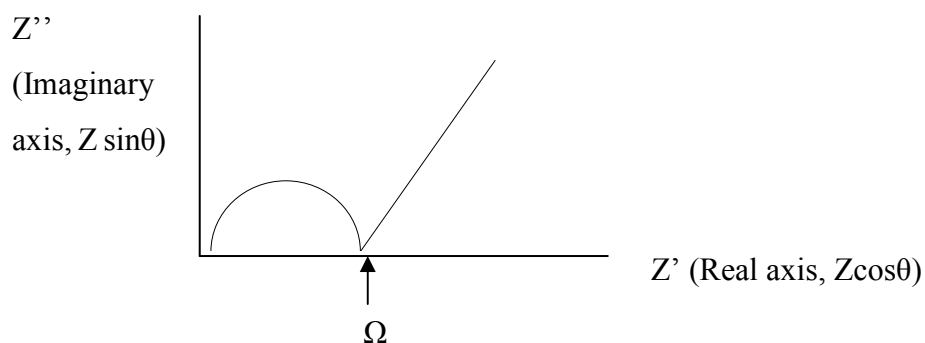


Figure 5.9: Typical Nyquist Plot

During the project the HP 4274A LCR meter was replaced by an Agilent 4284A instrument. A number of samples were remeasured using the new instrument and excellent correlation was found between the two meters. A standard resistance was also tested on both instruments and the actual discrepancy measured was 0.01% over the range 1 kHz to 100 kHz.

5.4.2.2 Solartron 1252A Frequency Response Analyser

The Solartron was connected to the cell by means of crocodile clips attached to the cell electrodes. The readings were automatically taken and the data converted to conductivity using the Z-plotTM function supplied by the manufacturer.

The conductivity results from the Solartron instrument were found to vary slightly from those measured using the HP and the Agilent instruments. The data reported later in this thesis are values from the HP and Agilent instruments. That from the Solartron is not recorded here because of the increased systematic error it would have introduced.

5.4.3 Methanol Permeation Measurements

The methanol permeation of the samples was determined by determining the rate of methanol migration as measured by change in refractive index. Samples were hydrated in deionised water for 16 hours at 25 °C and excess water was removed by paper towel. The membrane was then placed in a split cell, one half containing deionised water and the other half 100 % methanol (See figure 5.10 and 5.11). The cell temperature was maintained at 25 °C by use of a water jacket. Both cell chambers were stirred continuously to prevent concentration gradient effects. Aliquots were withdrawn from the water-side of the cell using a glass rod at 10 minute intervals for the first 1.5 hours of the test and thereafter in half hourly intervals until 3 hours total had lapsed.

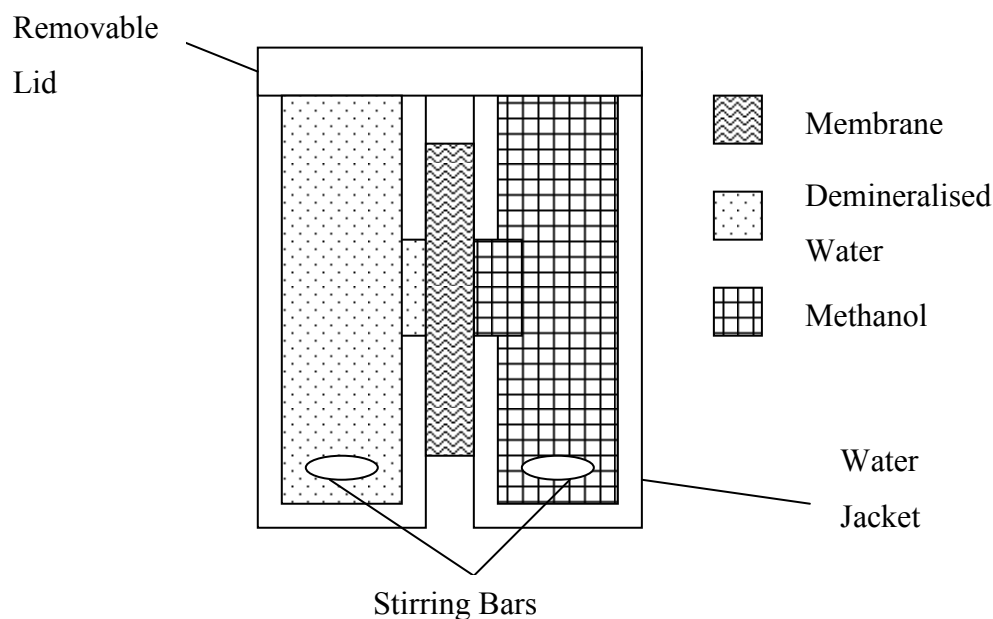


Figure 5.10: Methanol permeation cell

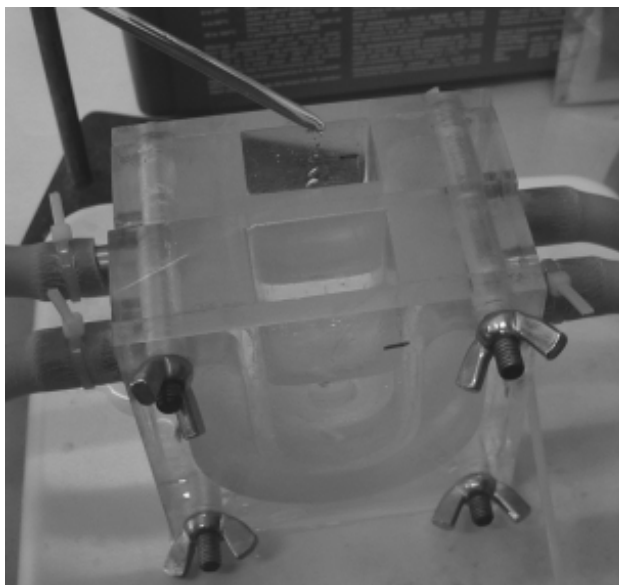


Figure 5.11: Methanol permeation cell, showing rod for extracting sample

The refractive index (RI_m) of the aliquots was measured using a Bellingham and Stanley refractometer (Model No.60) and the change in refractive index ($RI_w - RI_m$) with time was calculated, where RI_w is the refractive index of water. The difference in refractive index was then related to concentration using previously obtained calibration data according to the method given in Appendix C). The gradient of the change in concentration with time is the diffusion coefficient DK ($\text{cm}^2 \text{s}^{-1}$).

5.5 Fuel Cell Testing

Two types of catalyst cloth were obtained from Lyntech. One was ELAT woven carbon cloth impregnated with 5 mg cm^{-2} platinum black (Pt), the other was ELAT woven cloth with 5 mg cm^{-2} platinum/ruthenium (Pt/Ru) impregnated. These were utilised as received. Both catalyst loaded cloths were treated with Nafion® solution in order to facilitate bonding with the other electrode components.

The membranes were hydrated in deionised water at 25 °C for at least 16 hours prior to being used. The samples were removed from the water, and excess removed with a paper towel. Membrane Electrode Assemblies (MEA) were then prepared for each sample, by placing catalyst cloth on either side of the membrane, Pt/Ru on the anode side, and Pt on the cathode side. The active area of the catalyst cloth was cut to be the same size as the electrode.

The MEA was placed in a fuel cell, and the cell was tightened by hand (as illustrated in figures 5.12 and 5.13). It was found that tightening with a torque wrench to give a constant clamping force tended to cause damage to the MEA. Further experiments showed that tightening by hand produced less damage and gave more reliable cell results. The fuel was fed to the anode side of the cell at 3.5 mL min⁻¹, and the cathode supplied with non-hydrated oxygen at 50 mL min⁻¹. These conditions were found to give the most stable Open Circuit Voltage (OCV).

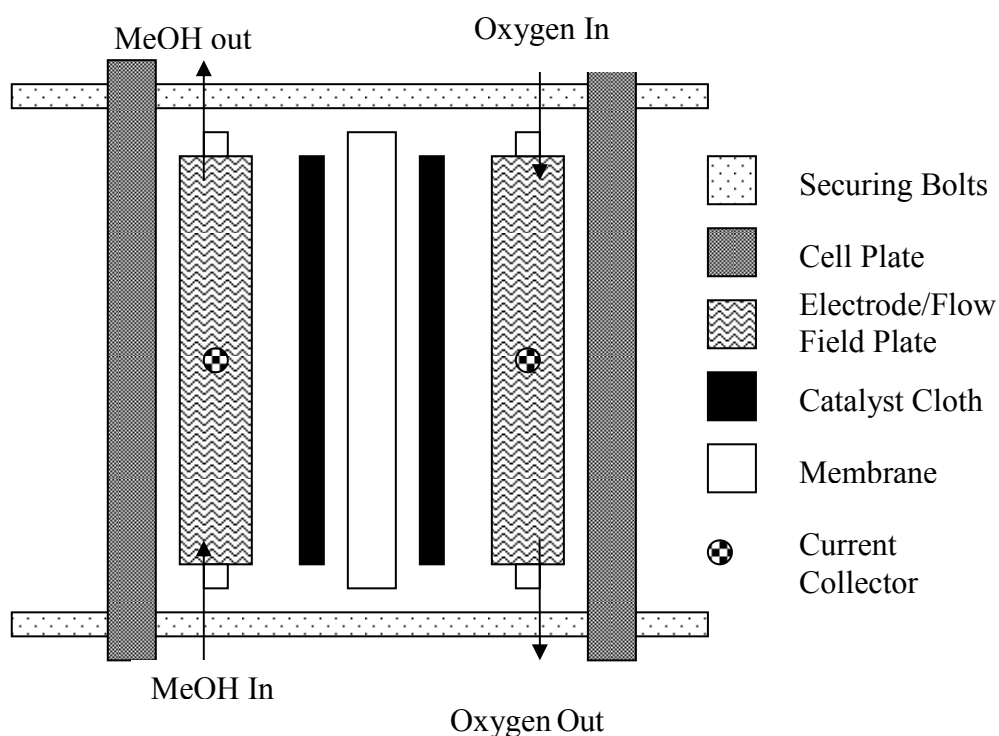


Figure 5.12: Diagram of fuel cell, top expanded view

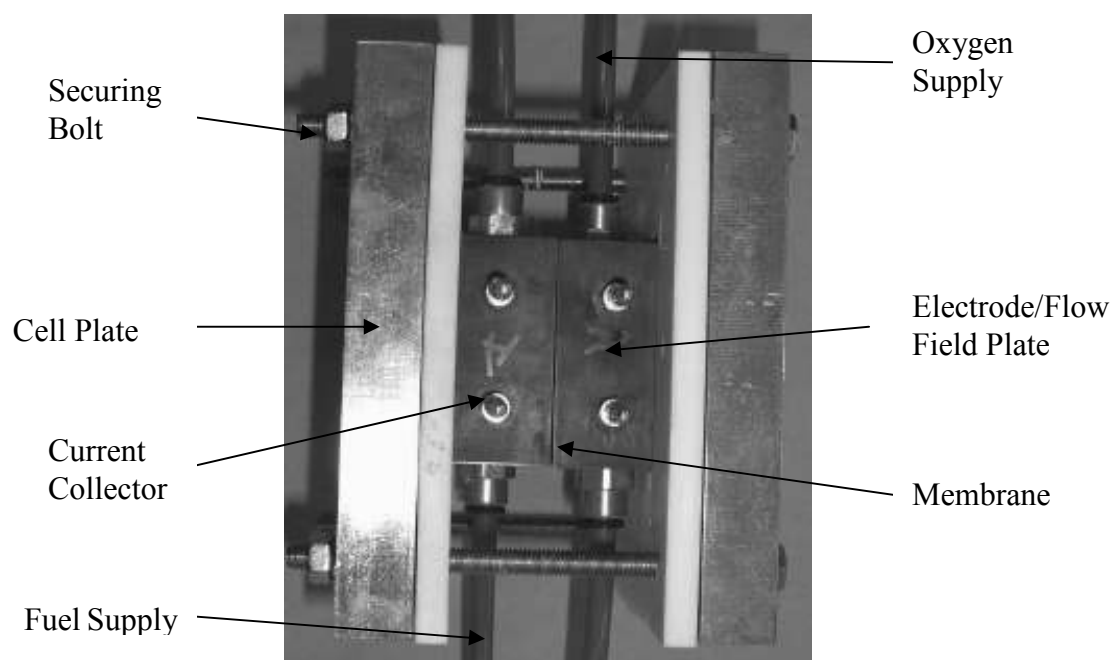


Figure 5.13: Photograph of Fuel Cell

The fuel cell was left to equilibrate for at least 2 hours, before the first polarisation curve was taken.

5.6 Water Electrolysis Testing

Samples were hydrated in deionised water for 16 hours and excess water removed by paper towel. A MEA was made constructed using the sample and Pt carbon cloth on both sides of the sample. The MEA was placed in an H-TECH water electrolyser and deionised water was supplied to both the anode and cathode compartments, as shown in figures 5.14 and 5.15. A variable voltage was applied to the cell and the current noted. The rate of production of gas was also noted.

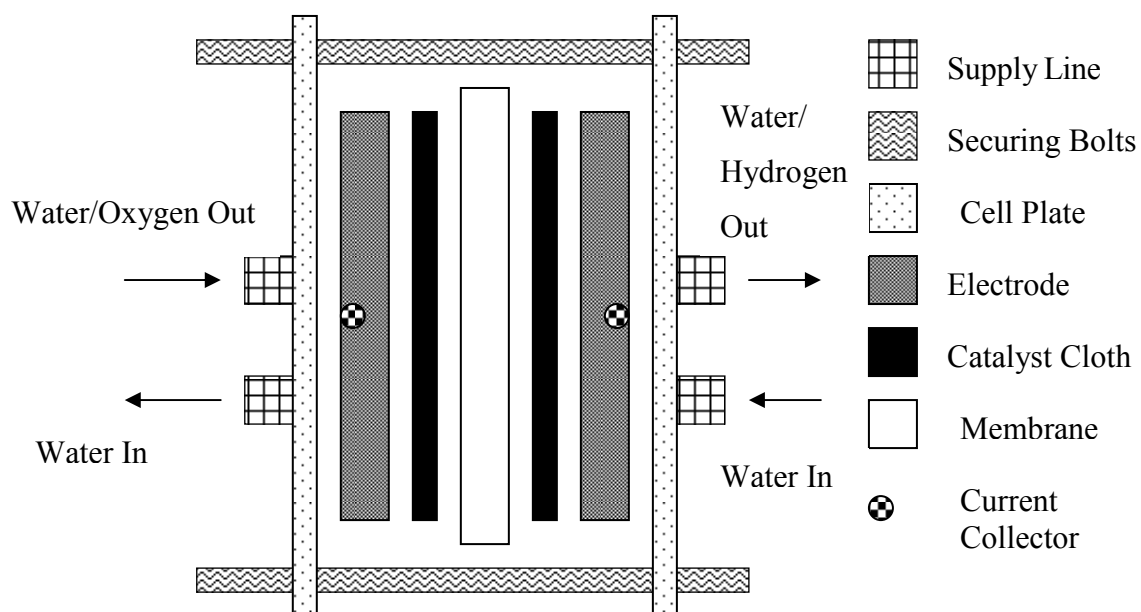


Figure 5.14: Water electrolysis cell diagram, top expanded view

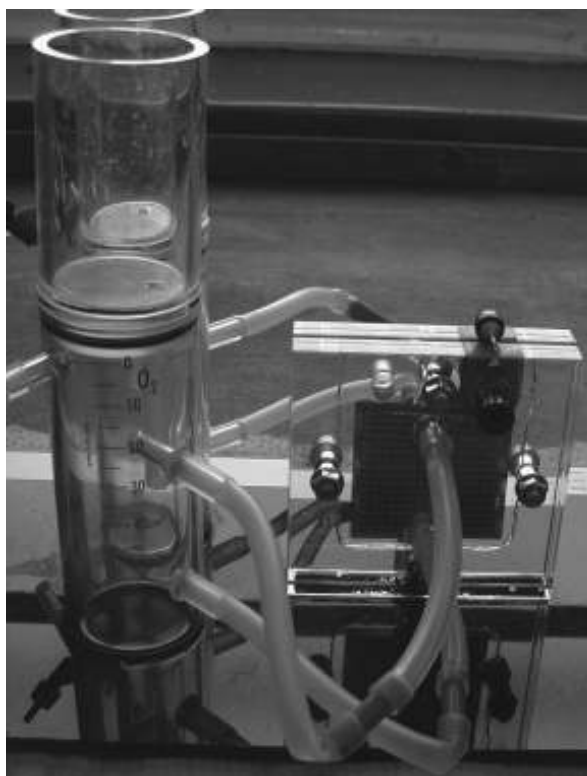


Figure 5.15: Water electrolysis cell and gas storage tanks

Although it would normally have been possible to analyse the gases by Gas Chromatography-Mass Spectrometry (GC-MS) through headspace analysis, in these experiments the volumes of the gases were measured by volumetric displacement of water and the composition confirmed by the use of lighted and glowing splints.

5.7 Soxhlet Extraction

It was considered important to determine not only the chemical stability of the new copolymers but also the efficiency of the polymerisation reactions. Thus samples were subjected to soxhlet extraction and the resulting liquors were analysed for composition.

Sections of rod were measured and weighed prior to extraction. Each section of rod was placed in a marked cellulose thimble and weighed. Glass wool was then placed over the sample to reduce the loss of solid material during extraction.

The thimbles were placed in a soxhlet extraction apparatus and set to reflux over an electric isomantle, as illustrated in figure 5.16. Samples were extracted over 48 hours with either methanol or toluene.

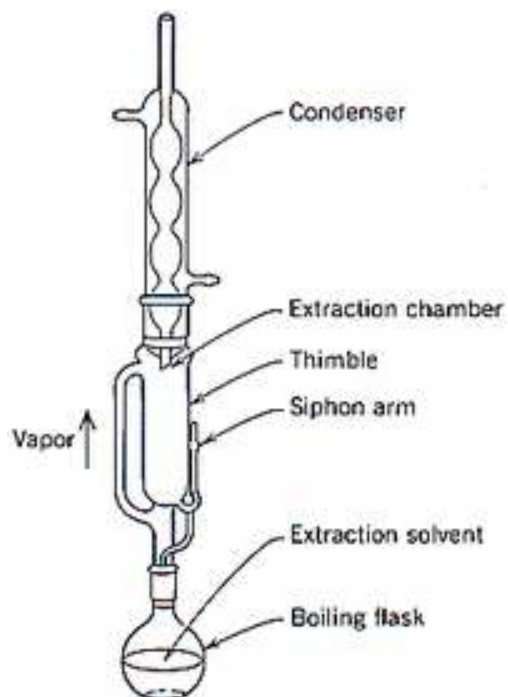


Figure 5.16: Soxhlet Apparatus

The samples were left to cool to room temperature and excess solvent removed. The thimble was then placed in an oven at 50 °C and the sample weighed after 2 days, and every 24 hours until a constant mass was recorded. The sample was then removed and reweighed. Percentage loss on extraction was calculated as follows:

$$[(W_o - W_e) / W_o] \times 100 \quad (5.4)$$

where W_o is the mass of the original sample and W_e is the mass of the sample after extraction.

A sample of the extracted liquor was analysed by HPLC, FT-IR and GC-MS

5.7.1 HPLC Analysis

HPLC analysis was undertaken using a reversed phase column, in an Alliance 2695 Separations Module coupled, with a 996 PDA detector. The column was an Intensil ODS2 5 μm , 250 mm length by 4.6 mm diameter and the mobile phase was 60 % methanol and 40 % demineralised water at 1 mL min⁻¹.

5.7.2 FT-IR Analysis

FT-IR analysis was undertaken using a Bruker Vector 22.

For solid samples 10 mg of the sample was placed in a crucible with 300 mg of dried potassium bromide. The mixture was then ground and mixed using a pestle and mortar. 55 mg of the resulting powder was taken and placed in a die and a disc pressed to 10,000 kg on a 13 mm die. The pressed disc was placed in the FT-IR and, as recommended by the manufacturer, 16 scans were taken of each sample.

For liquid samples 10 drops (approx 1 mL) were placed on a sodium chloride disc to increase the recorded signal. A second sodium chloride disc was then placed on top of the first and both placed in the FT-IR. 1000 scans were taken of each sample to boost the signal and the background removed from the samples spectrum.

A background spectrum was taken before the sample measurement to assess the absorption due to the sodium chloride discs.

5.7.3 GC-MS Analysis

GC-MS analysis was undertaken using a Fisons CG 8000^{TOP} coupled to a Fisons Voyager MS with a Fisons AS800 auto sampler.

The GC column used was a RTX-5 SILMS, 15 metres, 0.25 mm ID, 0.25 μm film thickness (df). Injector temperature was 250 °C with a split ratio 50:1 and a 1 μL injection volume. The oven temperature profile was 50 °C hold for 1 min, ramp 20 °C min^{-1} to 200 °C, hold for 10 min. The mass spectrometry acquisition was held in EI+ mode with a scanning range of 12-250 m/z (where m = mass and z = charge).

Chapter 6 . Results and Discussion

6.1 Polymerisation

Four blended systems were created for this project based on the monomers:

- 2-Phenyl-Oxazoline (PhOX)
- Aniline (AI)
- 2-Methyl-2-Oxazoline (MeOX)
- 4-Vinyl Pyridine (VPy)

The systems were polymerised by means of:

- gamma radiation
- thermal initiation
- microwave initiation

Characterisation of the copolymers was carried out to determine equilibrium water content upon hydration, thickness increase upon hydration, ionic conductivity and methanol permeation rate. Based on these values the suitability of these materials for use as anionic solid polymer electrolytes in direct methanol fuel cells was assessed and the choices made for fuel cell testing. A second smaller selection of samples was made for testing in a water electrolyser.

6.1.1 Gamma Radiation Polymerisation

The majority of compositions subjected to gamma radiation (γ -radiation) underwent a change of state from liquid to solid, and this is summarised in table 6.1. . Materials were irradiated to approximately 25 and 50 kGy. 25 kGy is the accepted sterilisation dose for medical products in the UK and as such is available in all commercial gamma sterilisation plants. 50 kGy simply equates to a double pass.

Table 6.1: Radiation curing of samples

Sample	Composition (Molar Ratio)	Total Dose (kGy)	Notes
04SJG008	PhOX (1)	30.2	Uncured, still liquid
04SJG007	NVP (1): PhOX (1)	52.0	Gelled, not solid
04SJG005	AN (1): NVP (1): PhOX (1)	3.0	Gelled, not solid
04SJG018	AN (6): NVP (8): PhOX (8): H ₂ O (11)	25.2	Top gelled, bottom still liquid
04SJG020	AN (1): AI (1)	25.2	Solidified, crumbles on handling
04SJG011	AN (11): AI (11): H ₂ O (13)	25.2	Solid with liquid containing within Brittle, possible exclusion of one reagent*
04SJG019	AN (1): NVP (1): AI (1)	25.2	Solidified, rigid
04SJG010	AN (1): NVP (1): AI (1): H ₂ O (2)	25.2	Solidified, malleable, white area, sticky
04SJG042	AN (6): NVP (6): AI (6): BV (1): H ₂ O (13)	26.9	Solidified, flexible.
04SJG046	AN (6): NVP (6): AI (6): BE (1): H ₂ O (13)	20.0	Small section gelled, extrudes on touch
04SJG050	AN (6): NVP (5): AI (6): BE (1): H ₂ O (13): AMX (0.1)	20.9	Only gelled at bottom, soft and sticky
04SJG054	AN (5): NVP (6): AI (6): BV (1): H ₂ O (24): AMX (0.1)	20.9	Solidified, soft and flexible
04SJG009	MeOX (1)	30.2	Solution uncured, still liquid. Liquid light blue
04SJG004	AN (20): MeOX (9)	25.0	Solid, brittle, unable to be handled.
04SJG016	AN (9): MeOX (9): H ₂ O (11)	25.2	Solidified, brittle and inhomogeneous
04SJG001	AN (1): NVP (1): MeOX (1)	3.0	Solidified, but soft
04SJG002	AN (1): NVP (1): MeOX (1)	25.0	Solidified, tough
04SJG015	AN (7): NVP (7): MeOX (7): H ₂ O (11)	25.2	Solidified, flexible
04SJG041	AN (7): NVP (7): MeOX (3): BV (1): H ₂ O (11)	26.9	Solidified, rigid
04SJG045	AN (7): NVP (7): MeOX (3): BE (1): H ₂ O (11)	20.0	Solidified, malleable
04SJG053	AN (7): NVP (7): MeOX (3): BV (1): H ₂ O (11): AMX (0.1)	20.9	Solidified, rigid

* Unknown which reagent might be excluded from reaction

Table 6.1: (Continued) Radiation curing of samples

Sample	Composition (Molar Ratio)	Total Dose (kGy)	Notes
04SJG049	AN (7): NVP (7): MeOX (3): BE (1): H ₂ O (11): AMX (0.2)	20.9	Solidified, but soft
04SJG021	AN (1): NVP (1): VPy (1)	25.2	Solidified, very hard
04SJG012	AN (1): NVP (1): VPy (1): H ₂ O (2)	25.2	Solidified, hard
04SJG043	AN (6): NVP (6): VPy (6): BV (1): H ₂ O (12)	26.9	Solidified, very hard
04SJG047	AN (6): NVP (6): VPy (6): BE (1): H ₂ O (13)	20.0	Solidified, very hard
04SJG052	AN (8): VPy (9): BE (1): H ₂ O (12):AMX (0.1)	20.9	Solidified, very hard
04SJG055	AN (5): NVP (6): VPy (6): BV (1): H ₂ O (12): AMX (0.1)	20.9	Solidified, very hard
04SJG051	AN (6): NVP (6): VPy (6): BE (1): H ₂ O (12): AMX (0.1)	20.9	Solidified, very hard
ITMSTD1	AN (15): NVP (9)	3.0	Solidified
ITMSTD2	AN (15): NVP (9)	25.0	Solidified, White areas
04SJG014	AN (14): NVP (7): H ₂ O (11)	25.2	Solidified, white area at bottom of
ITMAE1A	AN: NVP: BV: H ₂ O: AMX [#]	26.9	Solidified, rigid
ITMAE7A	AN: HEMA: BV: H ₂ O: AMX [#]	26.9	Solidified, rod rigid with white areas
ITMAE2A	AN: NVP: BE: H ₂ O:AMX [#]	20.0	Solidified, rigid
OR-10A	AN: NVP: AMPSA: H ₂ O: AMX [#]	26.9	Solidified, rod malleable

[#] Commercial in Confidence, Confidentiality agreement with ITM Power PLC.

From the data in table 6.1 it can be seen that 2-Phenyl 2-Oxazoline (PhOX) did not polymerise. This may be explained by the presence of the phenyl group, which may lead to the resonance stabilisation of free radicals^[103]. Alternatively steric hindrance, the physical blocking of a reaction due to molecule size, may be responsible, as indicated in figure 6.1.

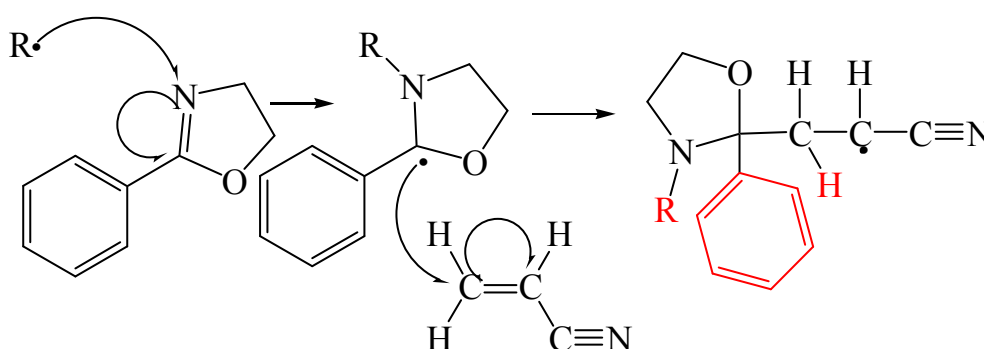


Figure 6.1: Possible free radical polymerisation of PhOX, showing possible steric hinderance of final product in red

The data also show that use of Aniline (AI) produced copolymers of variable consistency under gamma radiation conditions. Sample conditions ranged from completely polymerised to materials that remained liquid. One sample produced a polymer with liquid within. Closer examination by repeating experiments and conducting a detailed analysis of the results failed to find discernable reasons for these variations. It is possible that one or more monomers were effectively excluded from the reactions due to phase separation within the sample mixture.

2-Methyl 2-oxazoline (MeOX) was known to polymerise by cationic ring opening^[82], though did not homopolymerise when exposed to γ -radiation, but did undergo copolymerisation in the presence of other monomers. This suggests that formation of

free radicals within the oxazoline molecule was not achieved, while the free radical copolymerisation of MeOX can be explained by the formation of free radicals on the other monomers, which then opened the double bond on the oxazoline ring, to promote the copolymerisation. This is illustrated in figure 6.2 for one possible reaction scheme.

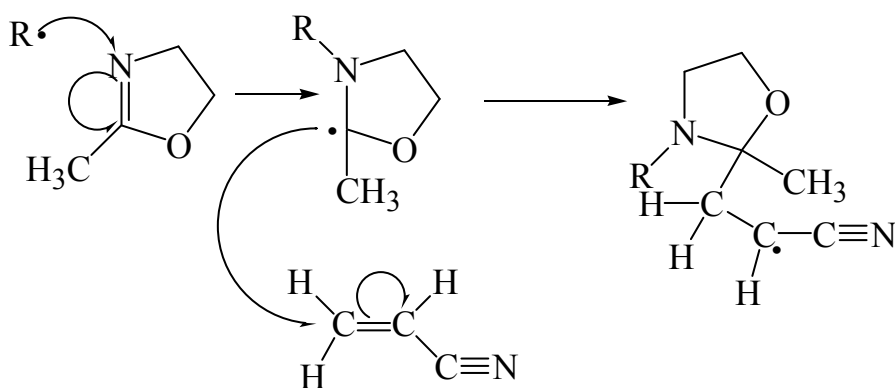


Figure 6.2 Possible free radical polymerisation between MeOX and AN, where R is a free radical formed by gamma radiation.

The copolymerisation of AN and MeOX produced a brittle material that was very difficult to handle. However, the addition of NVP to this system rendered the material more manageable. This system became one of the major copolymers studied in this work and from here on the copolymer containing MeOX and NVP, in varying compositions, is called the MeOX system.

Sample 04SJG053 containing MeOX copolymer was refluxed under soxhlet conditions with two separate solvents. HPLC analysis of the liquors was undertaken and the results showed that no MeOX was present in either solvent, suggesting that the MeOX was fully incorporated in the copolymer. This was to be confirmed by solid state NMR, but the technique was unavailable at the time of analysis.

The compositions containing 4-vinyl pyridine (VPy) generally polymerised well using gamma radiation, the exception being those that received low total doses. The resulting copolymers often contained voids caused by the production of entrapped hydrogen from radical formation, as discussed earlier. By lowering the dose rate of the radiation fewer free radicals were produced in unit time, thus giving time for the hydrogen gas to diffuse out of the system and thereby reduce the occurrence of voids.

Although VPy is known to generate soft homopolymers, (as previously discussed outlined in Chapter 4) hard, rigid copolymers were produced. These materials were hydrophilic in nature and became more flexible on hydration in demineralised water.

Production of membranes using gamma radiation was undertaken with various compositions. It was noted that the difference in dose rate between the edge and the centre of the membrane (caused by the geometry of the irradiation source) caused a difference in polymerisation across the membrane. The centre area of the membrane received a higher total dose, thus producing thicker polymer when compared to the edges of the membrane. This effect could be overcome by using a different source geometry to achieve a more uniform dose rate across the membrane area.

6.1.2 Thermal Polymerisation

Initially thermal polymerisation was undertaken on a basic AN:NVP system in order to gain confidence in the thermal polymerisation process. The results are given in table 6.2. Unsurprisingly, in the absence of a thermal initiator none of the monomers copolymerised when heated to 80 °C. This indicated that the thermal curing of these

monomer systems proceeded via a free radical process (since without a free radical initiator no reaction occurred).

Table 6.2: Thermal curing of samples

Sample	Composition (Molar Ratio)	Temperature (°C)	Time in Oven (h)	Notes
04SJG025	AN (11): NVP (12)	70-80	168.0	Liquid
04SJG028	AN (14): NVP (14): AIBN (0.06)	40	17.5	Solidified
04SJG026	AN (14): NVP (14): H ₂ O (6)	70	156.5	Liquid
04SJG027	AN (14): NVP (14): H ₂ O (7): AIBN (0.06)	40	1.33	Solidified

In the presence of a thermal initiator copolymerisation was possible at temperatures below 80 °C. The inclusion of 5 % w/w (0.06 molar ratio) azo-bis-isobutyronitrile (AIBN) produced an exothermic reaction, which in turn produced a final product with voids, presumed to be produced by the nitrogen by-product of the initiator (See section 2.4.5). Reducing the amount of thermal initiator to 1.5 % w/w produced fewer voids in the copolymers.

Initial thermal trials utilising AIBN as the free radical initiator produced a sticky membrane, possibly due to the AIBN decomposing over time, leading to less than 100 % of the AIBN used being active. This was tested by the use of a newer batch of AIBN, which led to solid membranes with a constant thickness. Unfortunately during the period of this project AIBN became commercially unavailable due to Control of Substances Hazardous to Health (COSHH) regulations on the carriage of the material and this limited the extent of further experiments with this compound.

Further thermal trials used the initiator ammonium persulphate and produced a solid membrane, although the thickness across the membrane area was variable.

6.1.3 Multi Mode Microwave Polymerisation

The exact power absorbed by a sample in the Proline 700 W multi mode microwave oven was determined using a modified technique of Watkins^[104]. The equation used by Watkins is given in equation 6.1.

$$P = \frac{Cm\Delta T}{\Delta t} \quad (6.1)$$

Where P is the power absorbed in Watts, C is the specific heat capacity of water (taken to be 4.18 J K⁻¹ g⁻¹), m is mass of water, ΔT is the change in temperature in °F, and Δt is the time. Assuming that water density is 1 g mL⁻¹, and using a pint of water (568 mL, 568 g), and converting temperature from °F to °C, with a standard unit of time as 60 seconds gives

$$P = \Delta T \times 39.6 \quad (6.2)$$

As figure 6.3 shows there is a linear relation between power absorbed and microwave setting. The standard deviation for this experiment was 0.17.

It was however noted that Watkins equation is correct only for water. The specific heat capacity of acrylonitrile (a major constituent in all of the copolymers) is given as 1.32 J K⁻¹ g⁻¹^[105]. This means that acrylonitrile (AN) requires less energy per gram to raise the temperature by one degree. Therefore less energy is required to be absorbed by the acrylonitrile than water to produce thermal decomposition of the initiator in the monomer solution. The question therefore arises as to the ability of AN to absorb the microwave

energy when compared to water. This led to an inability to accurately define the amount of power absorbed by a solution to achieve polymerisation, a fact also recorded in the literature^[63] as outlined in section 3.3.1. The given total energy absorbed henceforth is based on water, to give a more accurate indication than quoting the microwave power setting and time irradiated.

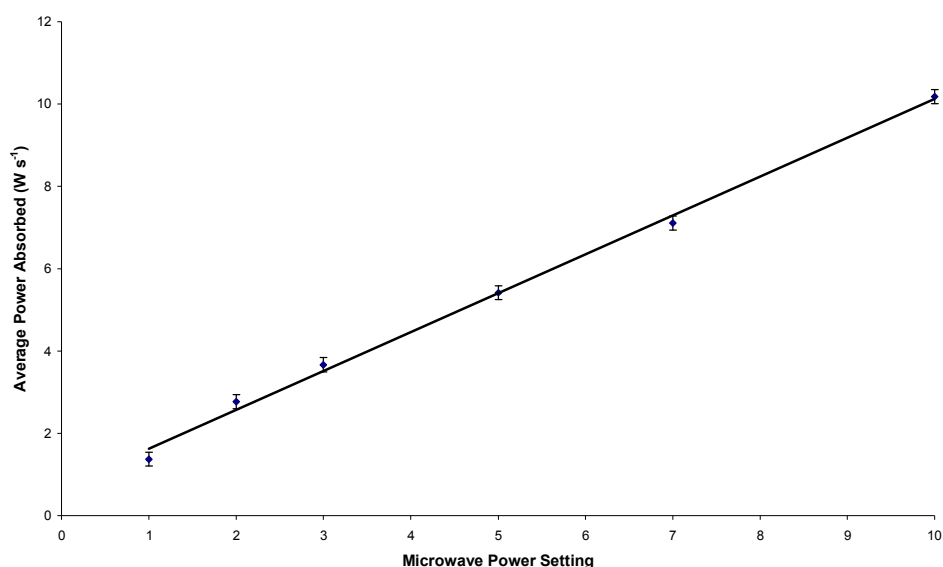


Figure 6.3: Average absorbed power of Proline 700 W multi-mode microwave

A total of 18 samples were prepared by multi-mode microwave radiation. Those listed in table 6.3 were the samples where a noticeable reaction occurred. Those not reported either showed no apparent sample heating or no change in state to produce a useful product.

Initial microwave polymerisation was undertaken with a conventional multi-mode microwave oven (see section 3.5) on a basic AN:NVP system. It was found that polymerisation by multi-mode microwave energy was not possible without the presence of a thermal initiator, as shown by table 6.3. This result strongly indicates that microwave polymerisation is a type of thermal polymerisation, as described in chapter 3.5.

Table 6.3: Microwave curing of samples

Sample	Composition (Molar Ratio)	Container	Total Energy Absorbed (Power setting)	Notes
04SJG023	AN (3): NVP (2)	sealed tube	2448 W (1)	No change. Post irradiated and cured.
04SJG024	AN (11): NVP (5): H ₂ O (9)	sealed tube	1509 W (1)	Liquid boiled.
04SJG033	AN (15): AIBN (0.003)	sealed tube	1221 W (10)	Solidified. Cracked and peeling.
04SJG030	AN (14): NVP (15): AIBN (0.06)	sealed tube	122 W (1)	Solidified. Exothermic reaction.
04SJG032	AN (15): NVP (16): AIBN (0.006)	open petri dish	163 W (1)	Solidified. Exothermic reaction with white fumes.
04SJG034	AN (16): NVP (16): AIBN (0.003)	open petri dish	305 W (10)	Solidified on cooling. White fumes.
04SJG035	AN (8): NVP (8): AIBN (0.0015)	open petri dish	101 W (10)	Solidified. Voids contained within.
04SJG029	AN (14): NVP (15): H ₂ O (6): AIBN (0.06)	open petri dish	81 W (1)	Solidified. Exothermic reaction.
04SJG036	AN (8): NVP (8): VAZO® (0.01)	open petri dish	216 W (5)	Solidified. White fumes.
04SJG037	AN (8): NVP (8): K ₂ S ₂ O ₈ (0.01)	open petri dish	610 W (10)	No change in state, although solution heated.
04SJG040	AN (8): NVP (8): K ₂ S ₂ O ₈ (0.02): H ₂ O (6)	open petri dish	209 W (3)	Sticky and extrudes on touch.
04SJG038	AN (8): NVP (8): (NH ₄) ₂ S ₂ O ₈ (0.01)	open petri dish	270 W (5)	Gel extrudes.
04SJG039	AN (8): NVP (8): (NH ₄) ₂ S ₂ O ₈ (0.02): H ₂ O (6)	open petri dish	162 W (5)	Sticky and extrudes on touch.

Also of interest was the fact that polymerisation occurred in the presence of oxygen, a known radical scavenger^[106]. It is suggested here that the faster rate of reaction when polymerising using a microwave overcomes the oxygen scavenger effect, because the diffusion of oxygen into the sample is slower than the polymerisation rate.

It was found that the concentration and type of thermal initiator changed the rate and degree of cure. It was difficult to measure the temperature of the monomer composition in the multi-mode microwave as the presence of a thermocouple inside the cavity caused arcing. It was also difficult to measure the temperature of the composition after the microwave energy had been imparted, as some materials were solid and others, whilst liquid, had cooled before the composition could be removed from the microwave cavity.

AIBN produced a high rate of reaction at high microwave power (average 10.2 W), polymerising in seconds, and even at low microwave powers (average 1.2 W) polymerisation still occurred. Unfortunately with AIBN concentrations above 2 % w/w uncontrollable exothermic reactions were observed, leading to a poor heterogeneous cure.

The alternative free radical initiator azo-bis(cyclohexane carbonitrile) (VAZO®) was not soluble in the sample matrices, which led to inhomogeneous final products. The reaction proceeded quickly with fumes being produced in shorter times and at lower microwave powers than used for AIBN. The products of these reactions contained voids. Reducing the initiator concentration reduced the rate of reaction and produced a more homogeneous product.

The use of the persulphate initiators required the presence of water, otherwise no polymerisation occurred. This indicates that the water in the sample was absorbing the microwave energy and when the temperature of the water was sufficient to decompose the persulphate initiator, free radicals were produced. Polymerisation by this method was therefore almost certainly of a thermal nature, similar to normal thermal oven curing processes. The major difference being the rate at which energy was being absorbed by the sample, being much higher in the case of the microwave initiation compared to the thermal oven.

It was observed that potassium persulphate was less soluble in water than the ammonium analogue, and therefore it was decided that ammonium persulphate initiator should be used as a thermal initiator for the duration of this project.

The use of ammonium persulphate free radical initiator led to a more homogeneous cure when compared to AIBN. Low concentrations (0.01 % w/w) of ammonium persulphate did not produce a solid product, rather a gel, which when left to settle over time allowed the gas trapped within the polymer to escape leaving a void-free final product. The gel could not be cured further by microwave or oven curing, probably suggesting that the persulphate initiator had been depleted in the initial polymerisation process. This argument was strengthened when it was found that the gel could be further cured using γ -radiation and also be remoulded into a different shape prior to the second stage curing.

Increasing the persulphate concentration above 1% w/w produced a solid product by microwave.

6.1.4 Single-Mode Cavity Microwave

As described in Chapter 3 domestic microwave ovens, such as those used in some early experimentation may not be particularly suitable for chemical reactions ^[61]. The main reason for the use of domestic microwave ovens by other researchers is the widespread availability of equipment and the low cost.

A pilot study for this project using a single-mode microwave (CEM Discovery Model) at the University of Hull showed that polymerisation of the monomers of interest was possible. Two samples (one MeOX and one VPy) were polymerised to a gel state within 5 mins and had cured to a solid final product within a further 2 mins at a 5 W power level. The final product had no voids within and appeared to have cured homogeneously. The major downside of the pilot study was the small volume of the single-mode microwave cavity, which had a sample size of only 5 cm³. Therefore there was insufficient copolymer to undergo extensive characterisation. Also, although the average conductivity of the MeOX sample was very high at 101.2 mS cm⁻¹ the mechanical stability of the polymer was very poor. The water content was measured at 477 % and the thickness increase upon hydration was 1300 %, quite unacceptable for this project.

It was therefore decided that further experimentation with a larger single-mode microwave cavity was justified in order to provide more data on suitability of the technique for the production of materials for fuel cell electrolytes. A study to build a large device was undertaken (See chapter 3.6) but, for reasons explained, the samples produced in this prototype cavity were unsuitable for further characterisation and testing.

6.1.5 Polymerisation Summary

- In view of the results in Table 6.1 2-Phenyl 2-Oxazoline (PhOX) and aniline (AI) were discarded at an early stage in this project. PhOX did not homo- or copolymerise and AI did not produce consistent results.
- Polymerisation of the monomer systems without a thermal free radical initiator was not thermally possible. The rate and percentage of cure, and hardness of the final polymer, depended on the concentration and type of thermal initiator used.
- 1 % w/w aqueous ammonium persulphate produced a solid final product. The presence of the water facilitated microwave heating of the ammonium persulphate, in turn causing its decomposition and the production of free radicals.
- The use of ammonium persulphate as a thermal free radical initiator led to products with varying thickness across the membrane.
- The production of membranes with uniform thickness was possible using the thermal initiator AIBN. The state of the final cured membrane depended on the age of the thermal initiator AIBN. The withdrawal from sale of this compound precluded further extensive experimentation with it.
- Small scale study using a single-mode microwave proved that homogeneous polymerisation was possible. Samples polymerised to a gel state within 5 mins and had cured to a solid final product within a further 2 mins at 5 W power level.

- Production of membranes using gamma radiation was not possible due to the particular design of the source, causing a marked difference in the received total dose across the membrane, leading to an inhomogeneous cure. This would be overcome by presenting the samples to a specially designed gamma source.

6.2 Materials Properties and Characterisation

The materials initially produced were screened to determine their suitability for use in a direct methanol fuel cell (DMFC). The tests used were equilibrium water content, dimensional stability (thickness increase upon hydration) and ionic conductivity, for some materials of particular interest this was extended to include methanol permeation.

From the initial screening of the wide range of copolymer materials prepared by different curing processes, the objective was:

- i) to be able to narrow down the choice of materials
- ii) prepare several optimised materials
- iii) characterise these materials and thereby validate their choice
- iv) test these materials in the DMFC and water electrolyser

An ideal material would have zero thickness increase on hydration, though a small amount of thickness increase, while not ideal might be acceptable. Wan *et al*^[107] produced an alkaline membrane with 425 % thickness increase, which was used in a fuel cell. This is considered to be too great for this project and only materials with linear thickness increase below 20 % were considered to be dimensionally acceptable.

The properties of copolymer produced by gamma radiation in terms of their water content, thickness increase and conductivity are given in table 6.4.

Table 6.4: Properties of materials polymerised by gamma radiation

Sample	Ionomer	System	Water content (%)	Thickness Increase (%)	Average Conductivity (mS cm ⁻¹)
04SJG012	Neutral	VPy	2.5	0.0	>0.01
04SJG015	Neutral	MeOX	43.5	37.1	>0.01
04SJG043	AEM	VPy-BV	29.4	19.3	4.1
04SJG047	AEM	VPy-BE	34.1	48.2	>0.01
04SJG041	AEM	MeOX-BV	95.1	263.6	nm [†]
04SJG045	AEM	MeOX-BE	nm [†]	nm [†]	nm [†]
04SJG055	AEM	VPy-BV-AMX	30.7	14.0	1.0
04SJG052	AEM	VPy-BE-AMX	35.3	14.4	0.3
04SJG053	AEM	MeOX –BV-AMX	53.5	23.9	5.8
04SJG049	AEM	MeOX-BE-AMX	nm [†]	nm [†]	nm [†]
ITMAE1A	AEM	NVP-BV-AMX	85.0	36.5	3.0
ITMAE2A	AEM	NVP-BE-AMX	89.4	13.2	1.8
ITMAE7A	AEM	NVP-HEMA-AMX	42.3	10.5	1.1

In samples with crosslinking agent and ionic exchange moiety absent, a small quantity of water content and thickness increase was observed (see table 6.4), most probably due to the hydrophilic monomers present.

[†] nm = not measured due to physical instability of material

Sample 04SJG013 (VPy) was dimensionally stable, physically robust, but conductivity was very low (below the measurable limits). In comparison the MeOX composition, 04SJG015, had high water content and was dimensionally unstable, but still achieved only a very low conductivity.

The addition of an ionic exchange moiety, such as (*ar*-vinyl benzyl)trimethyl ammonium chloride (BV) increased water content and decreased dimensional stability. It was noted that the samples containing MeOX were more dimensionally unstable in comparison to the VPy system. The physical instability of these MeOX:BV samples prevented their full characterisation.

The addition of 2-(dimethylamino)ethyl methacrylate (BE) to the VPy system produced a small rise in conductivity, water content, thickness increase and the material was dimensionally stable. In contrast, the addition of BE to the MeOX system caused a significant thickness increase resulting in material break up on immersion in water and, as a result, no further characterisation measurements were possible.

To prevent the excessive swelling and break up, a crosslinking agent, allyl methacrylate (AMX) was added to both the MeOX and the VPy systems. The resulting MeOX copolymer was still unable to retain its shape, and the MeOX : BE copolymer was therefore discarded as an unsuitable formulation for a cell membrane in terms of dimensional stability.

Conversely the addition of AMX to the VPy system reduced the thickness increase and maintained water content, which increased conductivity. However, the conductivity value was too low to act as a membrane for a direct methanol fuel cell. The VPy:BE formulation was therefore also dismissed. This finding was further supported by the low conductivity found in the proprietary material ITMAE2, supplied by ITM Power plc, which was also known to contain BE.

Summarising

- The addition of hydrophilic monomers or ionic exchange moieties increased the amount of water absorbed within the samples, but at the expense of their physical stability. This could be counter-acted by the addition of a crosslinking agent AMX.
- The use of BE as an ion exchange moiety was not successful and discontinued; the emphasis was placed on (ar-vinylbenzyl)trimethyl ammonium chloride (BV)

6.3 Effect of Monomer Concentration

The effect of the concentration of each of the system components on the sample was investigated by varying the concentration of each one in turn, keeping all other variables constant. The results are shown in a series of graphs which depict the percentage change in the parameters of water content and thickness increase together with the measured value of conductivity. The use of the percentage change notation on the ordinate axis was adopted so as to fit the data on a single graph for easy comparison.

The baseline materials for each system is as follows:

- MeOX system: 0.095 M AN, 0.091 M NVP, 0.038 M MeOX, 0.014 M BV, 0.200 M H₂O and 0.001 M AMX
- VPy system: 0.095 M AN, 0.095 M VPy, 0.022 M BV, 0.115 M H₂O and 0.001 M AMX.

6.3.1 Effect of Acrylonitrile (AN) Concentration

The data are summarised in figure 6.4. It can be seen that increasing the concentration of acrylonitrile (AN) in the VPy system caused a decrease in water content and conductivity, as expected. ⁻OH Ions are expected to be more mobile in water than in solid copolymer, therefore as the water content decreased the conductivity also reduced, due to the lack of ion mobility.

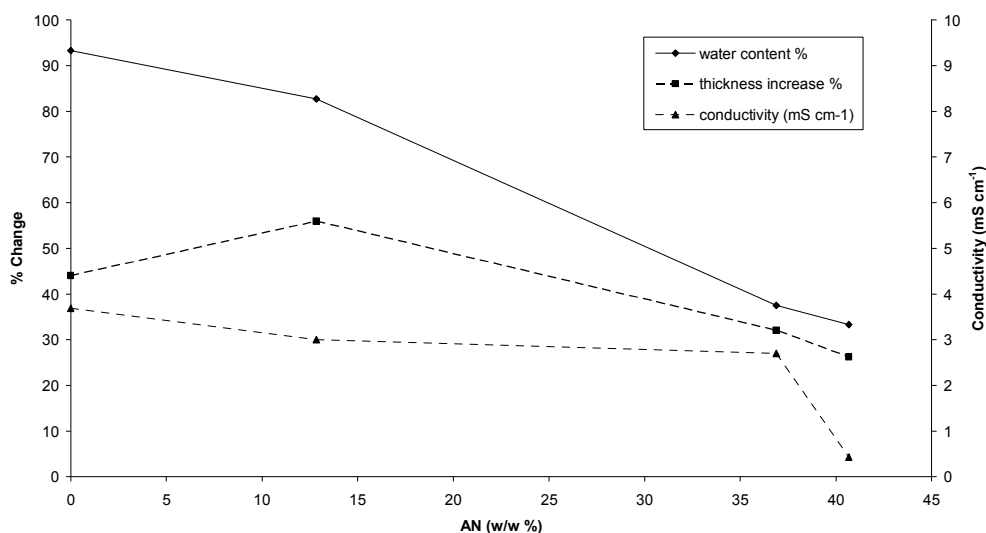


Figure 6.4: Effects of variation in concentration of AN in a VPy system

The dimensional stability, as evidenced by the membrane swelling, initially decreased with increasing AN concentration, but then increased as expected. The initial rise may be due to

a phase separation, resulting in the production of large areas of homopolymer as recorded in the literature for similar blended polyelectrolytes^[99].

As with the VPy system, increasing AN concentration in the MeOX system initially increased the water content, thickness and conductivity as shown in figure 6.5. Also further increases in the concentration of AN caused an increase in the hydrophobic nature of the polymer and therefore a decrease in water content, thickness increase and conductivity, again analogous behaviour to the VPy system.

From these experiments it is clear that in order to maintain an acceptable conductivity the maximum level of AN in the copolymer should not exceed ~12 % w/w for both the VPy and MeOX systems.

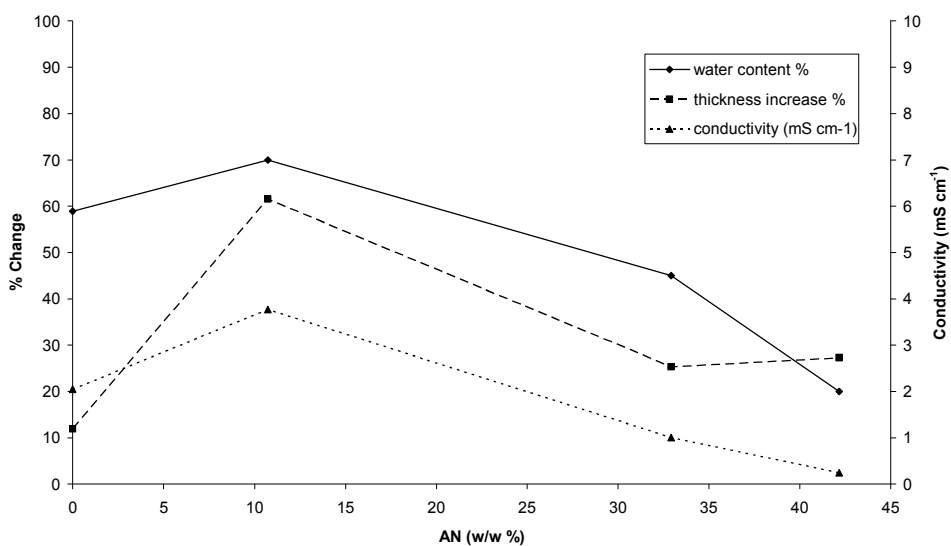


Figure 6.5: Effects of variation in concentration of AN in a MeOX system

6.3.2 Effect of N-Vinyl Pyrrolidone (NVP) Concentration

The addition of the hydrophilic monomer NVP into a MeOX system caused an initial increase in water content (see figure 6.6), but further increases in the concentration of NVP produced no further increase in water content. However, increasing the NVP concentration appeared to cause a small reduction in thickness increase and conductivity, which was unexpected.

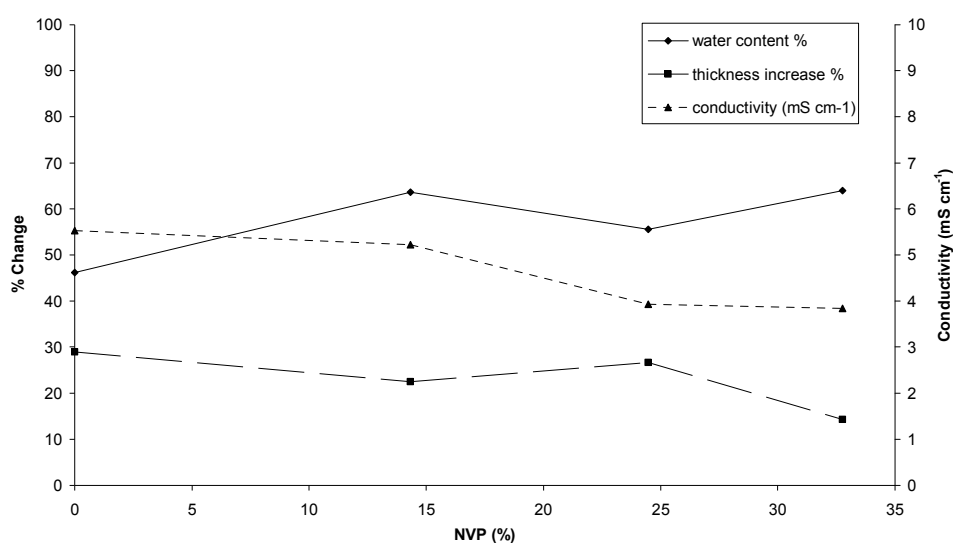


Figure 6.6: Effects of variation in concentration of NVP in a MeOX system

In the absence of NVP, high conductivity and good dimensional stability were achieved. Unfortunately this material was brittle and difficult to handle. Increasing the NVP concentration to 15% w/w improved the physical stability of the copolymer whilst maintaining the other properties at acceptable levels. Further increases in the NVP concentration reduced both the water content and the conductivity of the system. Comner *et al*^[108] also reported that conductivity decreased with a fall in water content, as the mobility of the ions became slower in the enlarged water volume.

Qiao *et al*^[99] also reported that blended polymers with large water content showed reduced conductivity. Qiao suggested that the charge carrier became diluted in the excess water, causing reduced conductivity, which he called ‘the dilution effect’. Qiao *et al*^[46] also suggested that conductivity was more influenced by thickness increase than water content, although no detailed explanation was given.

In line with the work of Qiao, for the copolymers in this project it is proposed that fast ion transfer is viable only if the fixed ion groups are within a close molecular distance and the ions may simply ‘float’ around in a relatively unchanged matrix. At this point, an excess of water may completely mask the ionic charge from the fixed ionic groups in the polymer. In effect the mobile ions might be considered to be completely surrounded by many layers of water molecules, which completely shield the ionic charge.

Therefore a large thickness increase would escalate the distance between the fixed ion groups to such an extent that the mobile ion is unaffected by the fixed ions, and therefore conductivity is reduced.

6.3.3 Effect of 4-Vinyl Pyridine (VPy) Concentration

Increasing the concentration of 4-vinyl pyridine (VPy) in the copolymer resulted in decreased conductivity. As can be seen from figure 6.7, water content and thickness increase on hydration also reduced on increasing the concentration of VPy.

The results indicate that the maximum level of VPy in the copolymer should not exceed ~15 % w/w, since above this level the conductivity falls rapidly.

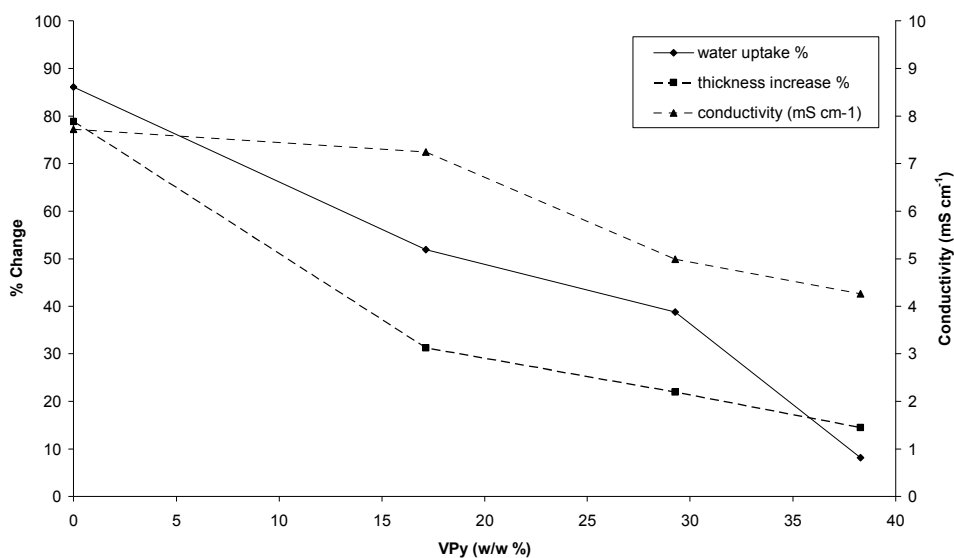


Figure 6.7: Effects of variation in concentration of VPy in a VPy system

6.3.4 Effect of 2-Methyl-2-Oxazoline (MeOX) Concentration

Increasing MeOX concentration had little effect on membrane thickness increase upon hydration, but unexpectedly decreased the water content slightly as shown in figure 6.8. This might indicate that the thickness increase was not due to a rise in water content, which stayed roughly constant.

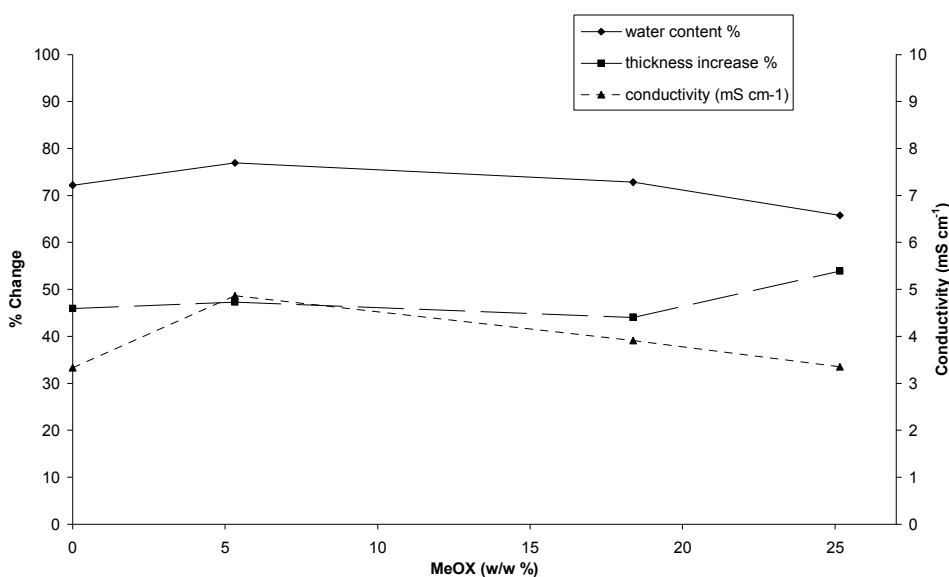


Figure 6.8: Effects of variation in concentration of MeOX in a MeOX system

The initial conductivity rise may be explained by the improved mobility of the counter ions, due to the slightly higher water content. The subsequent decrease in conductivity can be explained by the slightly increased volume of polymer (larger thickness increase), creating a greater distance between fixed ions, thus making the mobility of the mobile ion more difficult (The dilution effect). The extra water uptake would create change the density of the polymer, and as pure water is highly resistive, increase resistance and therefore reduce conductivity. From these experiments it is clear that the maximum level of MeOX in the copolymer should not exceed ~5 % w/w, as after this the conductivity drops markedly.

6.3.5 Effect of (ar-Vinylbenzyl)trimethyl Ammonium Chloride Concentration

Increasing the (ar-vinylbenzyl)trimethyl ammonium chloride (BV) concentration in the VPy system resulted in marked increase in water content, thickness increase, and conductivity (see figure 6.9). Similarly, increasing BV concentration in the MeOX system also increased the membrane swelling, the water content and conductivity (see figure 6.10).

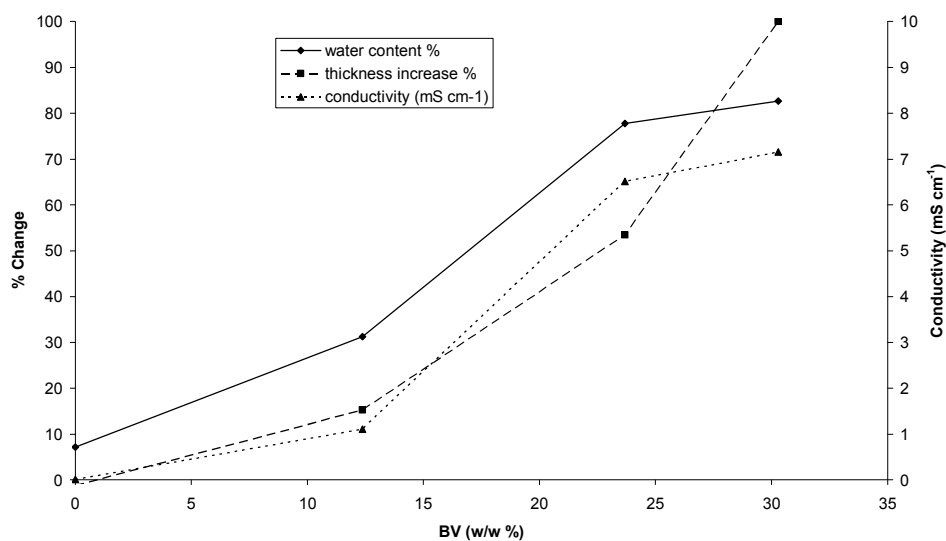


Figure 6.9: Effects of variation in concentration of BV in a VPy system

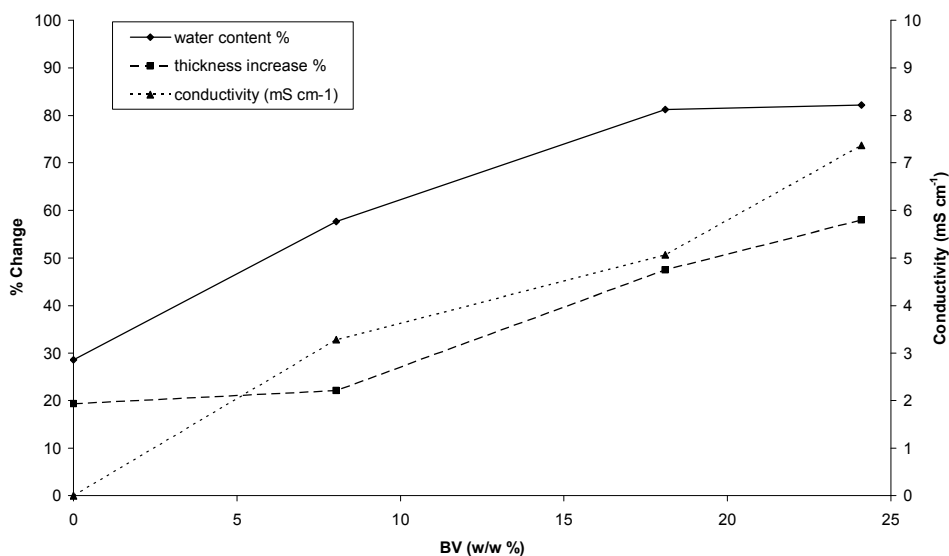


Figure 6.10: Effects of variation in concentration of BV in a MeOX system

Comparing the data in figures 6.9 and 6.10, the rate of increase of the measured parameters is more pronounced in the VPy system than for the MeOX system, particularly between 8 and 18 % w/w of BV.

To achieve high conductivity requires the maximum amount of ionic moiety (BV) and the results predict that this would produce a material with very high water content but poor dimensional stability, though the addition of other hydrophobic and/or crosslinking agents may be expected to improve the stability. As a general rule it is concluded that the amount of BV in the copolymer should be optimised in order to ensure maximum conductivity.

However, in further experiments it was shown that simply increasing concentration of BV in both MeOX and VPy systems also increased the methanol permeation rate of the samples (See figure 6.11), probably due to the miscibility of methanol with water.

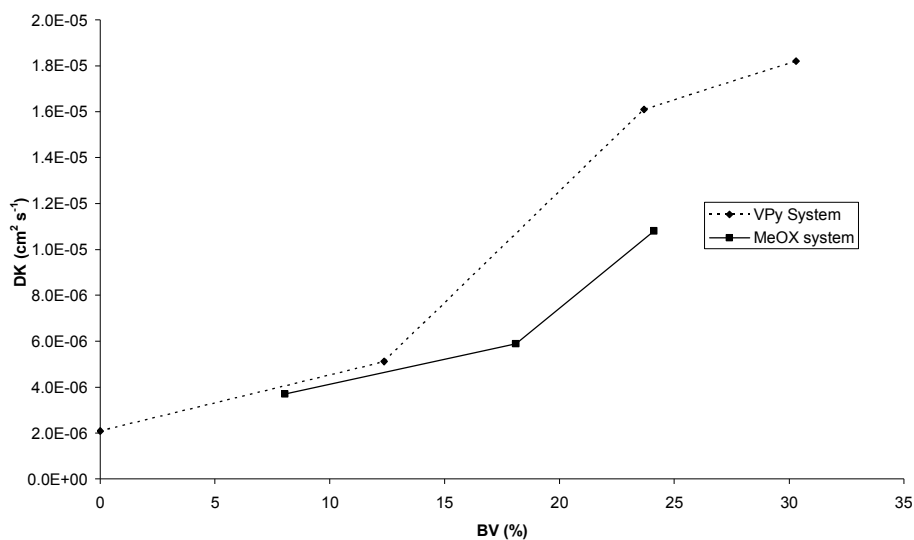


Figure 6.11: Methanol permeation (DK) with increasing BV concentration

The MeOX samples generally had a lower permeation to methanol than the VPy copolymer system and the data showed that for minimum methanol permeation the BV concentration should ideally be below ~18%. This is in good agreement with the working range for best dimensional stability and acceptable ionic conductivity.

6.3.6 Effect of Allyl Methacrylate (AMX) Concentration

It was expected that by increasing the concentration of AMX, which is known to be a highly reactive monomer^{[109],[100]}, would produce a three dimensional crosslinked polymer, with a tighter network with minimum increase in water content and thickness.

Low concentrations of allyl methacrylate (AMX) in the VPy system led, as expected, to reduced swelling and improved dimensional stability, but with reduced conductivity. This continued until approximately 5 % w/w (See figure 6.12). Thereafter, at concentrations above 5 % w/w the dimensional stability was slightly improved, while the conductivity dropped significantly. This compared with the material with no crosslinker which had a dimensional stability so poor it could not be tested further.

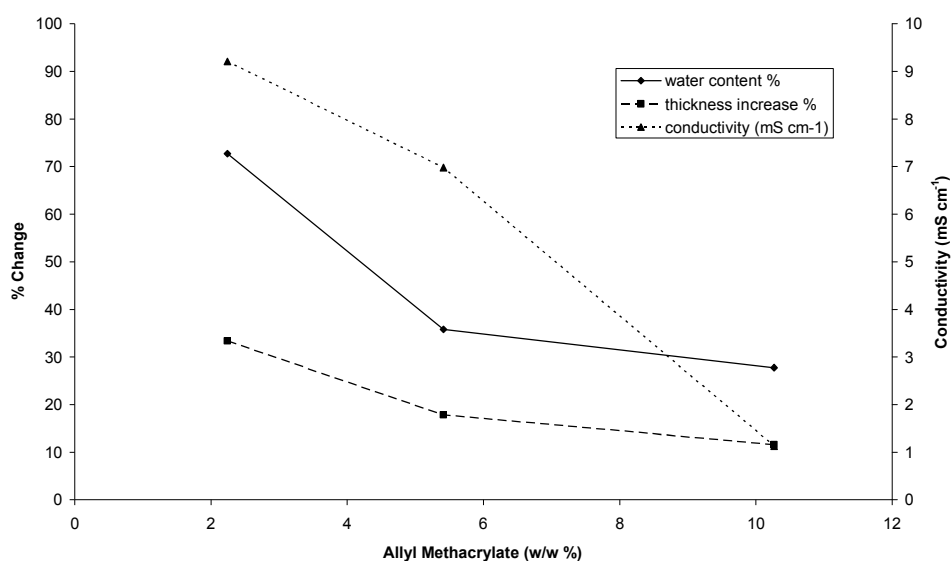


Figure 6.12: Effects of variation in concentration of AMX in a VPy system

In the MeOX system increasing the concentration of AMX, as shown by figure 6.13, had the effect of decreasing water content until approximately 5 % w/w, similar to the behaviour in the VPy system. Above 5 % w/w no further effect on water content was noted.

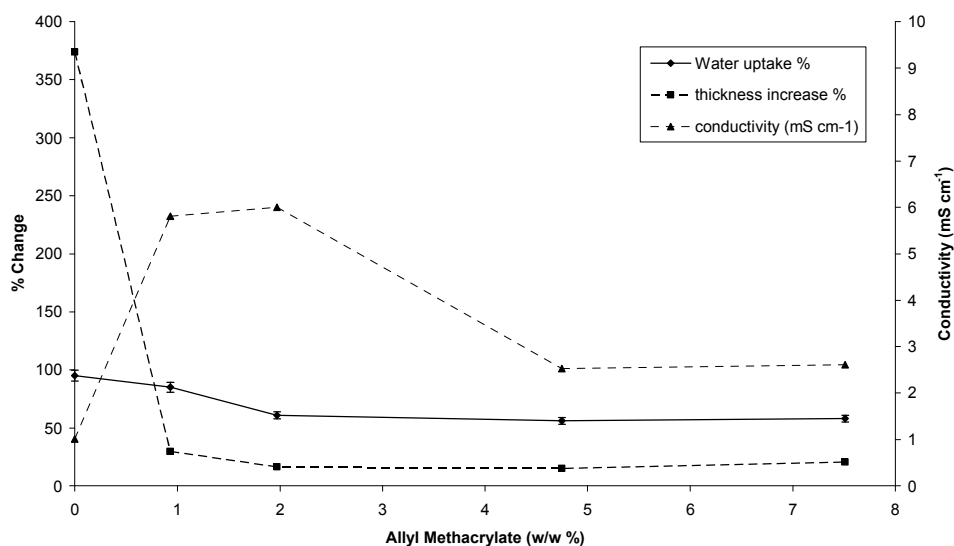


Figure 6.13: Effects of variation in concentration of AMX in a MeOX system

The swelling of the copolymer was dramatically reduced on the addition of 1 % w/w AMX. Further increases in the concentration to 5 % w/w showed that the dimensional stability increased steadily, above this concentration the opposite effect was observed with dimensional stability decreasing.

The change in conductivity with increased concentration of AMX had no immediately discernable pattern, but the shape of the curve may be explained in the following way: the low conductivity at 0 % w/w AMX may be due to the large thickness increase which increased the distance between fixed ions, retarding the Grotthus 'hopping' mechanism of ion transfer. As the AMX concentration increased, the space between the fixed ions was reduced and the conductivity increased. As the AMX concentration approached 5 % w/w the conductivity decreased due to the increase of a three dimensional crosslinked network within the sample, which in turn reduced the ion mobility and thus conductivity.

The number of available crosslinking sites can be calculated from the molar concentration of the AMX. For this calculation all crosslinking sites are considered to be active. The relationship between water content and amount of available crosslinking sites is shown in Figure 6.14. It indicates that a predictable pattern may exist for controlling the water content and thus the ionic conductivity of this polymer system by the use of a crosslinking agent at concentrations below 0.02 moles (0.05 % w/w)

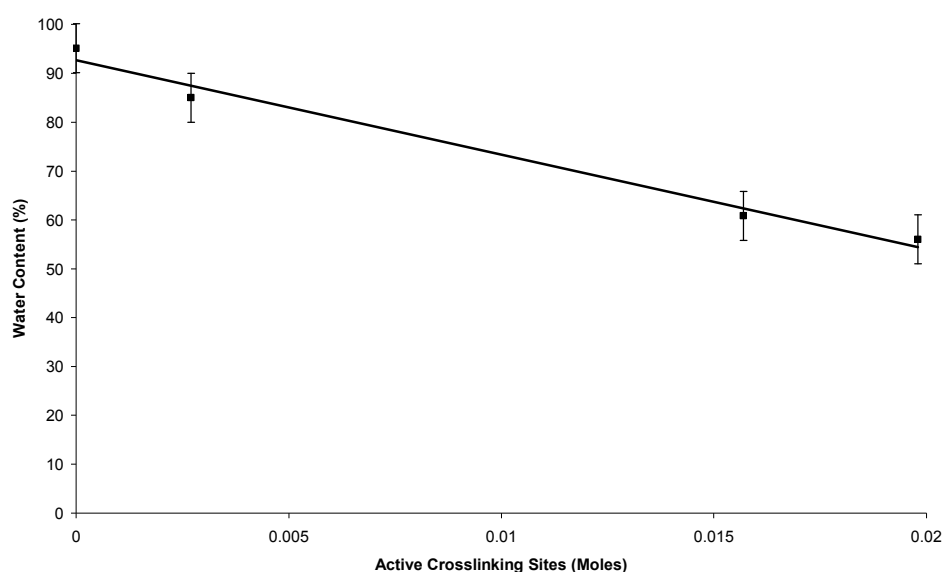


Figure 6.14: Copolymer Water content with moles of AMX crosslinking sites

The evidence from both MeOX and VPy systems suggest that varying AMX past 5 % w/w (0.20 moles for both systems) had a deleterious effect on dimensional stability, water content, and conductivity. This indicates that the maximum concentration of AMX in an ideal copolymer sample should not exceed a value of 5 % w/w.

6.3.7 Ideal Material Composition

From the above experimental data and analysis a concept model was developed in order to predict the composition of each component in the copolymer, necessary to produce an ideal material with high conductivity, high water content and high dimensional stability. In so doing it was clear that the predicted concentrations did not sum to 100 % w/w, and extra AN was therefore added to provide a stable material. The predicted values for each material component were as follows:

- AN 30-40 % w/w (to stabilise thickness increase of the hydrophilic contents in VPy and MeOX systems.)
- VPy 10-20 % w/w (to maintain high conductivity and water content.)
- NVP 15 % w/w (to reduce brittle nature of MeOX copolymers.)
- MeOX 5-10 % w/w (to maintain high conductivity high.)
- BV 20-30 % w/w (to avoid poor dimensional stability.)
- AMX 5 % w/w (to achieve the desired properties of water content and thickness increase in both VPy and MeOX systems.)

For a VPy based system this translated to an ideal mass composition of 20 g of AN, 10 g of VPy, 15 g of BV, 2.5 g of AMX and 2.5 g of H₂O, or a molar ratio of 0.378 M AN, 0.10 M VPy, 0.07 M BV, 0.02 M AMX and 0.139 M H₂O.

For a MeOX based system the composition was 20 g of AN, 7.5 g of NVP, 5 g of MeOX, 12.5 g of BV, 2.5 g of AMX and 2.5g of H₂O or a molar ration of 0.378 M AN, 0.07 M NVP, 0.06 M BV, 0.02 M AMX and 0.139 M H₂O

6.4 Optimisation of Materials

From the above data two optimised polymeric membrane materials were produced within the composition ranges given, these are summarised in table 6.5. To test the hypothesis two further samples were also produced with the hydrophobic/hydrophilic monomer ratio reversed. In the table samples 06SJG017 and 06SJG019 were the predicted materials, and samples 06SJG018R and 06SJG020R the materials with reversed monomer ratio (R depicting the reversed monomer ratio). All samples were cured by an identical gamma radiation process as outlined in section 5.1.2.

The materials were then characterised and compared to the data predicted for their respective compositions, as shown in table 6.6.

Table 6.5: Ideal polyelectrolyte systems

Sample	AN (g)	VPy (g)	NVP (g)	MeOX (g)	H ₂ O (g)	BV (g)	AMX (g)
06SJG017	20.00	10.00			5.04	12.65	2.50
06SJG018R	10.00	20.00			5.00	12.66	2.51
06SJG019	20.00		7.50	5.04	5.02	10.34	2.52
06SJG020R	10.00		17.51	5.02	5.34	10.27	2.50

Table 6.6: Characterisation of optimised samples

Sample	Water Content (%)		Thickness Increase (%)		Conductivity(mS cm ⁻¹)	
	Predicted	Measured	Predicted	Measured	Predicted	Measured
06SJG017	61.8	89.4	46.0	116.5	6.7	16.3
06SJG018R	60.3	66.7	41.0	51.6	5.5	11.0
06SJG019	67.8	5.9	33.0	16.1	4.6	1.5
06SJG020R	67.0	75.4	35.6	44.1	3.9	7.7

The VPy system with high ratio of hydrophobic monomers (06SJG017) had a water content, thickness increase and conductivity all above the predicted data. Unfortunately the material was physically unstable and was damaged on handling, due to its large swelling. Surprisingly the addition of more hydrophilic monomer VPy (06SJG018R) resulted in a reduction in water content, thickness increase and conductivity leading to a more physically stable and robust sample. The predicted data for this material was closer to the measured data than before, but once again all measured data was higher than the predictions.

As can be seen from table 6.6, water content in three of the four samples was higher than predicted, only sample 06SJG019 containing MeOX resulted in lower water content than

expected. This material had a low concentration of hydrophilic monomers possibly explaining the reduced water content, and hence low thickness increase and low conductivity. When the ratio between hydrophilic and hydrophobic monomers was altered to a more hydrophilic matrix (06SJG020R) the water content, thickness increase and conductivity rose considerably and above predicted values, suggesting that the hydrophilic materials within the copolymer have greater effect than the hydrophobic materials on the samples water content, thickness increase and conductivity.

One explanation for the lack of predictability observed in these samples is that the simplistic model does not take into account the interactions of the monomers at differing concentrations, nor the ability of the copolymers to form areas of homopolymer at low concentrations of monomer. It was noted that the materials with the reversed ratio of hydrophobic/hydrophilic monomers were in fact more suited as anionic solid polymer electrolytes for direct methanol fuel cells, probably due to the more homogeneous nature of the material. This suggests that the hydrophilic monomers within the copolymer have a greater effect on the materials characteristics than the hydrophobic monomers, and a greater account of this should be taken in a refinement of the predictions.

6.5 Effect of Crosslinking Agent

As seen in section 6.3.6 the effect of crosslinking available sites had a significant effect on the copolymer matrix. Therefore the type of crosslinking agent, with different numbers of available crosslinking sites, was studied on both the MeOX and the VPy system and the results compared to allyl methacrylate (AMX). The different agents studied were 2,4,6-triallyl-1,3,5-triazine (TT, see section 4.5.2) and 1,3,5-triallyl-1,3,5-triazine-2,4,6-(1H, 3H,

5H)-trione (TTT, see section 4.5.3). All samples received a gamma radiation dose of 25.3 kGy.

6.5.1 Effect of Crosslinking Agents on the VPy System

Five samples were produced by gamma radiation with various crosslinking agents, based on the baseline VPy system as described previously in section 6.3. The crosslinking agent was varied but with its mass kept constant (1.25 g). Molar compositions of these materials are described in table 6.7 below.

Table 6.7: Material composition for crosslinking studies of VPy system

Sample	AN (M)	VPy (M)	BV (M)	H ₂ O (M)	Crosslinker (M)
05SJG048	0.095	0.095	0.023	0.115	0.01-AMX
05SJG049	0.095	0.095	0.024	0.118	0.005-TT
05SJG051	0.095	0.096	0.022	0.115	0.005-TTT
06SJG006	0.095	0.096	0.025	0.120	
ITMAE1	Commercial in confidence				

As shown in figure 6.15, the water content of the hydrated samples was similar for all copolymers produced, with the exception of 05SJG048 and ITMAE1 which contained AMX and had reduced water content. Sample 06SJG006 with no crosslinker, had a very poor dimensional stability, and the addition of TT or TTT improved the dimensional stability only slightly. The dimensional stability of the material with AMX (05SJG048) was further improved over the materials with TT and TTT, though not enough to be considered ideal as a solid polymer electrolyte when compared to the proprietary ITMAE1 which is also known to contain AMX.

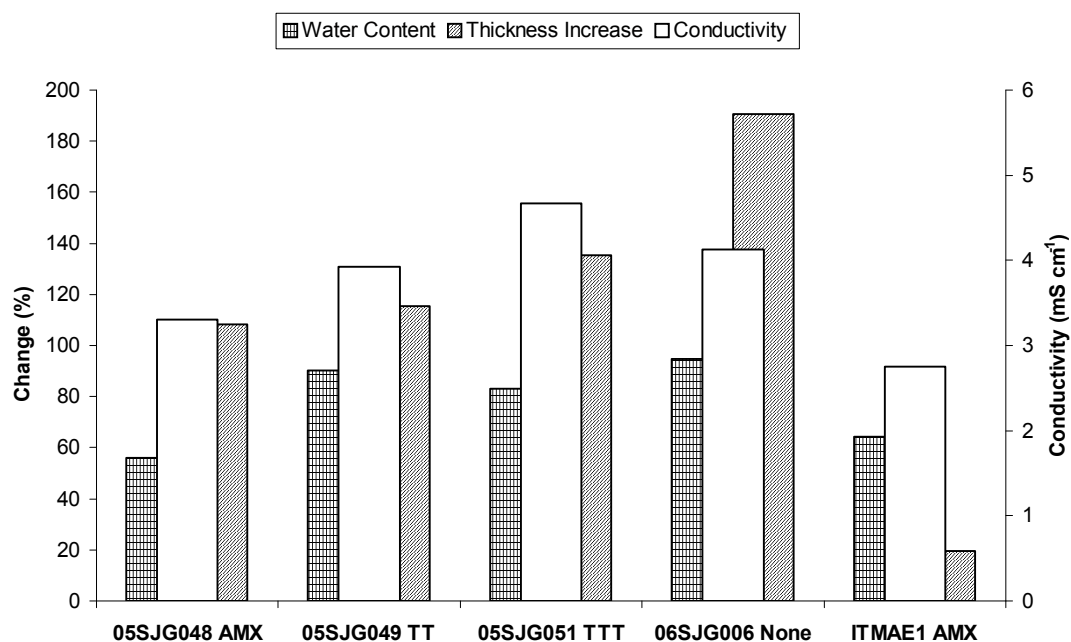


Figure 6.15: effects of crosslinking agent on VPy system

Unsurprisingly, given the similar water contents of the copolymers, the difference in conductivity was small.

Although the same mass of crosslinker was used, the molarities of the crosslinking sites differed due to molecular weight and number of crosslinking sites. AMX has two sites, giving 0.0198 M of sites in 05SJG048. TT and TTT have three sites, giving approximately 0.015 M of sites in 05SJG049 and 05SJG051. Hence 05SJG048 had nearly one third more available crosslinking sites than 05SJG049 and 06SJG051 and this may account for the low water content and thickness increase changes seen.

6.5.1.1 Effect of Crosslinking Agents on Methanol Permeation in the VPy system

Over a test period of three hours (see chapter 5.5.3) it was noted that sample 05SJG049 had zero methanol permeation, as shown in Figure 6.16. This suggests that copolymers

containing TT may have low methanol permeation rates. Sample 05SJG051 containing TTT also showed low methanol permeation characteristics. Both TT and TTT have 3 active sites, suggesting that the use of 3-dimensional crosslinking agents may lead to copolymers with lower methanol permeation rates.

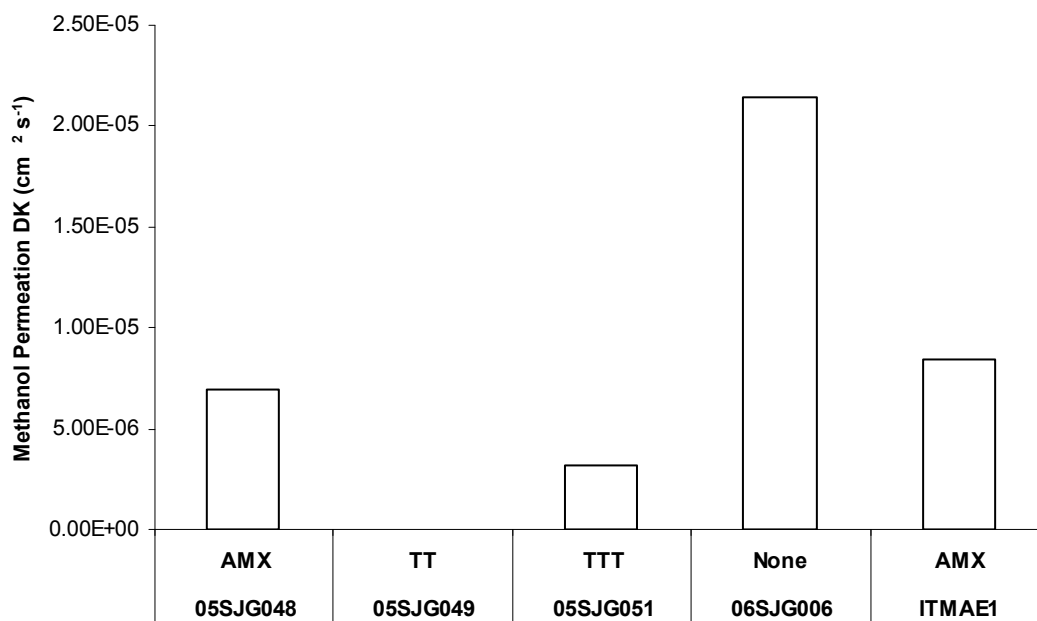


Figure 6.16: Methanol permeation for VPy system with different crosslinking agents

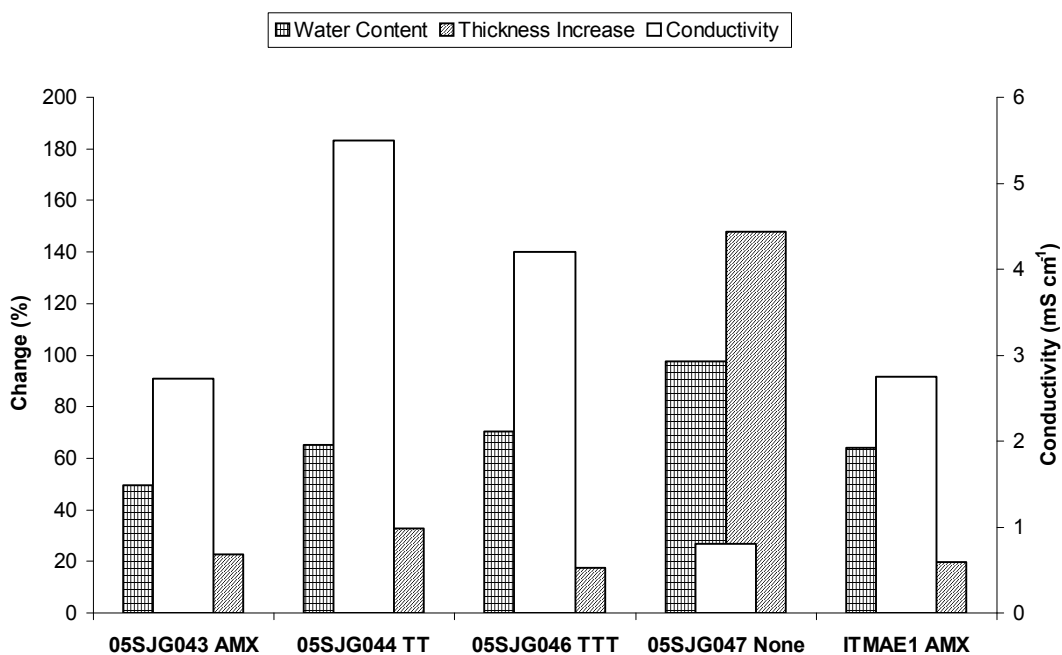
6.5.2 Effect of Different Crosslinking Agents on the MeOX System

Five samples based on the baseline MeOX system as described previously in section 6.3, were produced by gamma radiation with various crosslinking agents. The crosslinking agent was varied, with mass kept constant (1.25 g). Molar compositions of these materials are detailed below in table 6.8.

Table 6.8: Material composition for crosslinking studies of MeOX system

Sample	AN (M)	NVP (M)	MeOX (M)	BV (M)	H ₂ O (M)	Crosslinker (M)
06SJG043	0.095	0.091	0.039	0.015	0.200	0.01-AMX
05SJG044	0.095	0.091	0.039	0.015	0.202	0.005-TT
05SJG046	0.095	0.091	0.039	0.015	0.200	0.005-TTT
05SJG047	0.095	0.091	0.039	0.015	0.198	
ITMAE1	Commercial in confidence					

All samples had increased water content compared to the sample containing allyl methacrylate (AMX) (05SJG043), but lower than 05SJG047 which contained no crosslinking agent. The dimensional stability with the addition of TT and TTT was improved when compared with 05SJG047, as shown in figure 6.17.

**Figure 6.17:** Effect of crosslinker on MeOX system

The ionic conductivity for 05SJG047 was low, which together with a high water content and high thickness increase on hydration, suggested that it suffered from the “dilution effect” as explain earlier in this chapter.

Samples containing TT and TTT had higher conductivities than 05SJG043 and the ITM proprietary sample ITMAE1, which both contained AMX, possibly due to the higher water content.

It is clear that the density of crosslinking inversely affects water content in the MeOX system, i.e. more crosslinks equals lower water content, as can be seen in figure 6.18. From this graph calculations showed that to reduced the water content by 1 %, the number of active AMX crosslinking sites should be increased by 5.6×10^{-6} M.

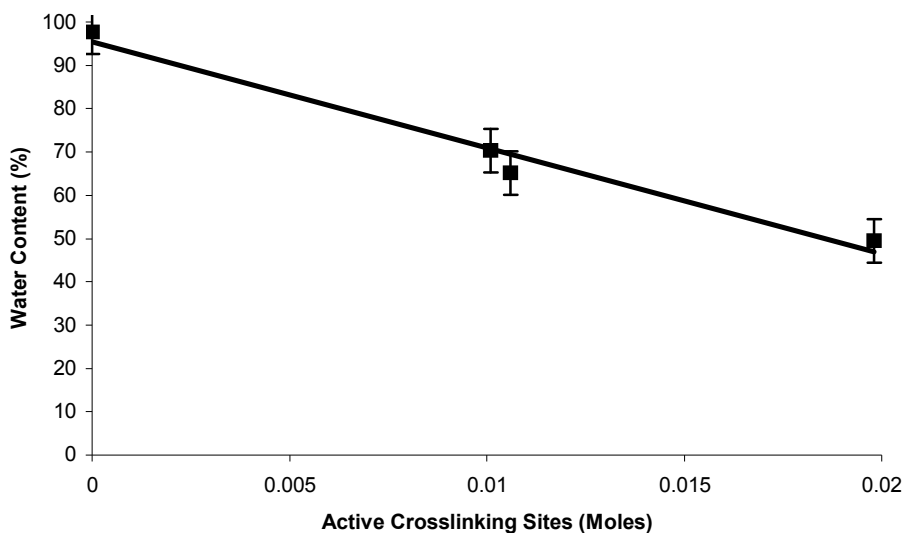


Figure 6.18: Water content against moles of active sites with various crosslinkers.

6.5.2.1 Effect of Crosslinking Agents on Methanol Permeation in the MeOX system

The results of methanol permeation measurements, shown in figure 6.19, show that the ITM proprietary material, ITMAE1, had a high methanol permeation. This suggests it may be unsuitable for use in a direct methanol fuel cell. When compared to sample 05SJG043, also containing AMX, it was clear to see the effect of MeOX on methanol permeation. The sample containing MeOX had a much reduced methanol permeation, suggesting that MeOX forms copolymers with low methanol permeation rates.

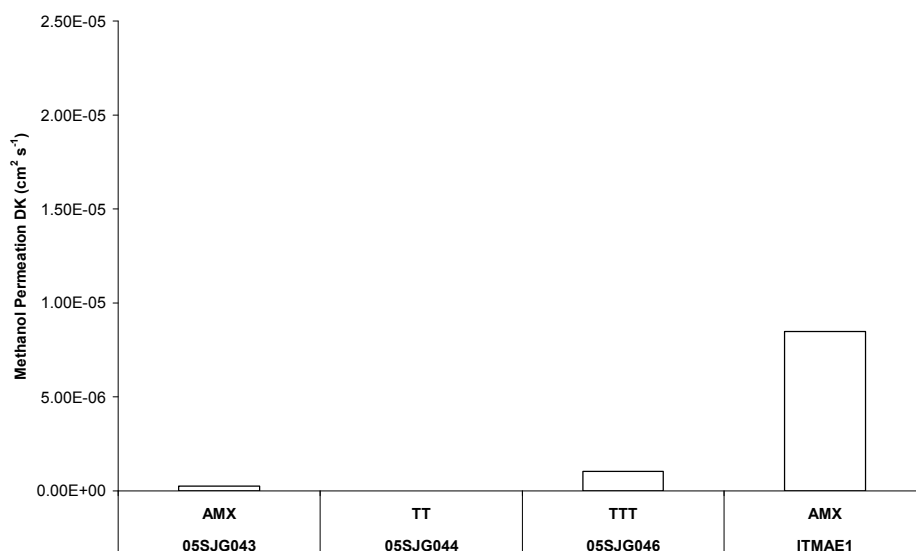


Figure 6.19: Methanol permeation for MeOX system with different crosslinking agents

Sample 05SJG044, containing TT, had zero permeation of methanol over the testing period. This was surprising considering its large conductivity and similar thickness increase and water content to both 05SJG043 and ITMAE1. It suggests that the combination of the MeOX system and TT has excellent methanol permeation barrier characteristics. To examine this further long term methanol permeation testing was undertaken on this sample (See section 6.8)

05SJG046 containing TTT, also had a low methanol permeation rate, although this was still higher than the 05SJG043 with AMX. The AMX crosslinked copolymer ITMAE1 had the worst methanol permeability coefficient.

The large thickness increase in 04SJG047 (no crosslinking agent) led to poor mechanical stability, and as such no further experimentation with the sample was able to be performed.

6.5.3 Comparison of the effects of Crosslinking agents in the VPy and MeOX Systems

Water content in the VPy system generally was much higher than in the MeOX system, suggesting that VPy is more hydrophilic than the MeOX:NVP mix.

Thickness increase in the VPy system was much larger than for the MeOX system, with the exception of the sample with no crosslinking agent. This adds further credence to the suggestion that VPy is more hydrophilic than the MeOX:NVP mix system.

An inverse linear relationship between water content and moles of active AMX crosslinking sites was discovered in the range up to 0.02 moles of active site in the MeOX system. This trend was also observed with differing crosslinking agents.

Ionic conductivity in the VPy system was generally higher than with the MeOX system, with the exception of 05SJG049, which contained TT. This may be due to the increased water content and thickness increase in the copolymers combining to improve ion mobility.

Methanol permeation for the VPy system was much larger than for the MeOX system. This is not surprising in view of the large thickness increase and water content of the VPy system samples.

6.5.4 Summary of Crosslinking Agents

The 2,4,6-triallyloxy-1,3,5-triazine (TT) crosslinked samples 05SJG044 and 05SJG049 showed zero methanol permeation during testing, whilst maintaining high water content, suggesting that TT improves the methanol permeation barrier properties of the copolymers which contain it. MeOX samples had high water content, and low dimensional swelling, but low conductivities, when compared to VPy analogue compositions, though MeOX copolymers had much reduced methanol permeation rates.

6.6 Effect of Crosslinking Radiation

Besides the addition of crosslinking agents during the copolymerisation of the MeOX and the VPy systems, it is widely known that gamma radiation can effectively crosslink a number of polymeric systems^[106].

To evaluate this in the context of this work the thermally polymerised sample 06SJG038 was separated into five pieces (1 control and 4 sets of test samples). The test samples were irradiated at 4.9 kGy h^{-1} , and each material removed at different total doses. The samples were subjected to the same characterisation as discussed earlier, together with a further test to measure the mass loss on solvent extraction as a means of determining the onset of radiation degradation if it occurred.

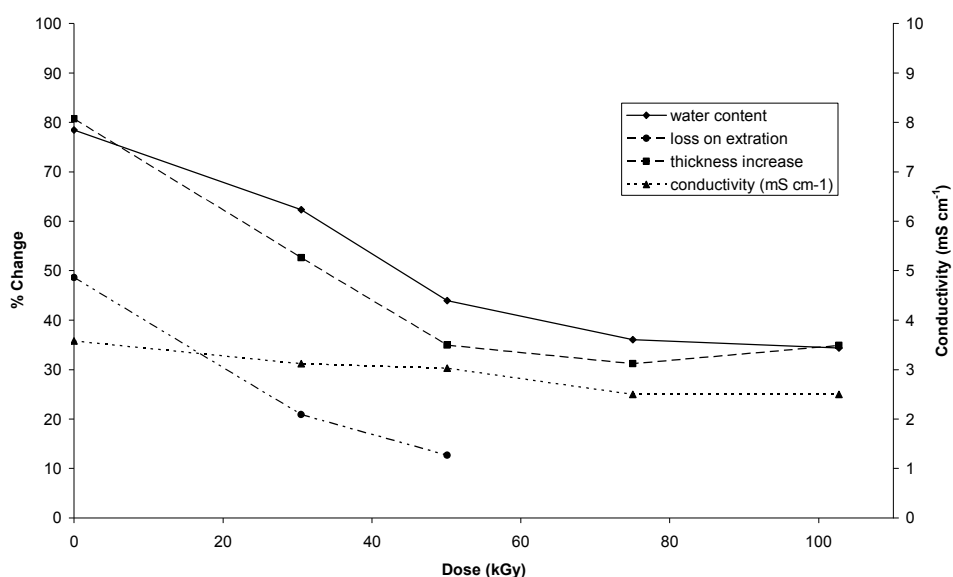


Figure 6.20: Effect of crosslinking radiation on 06SJG038

As can be seen from figure 6.20 the percentage mass loss on extraction was reduced with increased total radiation dose, indicating that no discernable degradation of the polymers occurred up to the maximum dose of 100 kGy.

Conductivity also reduced with increased total dose. Water content decreased as expected, due to the increase in crosslink density.

Of more interest was the effect of radiation dose on methanol permeation. Before radiation the methanol permeation was low ($5.96 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) when compared to standards such as ITMAE1 ($8.49 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) or cationic exchange membranes such as Nafion® 117 ($8.45 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$).

However, further significant reductions were noted as the radiation dose increased as shown in figure 6.21.

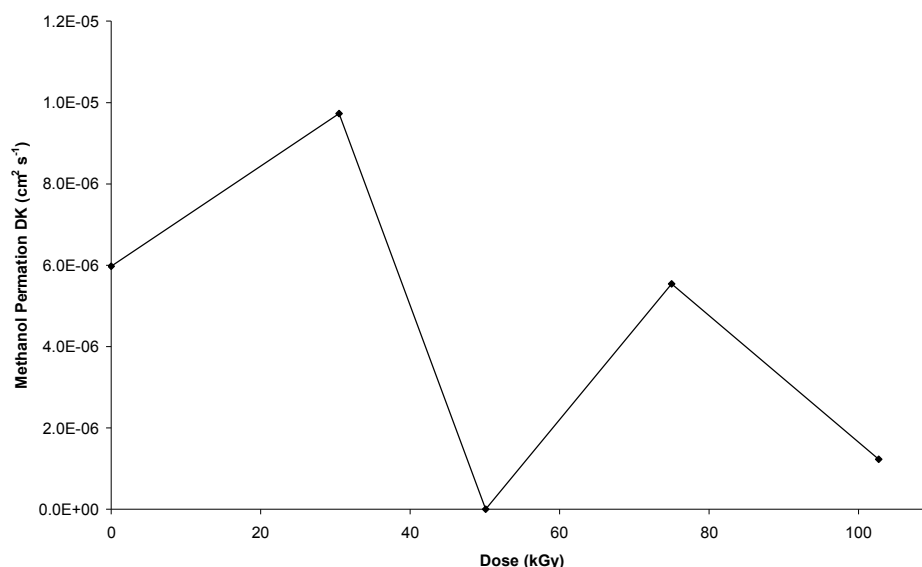


Figure 6.21: Effect of crosslinking radiation on 06SJG038 methanol permeation

No permeation was recorded for 06SJG038 after 50 kGy of radiation and after 3 hours of testing (see further long term testing in section 6.8). This is in accord with Qiao *et al*^[99] who also reported that the methanol permeation barrier could be improved by adjusting the crosslinking density of membranes, in their case using blended polymers and a crosslinking agent rather than radiation.

It is therefore suggested that the cumulative effect of the radiation on 06SJG038 at total doses where the permeation was high was probably chain scission, and where the permeation rates was low was crosslinking.

Two further samples were subjected to radiation doses up to 50 kGy. Figure 6.22 also indicates that for these samples a total dose of 50 kGy can produce materials with zero methanol permeation (as measured over 3 hours), suggesting that thermally polymerised

materials could be beneficially irradiated to a total dose of 50 kGy, to produce very low methanol permeation membranes.

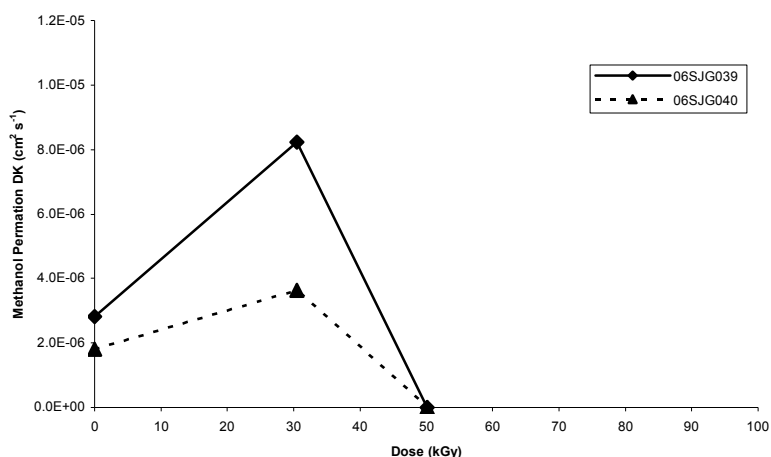


Figure 6.22: Effect of radiation on samples containing MeOX

6.7 Analysis of Extracted Liquors

In order to follow the potential degradation during irradiation of the membrane systems the liquors from the soxhletted materials were analysed by various methods to determine what material was lost on extraction.

6.7.1 HPLC Analysis

HPLC analysis of liquors from sample 06SJG038J (0 kGy) showed a peak with the same retention time as the NVP standard (3.95 mins), suggesting the presence of NVP. This indicated that NVP was not fully copolymerised into the copolymer. No other material was detected. (See appendix D for typical HPLC chromatogram).

Sample 06SJG038K (30.5 kGy) showed a peak with at 3.41 mins, similar to AN at 3.59 mins. The HPLC also had a UV detector as well as the normal FID detector, which showed a comparable UV profile to AN (Sample peak absorption 211 nm, AN standard 213 nm). The UV profile of the sample also had a secondary peak at 261 nm, not seen on any standard, suggesting a new product had been extracted. No other material was detected, indicating that higher total doses of radiation acted to polymerise NVP into the matrix. (See Appendix D for typical UV profile graph). It is possible that the new material seen was a homopolymer of AN, with the extended retention time due to increased molecular weight

Sample 06SJG038L (50.1 kGy) showed a peak with retention time of 5.64 mins. TT standard had a similar retention time of 5.81 mins, but the UV profile of both materials was distinctly different, suggesting that the material detected was not TT. The retention time was longer than small molecules such as AN or VP, suggesting a larger (molecular weight) partially copolymerised product, was responsible.

6.7.2 FT-IR analysis

Analysis of 06SJG038J liquors identified the presence of several key groups which were present in the monomers used to produce the copolymer, as shown in table 6.9. The peaks present suggested that a derivative of TT was extracted from the sample. FT-IR analysis does not conclusively confirm the HPLC data that NVP was also extracted from 06SJG038J. (A typical FT-IR spectrum is shown in Appendix D).

Table 6.9: FT-IR analysis for 06SJG038J

Wavenumber (cm ⁻¹)	Possible Stretch	Possible Source
2980-2850	CH	All monomers
2260-2240	Nitrile (C≡N)	Thermal initiator product (see section 2.3.4)
1470-1450	CH ₂	All monomers
1400-1360	CH ₃	All monomers
1300-1000	Ether (C-O-C)	Ether linkage present in crosslinking agent TT
850-830	1,3,5-tri substituted benzene	Derivative of TT

Liquors from sample 06SJG038K and 06SJG038L showed a spectra with no stretching of the carbon-nitrogen triple bond at 2260-2240 cm⁻¹, no stretch at 1300-1000 cm⁻¹ corresponding to an ether linkage, and the strong stretch at 850-830 cm⁻¹ usually indicative of a 1,3,5-tri substituted benzene was also absent (see table 6.10).

Table 6.10: FT-IR analysis for 06SJG038K and 06SJG038L

Wavenumber (cm ⁻¹)	Possible Stretch	Possible Source
2980-2850	CH	All monomers
1470-1450	CH ₂	All monomers
1400-1360	CH ₃	All monomers

It is possible that a derivative of TT was extracted from the sample with no crosslinking radiation. The results do however corroborate the data from HPLC studies that radiation copolymerises unreacted monomers in the thermally cured materials.

6.7.3 GC-MS Analysis

Gas Chromatography-Mass Spectrometry (GC-MS) experiments were also undertaken on the extracted liquors. MS and daughter ion analysis of large peaks (abundance above 15 %) with high probability matches (above 90 %) are shown in tables 6.11 to 6.13. (A typical GC-MS chromatogram is shown in Appendix D).

Table 6.11: GC-MS analysis of peaks for sample 06SJG038J (0 kGy)

Retention time (mins)	Approximate Relative Abundance	Mass Ion	Suggested Material	Probability (%)
4.06	23	205	Azo-bis-isobutyronitrile (AIBN)	93.2
5.10	100	111	N-vinyl-2-pyrrolidone	90.6
8.15	18	172	2,4,6-trimethoxy-1,3,5-triazine	93.25

Table 6.12: GC-MS analysis of peaks for sample 06SJG038K (30.5 kGy)

Retention time (mins)	Approximate Relative Abundance	Mass Ion	Suggested Material	Probability (%)
4.06	97	199	Azo-bis-isobutyronitrile (AIBN)	92.18
5.09	100	111	N-vinyl-2-pyrrolidone	93.99
8.15	67	172	2,4,6-trimethoxy-1,3,5-triazine	98.00

Table 6.13: GC-MS analysis of peaks for sample 06SJG038L (50.1 kGy)

Retention time (mins)	Approximate Relative Abundance	Mass Ion	Suggested Material	Probability (%)
4.06	68	165	Azo-bis-isobutyronitrile (AIBN)	94.6
5.09	52	111	N-vinyl-2-pyrrolidone	92.0
8.15	43	172	2,4,6-trimethoxy-1,3,5-triazine	94.4

The NVP peak present in sample 06SJG038L was reduced in comparison with the other samples. Polymerisation products such as undecane were seen in 06SG038K and 06SJG038L at low abundances.

6.7.4 Summary of Extraction Analysis

Summarising the results of the sample analysis it can be said that:

- NVP was not fully polymerised in sample 06SJG038J. It is also suggested that analogues of AIBN and TT were extracted from the copolymer.
- NVP was not fully polymerised in samples 06SJG038K or 06SJG038L. polymerisation products were seen but it was difficult to confidently predict which materials they might be.
- NVP was present in the eluate (06SJG038J) and was thus not fully incorporated in the unirradiated sample.
- Crosslinking radiation produced unknown materials with similar properties or functional groups to the monomer reagents, which were extracted from the copolymer. Analysis of the exact nature of these materials was inconclusive.

6.8 Long Term Methanol Permeation Testing

Various samples were noted to have unmeasurable (very low) methanol permeation rates during the normal 3-hour test period. Extended methanol permeation studies were therefore undertaken on two of these samples, 06SJG038 (50 kGy) as discussed in section 6.5 and sample 05SJG044 (crosslinker TT) as previously discussed in section 6.4.2.1. This was

carried out in order to determine at what point (if any) methanol permeation occurred and any consequent permeation rate of the materials.

The test conditions were kept the same as previously with an aliquot of sample taken every 90 mins for 8 hours and its refractive index measured. After 8 hours of testing the cell was left running for a total of 24 hours and a further aliquot taken.

For sample 06SJG038I it was observed that it took 6.5 hours before any measurable permeation occurred. Permeation over the next few hours occurred at a slower rate than other materials such as Nafion® 117. The average permeation rate over 24 hours was low and found to be $1.06 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, compared to Nafion® 117 ($8.45 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$).

No methanol permeation over 8 hours was observed for sample 05SJG044, but after 24 hours the average permeation rate was found to be $1.31 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, which was still lower than Nafion® 117.

The results suggest that these materials which show zero permeation over 3 hours could be utilised in a direct methanol fuel cell with a higher concentration of methanol (>10 M) than normally considered possible with existing membranes, which would suffer unacceptable parasitic methanol crossover at such high concentrations.

6.9 Membrane Production for Fuel Cell Testing

Both VPy and MeOX system materials were produced by thermal initiation in the form of membranes, as discussed in section 5.1.5. The materials were split into smaller sections and

various radiation treatments undertaken prior to hydration for characterisation and fuel cell testing.

It was observed upon hydration that the physical stability of the membranes containing VPy was poor. The materials broke on handling and were unable to be tested in a fuel cell environment. Therefore at this stage the VPy system was discarded from further testing and only the MeOX system was carried forward.

6.10 Fuel Cell Testing

Initial fuel cell testing was undertaken with a small circular cell (electrode area 0.785 cm^2). However a number of difficulties were found when using this cell, particularly in the ability to ensure good electrical contact between the MEA and the cell electrodes. To overcome this problem further testing was undertaken with a fuel cell with Poco graphite current collectors, with a flow field design machined into each collector as pictured in figure 6.23. The active area of this cell was 12.25 cm^2 .

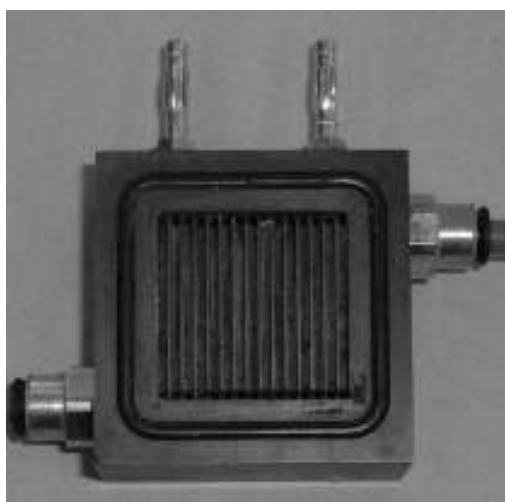


Figure 6.23: Flow field plate for fuel cell

For comparison the 2 commercial membranes ADP-100 and Nafion ® 117 were included as benchmarks.

Using the set-up described in chapter 5 and figure 5.9 the membranes given in table 6.14 were tested. The choice of the membranes for testing was made on the basis of the properties of high conductivity, low methanol permeation and good dimensional stability.

The test conditions, as discussed in section 5.6, were as follows:

- MEA made from Lyntech carbon cloth with 5 mg cm^{-2} platinum black (Pt) on the cathode and 5 mg cm^{-2} platinum/ruthenium (Pt/Ru) on the anode.
- The aqueous fuel (4 M MeOH/ 1 M NaOH) was fed to the anode side of the cell at 3.5 mL min^{-1} , and the cathode supplied with non-hydrated oxygen, standard temperature and pressure at 50 mL min^{-1} .

It was expected that open circuit voltages (OCV) would not be close to the theoretical maximum of $\sim 1.2 \text{ V}$, due to non-optimised construction of the MEA and the subsequent affect on catalysis. OCV's were expected to be in the range $0.7\text{-}1.0 \text{ V}$ (as reported in the literature). As regards energy density it was expected that, because the materials were of high anionic conductivity and low methanol permeation, high concentrations of methanol could be used, and energy densities in the region of 10 mW cm^{-2} would be achieved.

Table 6.14: Samples tested under alcohol fuel cell conditions

Membrane No.	Membrane Composition	Radiation Dose (kGy)	Conductivity (mS cm ⁻¹)	Methanol Permeation (cm s ⁻¹)	Thickness Increase (%)
06SJG038O	MeOX/TT	50.1	4.9	Below measurable limit ^o	31.1
06SJG038P	MeOX/TT	0.0	3.1	3.38x10 ⁻⁶	18.4
06SJG041J	MeOX/X	0.0	7.9	Below measurable limit ^o	9.4
06SJG041K	MeOX/X	50.1	6.8	Below measurable limit ^o	70.0
06SJG041M	MeOX/X	0.0	6.4	Below measurable limit ^o	68.7
ADP-100	AEM	0.0	2.4	3.63x10 ⁻⁶	7.8
Nafion® 117	CEM	0.0	43.7	8.45x10 ⁻⁶	9.3

The open circuit voltage (OCV) of 06SJG038O reached a constant voltage of 0.55 V after 30 mins at 24 °C and the polarisation curves were taken after equilibration at OCV. The results are shown graphically in figure 6.24 for cell temperatures of 24 °C, 70 °C and 80 °C (the current-voltage curves refer to the left hand axis, the power-current curves to the right hand axis).

^o Over 3 hour test period

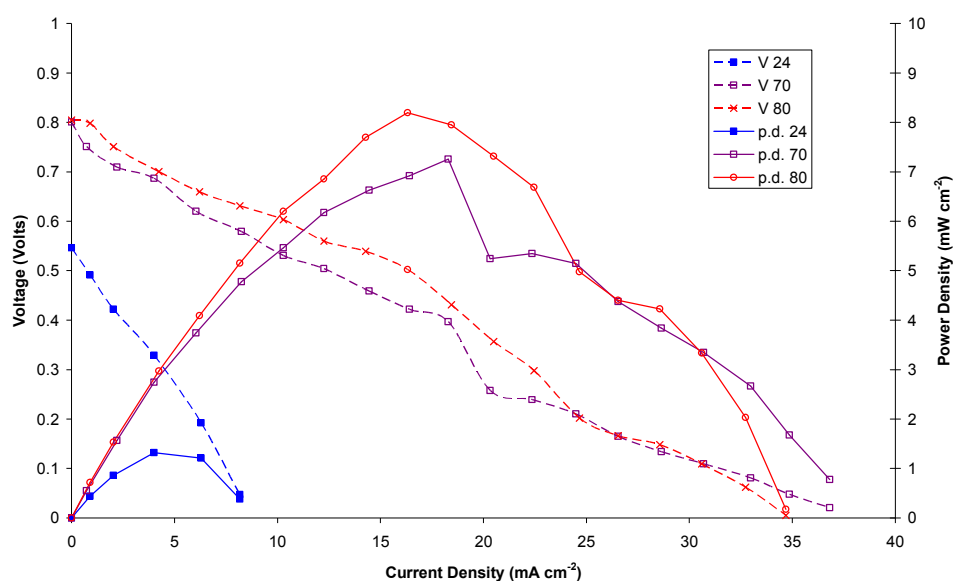


Figure 6.24: Comparison of polarisation curves for 06SJG038O at various temperatures

Clearly as temperature increased OCV and peak power density (p.d.) increased, mostly likely due to faster electrode kinetics of the catalyst.

As the methanol permeation of 06SJG038O had been previously shown to be low, the concentration of methanol in the fuel was increased to 10 M, whilst keeping the hydroxide concentration constant at 1 M.

The results are shown graphically in figure 6.25 for cell temperatures of 24 °C, 61 °C and 81 °C, and the effect of temperature can clearly be seen. The effect on p.d. of the increased methanol concentration is small but significant and is shown more clearly in figure 6.26.

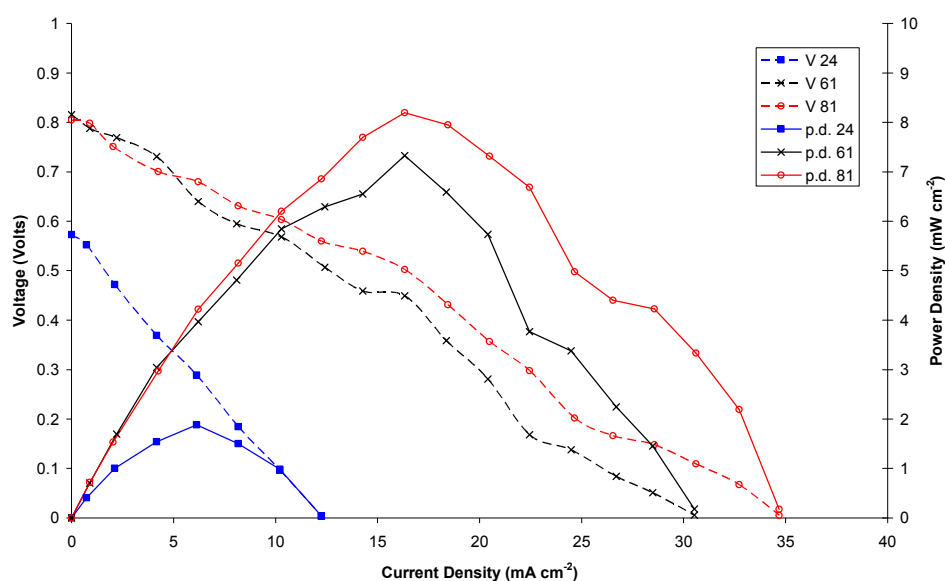


Figure 6.25: Comparison of polarisation curves for 06SJG038O at various temperatures with 10 M MeOH/1 M NaOH

However, at lower temperatures, the OCV was higher with low methanol concentrations.

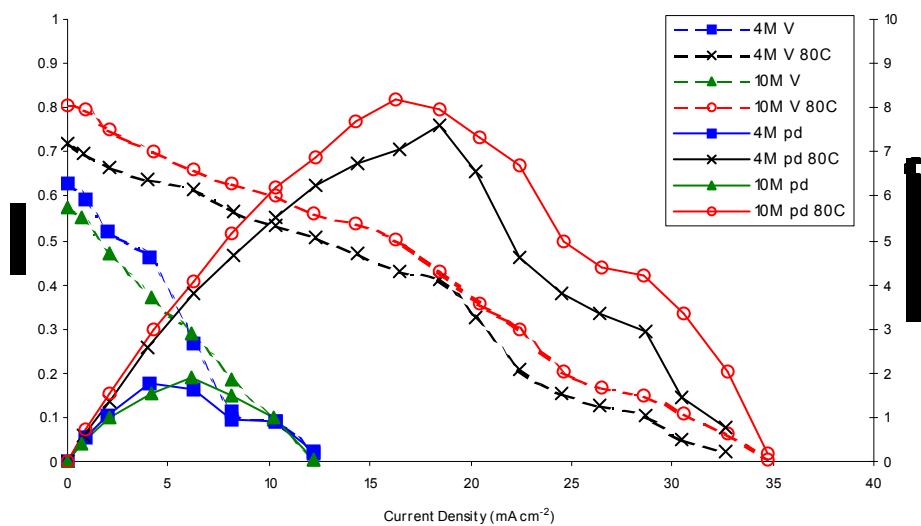


Figure 6.26: Comparison of polarisation curves for 06SJG038O at approx 24 °C and 80 °C with various molarities of methanol fuel

This may be because pure methanol is a desiccant and as such very high aqueous concentrations may have removed water from the membranes and caused an increase in the membrane resistance and hence a reduction in conductivity.

To test this, the cell was left to equilibrate with 24.14 M[‡] methanol overnight in a static fashion, and after 16 hours the OCV had risen to 0.75 V. No sign of mass methanol crossover was evident, with the oxidant waste pipe dry.

However, further testing was not possible due a hole in the membrane (noted upon removal). The cathode and MEA was dry, suggesting no methanol permeation had taken place. The anode was also dry suggesting that even when supplied with fresh fuel the membrane was drying out. It became apparent that the internal resistance of the cell had risen overnight, causing a poor cell performance.

It was also noted that the catalyst cloth had swollen into the flow channels of the cell (see figure 6.27). This was more pronounced on the cathode side of the MEA.



Figure 6.27: 06SJG038O MEA after cell testing

[‡] Pure methanol is 24.72 M.

The membrane 06SJG038P had a slightly lower conductivity than 06SJG038O but with 4 M MeOH/ 1 M NaOH showed a slightly higher OCV both at 24/25 °C and at 60/61 °C. However the max p.d at 60/61 °C for 06SJG038O was significantly higher than 06SJG038P. Figure 6.28 shows the data from polarisations at 25 °C, 50 °C and 60 °C for 06SJG038P. Once again the effect of temperature can be seen.

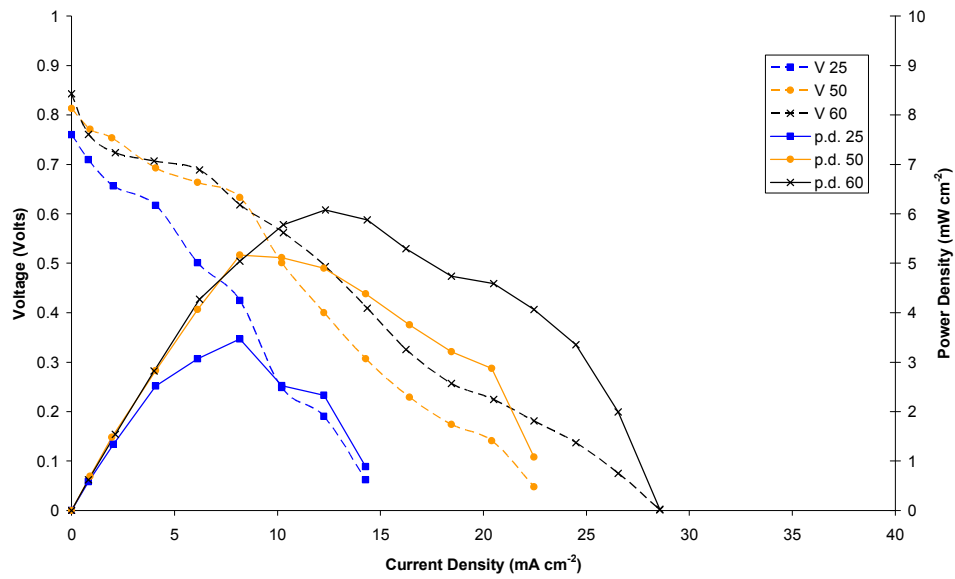


Figure 6.28: Comparison of polarisation curves for 06SJG038P for various temperatures

Prabhuram *et al*^[110] suggested the optimum methanol:hydroxide ratio was 1:1, and that peak p.d. could be achieved with 6M concentration. To test this hypothesis the fuel feed to 06SJG038P was changed to 6 M MeOH/ 6 M NaOH.

The OCV increased to 0.92 V and then stabilised at 0.86 V at 25 °C. However, a full polarisation was not possible. The MEA was removed from the cell and a tear through the membrane was noted (see Figure 6.29). This would have allowed fuel to cross the cell.

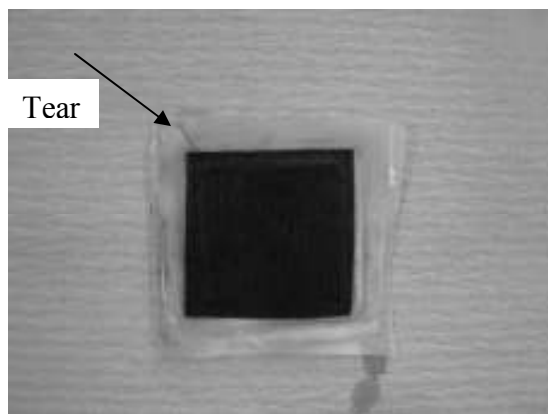


Figure 6.29: 06SJG038P MEA after fuel cell testing. Tear visible in top left hand corner.

Upon drying sodium hydroxide crystallised on both anode and cathode (see figure 6.30) and was suspected that the membrane had degraded in the concentrated alkali solution.

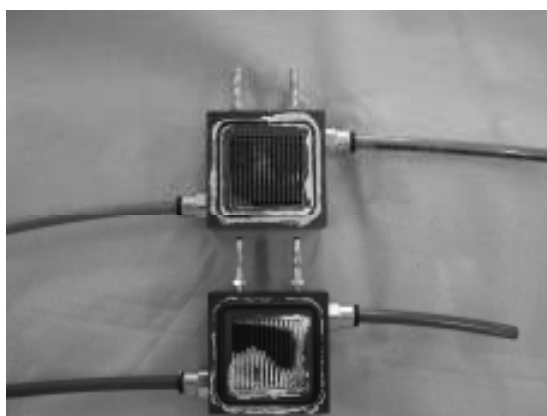


Figure 6.30: Top-anode, Bottom-cathode after contact with 6M MeOH/6 M NaOH solution

To examine this possibility the membrane was placed in 6 M MeOH/ 6 M NaOH electrolyte for 48 hours at 40 °C. The material lost 33.6 % of its mass and 6.5 % in thickness. Further investigation revealed the work of Bauer *et al*^[34] who suggest that the degradation of materials containing quaternary ammonium ions, such as in 06SJG038P, in the presence of a strong alkali, takes place by the Hoffman degradation.

The membrane 06SJG041J is a MeOX copolymer with higher conductivity than either 06SJG038O or 06SJG038P. The polarisation curve of 06SJG041J at 24 °C with 4 M MeOH/ 1 M NaOH is shown in figure 6.31.

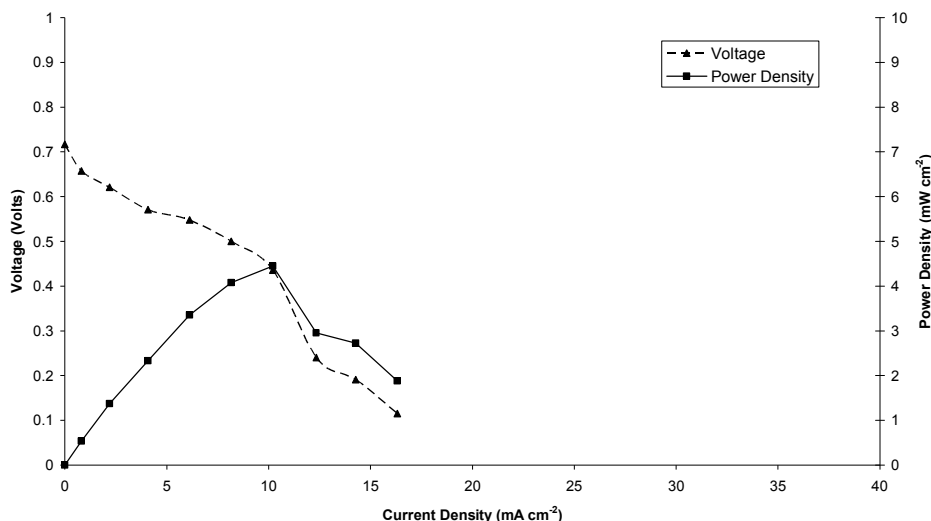


Figure 6.31: Polarisation curve of 06SJG041J

Increasing the methanol and sodium hydroxide concentrations to 6 M MeOH\ 6 M NaOH had the effect of increasing the peak OCV to a stable 0.93 V at 25 °C. However as before, no current could be drawn from the cell, and removing the MEA from the cell revealed a hole consistent with membrane degradation. Once again the change to a high concentration alkaline fuel may have caused damage to the membrane.

The material 06SJG041K had similar conductivity, and methanol permeation characteristic to 6SJG041J. In the fuel cell tests a clear trend between temperature and OCV and peak p.d. was established as can be seen in figure 6.32. For clarity, figure 6.33 shows the effect of temperature on the maximum power density achieved with 06SJG041K using 4M MeOH/1 NaOH as the fuel.

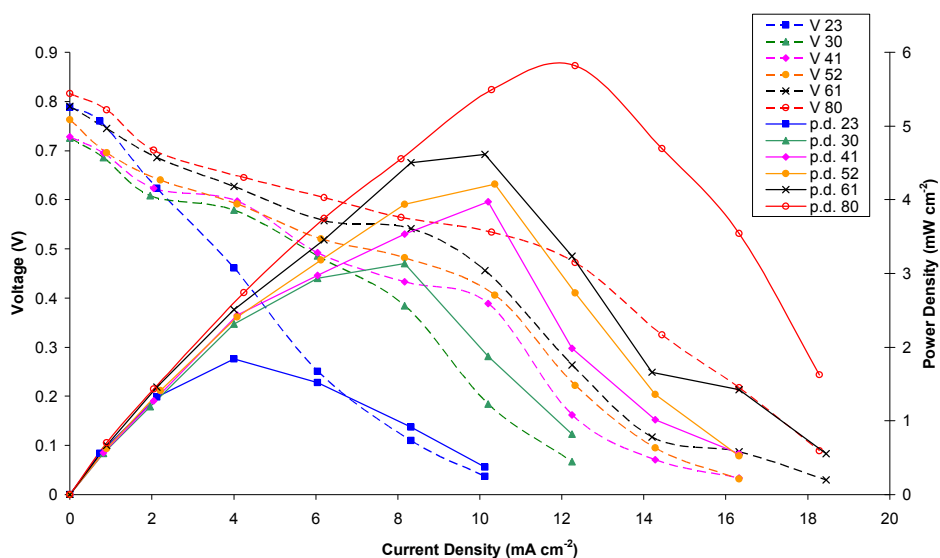


Figure 6.32: Comparison of polarisation curves at various temperatures for 06SJG041K (note reduced axis compared with similar figures, for clarity of presentation)

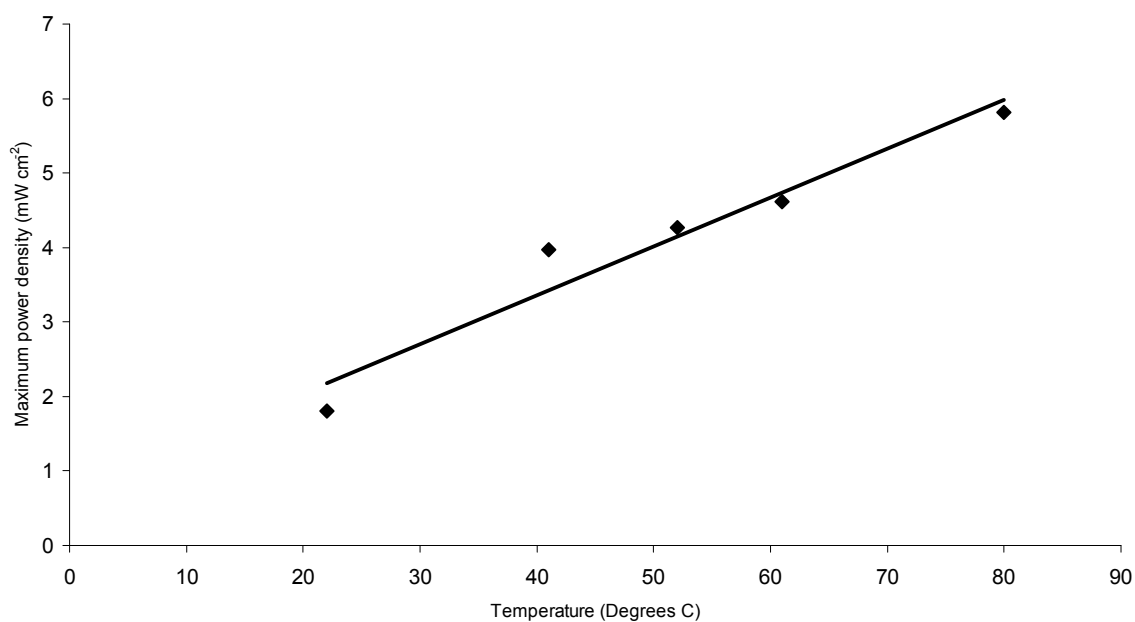


Figure 6.33: Temperature versus max power density for material 06SJG041K with 4M MeOH/1M NaOH

The highest OCV and peak p.d. was achieved at 80 °C, 0.816 V and 5.82 mW cm⁻² respectively.

06SJG041M was similar in composition to 06SJG041J and 06SJG041K. Polarisation curves were undertaken at 25 °C, 60 °C and 80 °C, as shown in figure 6.34.

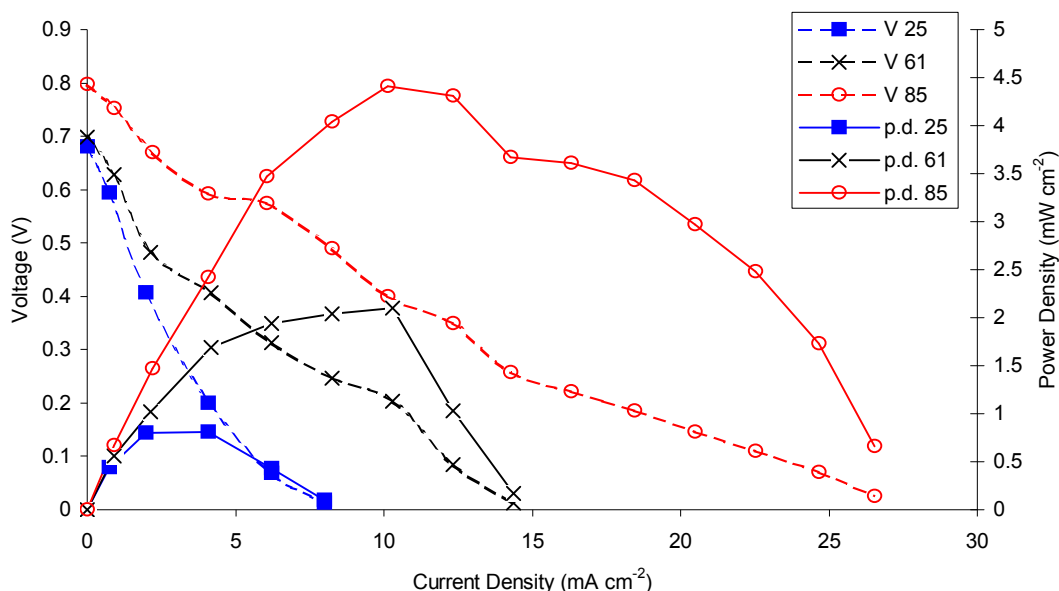


Figure 6.34: Comparison of polarisation curves for 06SJG041M at various temperatures, note reduced axis for clarity of graph.

As expected the highest OCV and peak p.d. was achieved at 80 °C, 0.798 V and 4.31 mW cm⁻² respectively. It is interesting to note that an increase in temperature from 25 °C to 61 °C increased the peak p.d. by only 0.46 mW cm⁻², whereas the smaller rise in temperature, from 61 °C to 80 °C lead to an increase in peak p.d. of 2.21 mW cm⁻². This is almost certainly because the activation energy for methanol reduction is temperature dependant.

Increasing the methanol concentration of the fuel to 10 M, while keeping and the sodium hydroxide concentration constant, gave the polarisation data as shown in figure 6.35.

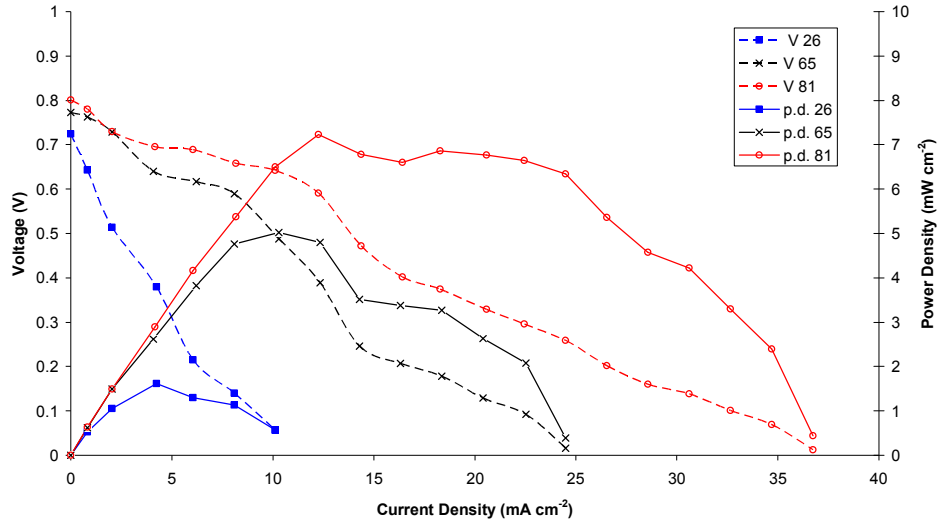


Figure 6.35: Comparison of polarisation curves for 06SJG041M at various temperatures with 10 M MeOH/ 1 M NaOH

The increase in methanol concentration does not affect OCV significantly, peak p.d. though at 81 °C was 7.24 mW cm^{-2} , up from 4.31 mW cm^{-2} with the lower MeOH concentration.

It is interesting to note that the peak p.d. at 65 °C with 10 M methanol is higher than that at a lower concentration (4 M methanol) at higher temperature, 85 °C, as shown by figure 6.36. This indicates that MeOH concentration may influence the cell output more than its operating temperature.

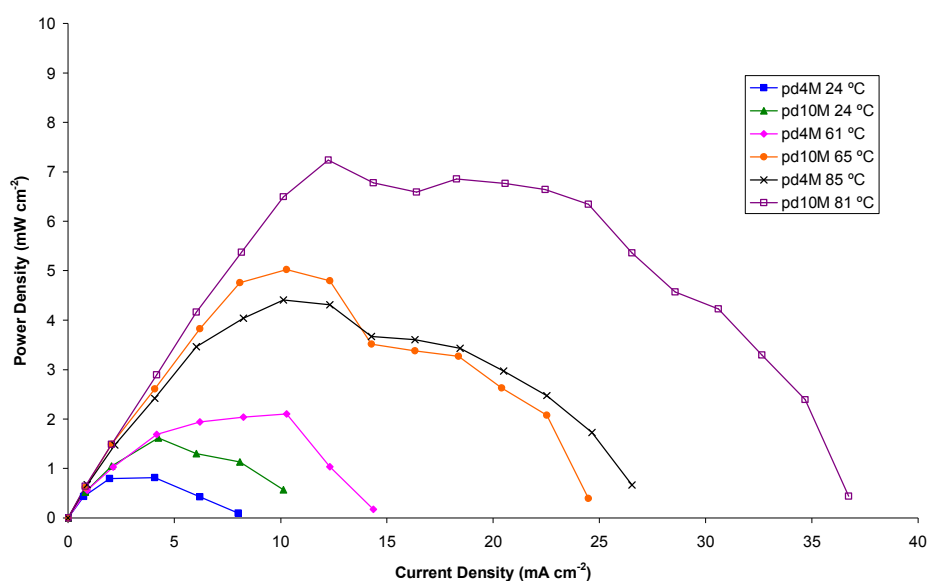


Figure 6.36: Comparison of power curves for 04SJG041M at various temperatures with 2 different fuel concentrations

More work on these materials would certainly lead to higher power densities. In particular the areas of improvement should be in the thickness uniformity of the membrane, a reduction in membrane thickness, thus its decreasing resistance, more reproducible MEA construction, leading to better three phase contact at the membrane-electrode interface and more accurate control of the level of hydration on the cathode.

As a benchmarking exercise the anionic exchange membrane ADP-100 from Solvay was tested under similar conditions. Polarisation using 4 M MeOH\ 1 M NaOH at 23 °C, 40 °C and 80 °C are shown in figure 6.37.

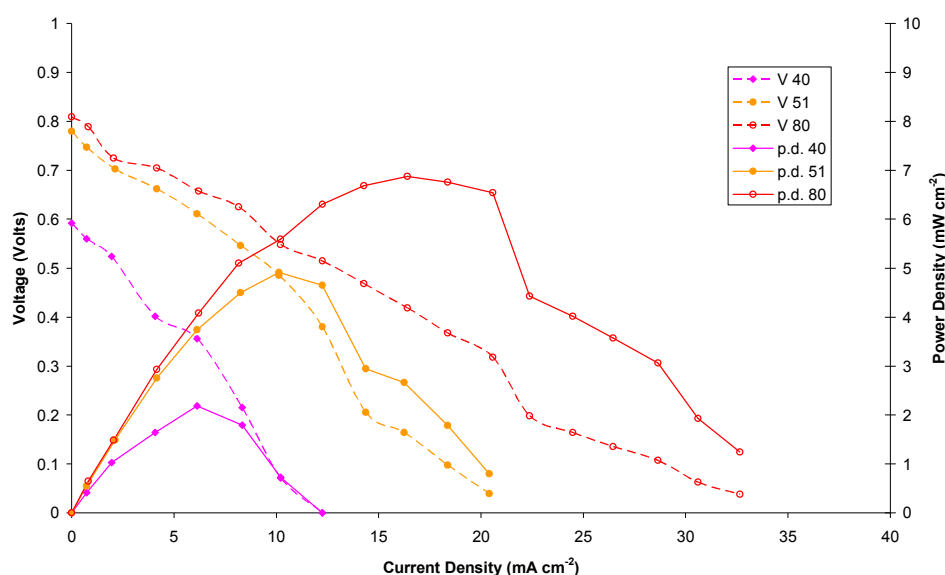


Figure 6.37: Comparison of polarisation curves for ADP-100 at various temperatures

The data from this graph show a peak OCV of 0.81 V and max p.d. of 6.9 mW cm^{-2} at 0.421 V at 80 °C. This is slightly lower than the data of Yu *et al*^[56]. They found a peak p.d. of 11.7 mW cm^{-2} with a lower concentration of methanol fuel 2 M MeOH/1 M NaOH. However, importantly, Yu also found that ADP was unstable in alkali solution and the peak p.d. dropped with time, which was also noted with the ADP-100 used here.

Also used as a benchmark was the commercial membrane Nafion® 117. As explained in chapter 2 this is a cationic exchange membrane, but it has been widely reported in the literature for all types of fuel cell operations. It has been included in this project simple to be able to compare any advances in membrane technology. The results of the performance of Nafion® in the project alkaline DMFC are shown in figure 6.38 for a fuel composition of 4 M MeOH/1 M NaOH.

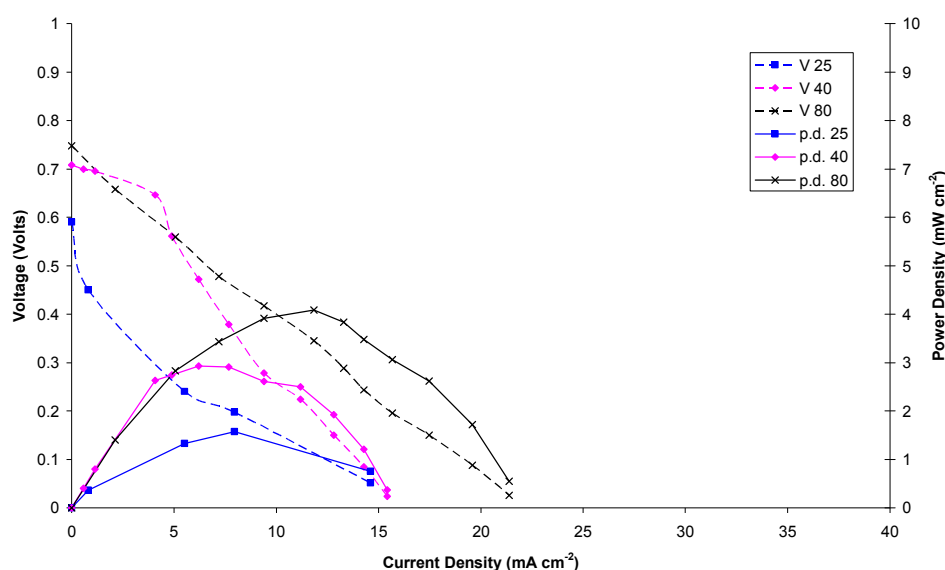


Figure 6.38: Comparison of polarisation curves for Nafion® 117 at various temperatures

As reported for the new membranes the effect of temperature on the power densities can be seen. Not shown in the figure, but importantly noted, was the fact that the peak p.d. reduced with time, probably due to the permeation of methanol across the membrane.

6.10.1 Comparison of Project Materials to Benchmark Standards

The cationic exchange membrane Nafion® 117 is known to have high methanol permeation, and therefore testing at high methanol concentrations was not undertaken. The peak power density (p.d.) at $\sim 80\text{ }^{\circ}\text{C}$ with 4M MeOH / 1 M NaOH (4.1 mW cm^{-2}) was lower than that of anionic exchange membranes such as ADP-100 (6.9 mW cm^{-2}) and 06SJG038O (7.6 mW cm^{-2}).

It is interesting to note that, at this methanol concentration, ADP-100 had a lower p.d. than 06SJG038O, but when the concentration was increased to 10 M MeOH, ADP-100 had a

higher p.d. However, the rise in MeOH concentration produced a serious side effect on the cell. Visible amounts of liquid (assumed to be methanol) were seen on the cathode after a few minutes and the peak p.d. of the cell dropped below that of 06SJG038O. This is in accord with the measured methanol permeation results where it was shown that ADP-100 had a higher MeOH permeation rate than 06SJG038O.

Examination of the ADP-100 MEA after removal from the fuel cell revealed that the membrane had discoloured to a brown colour, consistent with degradation of the polymer as reported by Yu *et al*^[56].

6.10.2 Comparison of Fuel Cell Tests

Table 6.15 below summarises the fuel cell data from the testing in section 6.8, 6.9 and 6.10.

6.10.3 A Comment on the Separators Incorporated in the MEAs

Samples 06SJG041J and 06SJG041M were made from the same copolymer composition, but containing different separator cloths. 06SJG041J used a woven hydrophilic nylon separator, whereas 06SJG041M used a nylon felt cloth. Both underwent testing at 25°C with 4 M MeOH / 1 M NaOH. Open circuit voltage (OCV) for the materials were similar (06SJG041J-0.717 V, 06SJG041M-0.719 V). However, the maximum-recorded power density (p.d.) was higher in the sample with the nylon woven cloth (06SJG041J-4.45 mW cm⁻², 06SJG041M-1.64 mW cm⁻²).

Table 6.15: Fuel cell test results

Sample	ADP-100			06SJG038P				06SJG038O								
System	AEM			MeOX / TT				MeOX / TT								
Separator	None			None				None								
Radiation (kGy)	None			None				50.1								
Fuel conc. (M)	4			4				24.14		10			4			
Temp (°C)	80	51	23	50	60	50	25	60	24	81	61	24	80	70	24	
OCV (V)	0.81	0.78	0.57	0.55	0.84	0.81	0.75	0.83	0.73	0.82	0.82	0.60	0.80	0.80	0.66	
Max p.d. (mW cm ⁻²)	6.88	4.91	0.03	2.06	6.08	5.2	3.84	N/A [∞]	2.33	8.20	7.33	1.77	7.62	7.26	1.89	
Voltage at max p.d. (V)	0.42	0.49	0.29	0.33	0.49	0.63	0.38	N/A [∞]	0.38	0.50	0.45	0.29	0.41	0.40	0.46	

[∞] Unable to obtain data due to cell failure

Sample	Nafion® 117			06SJG041M						06SJG041K						06SJG041J
System	CEM			MeOX / X						MeOX / X						MeOX / X
Separator	None			Felt						White						White
Radiation (kGy)	None			None						50.1						None
Fuel conc. (M)	4			10			4			4						4
Temp (°C)	80	40	25	81	65	26	80	61	25	80	61	52	41	22		24
OCV (V)	0.75	0.71	0.59	0.80	0.77	0.73	0.80	0.70	0.72	0.82	0.79	0.77	0.73	0.78		0.72
Max p.d. (mW cm ⁻²)	4.08	2.93	1.57	7.24	5.01	1.61	4.31	2.10	1.64	5.82	4.62	4.27	3.97	1.80		4.45
Voltage at max p.d. (V)	0.35	0.47	0.20	0.59	0.49	0.38	0.35	0.20	0.40	0.47	0.46	0.41	0.39	0.45		0.44

Table 6.15: Fuel cell test results (Continued)

The felt may have also caused a wicking effect of the liquid fuel into the MEA, placing physical strain on the polymer membrane. This resulted in polymer chain scission leading to break up of the membrane, as shown in figure 6.39.



Figure 6.39: Sample showing break-up of membrane due to physical stress after hydration

By contrast no physical break up of samples containing the woven nylon cloth was observed, suggesting that a wicking felt is a poor choice of material for imparting strength to a membrane and may have adverse effects on a materials performance in a fuel cell.

6.10.4 A Comment on the use of Crosslinking Radiation for Fuel Cell Membranes

As shown previously in section 6.6 sample 06SJG038 containing MeOX and receiving 50 kGy of radiation had lower methanol permeation than the equivalent sample receiving no dose. The improved performance at 24 °C may therefore be due to the lower methanol permeation of the crosslinked material.

6.10.5 Comparison of Fuel Cell Data Collected During this Project and Literature

Comparison of testing to literature values proved to be difficult due to differences in the testing procedures used. There were differences in preparation of the membrane and MEA,

(such as hydration of the membrane, size of MEA and type and loading of catalyst cloth), differences in fuel cell and flow field design (such as serpentine flow field, parallel flow, square cell, circular cells) and finally different test conditions for operation of the cell (such as temperature, pressure, fuel concentration, hydration of oxidant). These varied operating conditions inevitably lead to a somewhat confusing picture for the direct comparison of fuel cell membrane materials.

Overcoming this problem would entail a standardised test for direct methanol fuel cell materials. A suggested ideal standard test (which excludes the design details of the cell, which are beyond the scope of this project) could be:

- Membrane hydrated in demineralised water for 24 hours at 25 °C.
- Production of an MEA using 5 mg cm⁻² Pt/Ru catalyst cloth on cathode and 5mg cm⁻² Pt catalyst cloth on anode. Catalyst cloth placed on membrane without pressure, heat or interfacial material such as Nafion® solution.
- Cell should be tightened to a given torque.
- Anode supplied with 99.9 % oxygen non-humidified at 50 mL min⁻¹ at 1 atm and 25 °C.
- Cathode supplied with aqueous 4 M methanol / 1 M sodium hydroxide at 5 mL min⁻¹ at 1 atm and 25 °C.
- Materials left in fuel cell environment at 25 °C at OCV for 1 hour to equilibrate.
- Polarisation curve taken at current increase of 1 mA s⁻¹.

6.11 Electrolyser Testing

Having evaluated a range of membrane direct methanol fuel cell, one membrane was tested in a water electrolyser as described in chapter 5. Membrane 06SJG044 was a MeOX based copolymer, thermally cured and crosslinked by gamma radiation (50 kGy). The test was an initial screening test and not intended to be as exhaustive as the fuel cell tests.

The electrolyte used for the initial test was deionised water. The relationship between voltage and current for 06SJG044 at 24 °C is shown in figure 6.40.

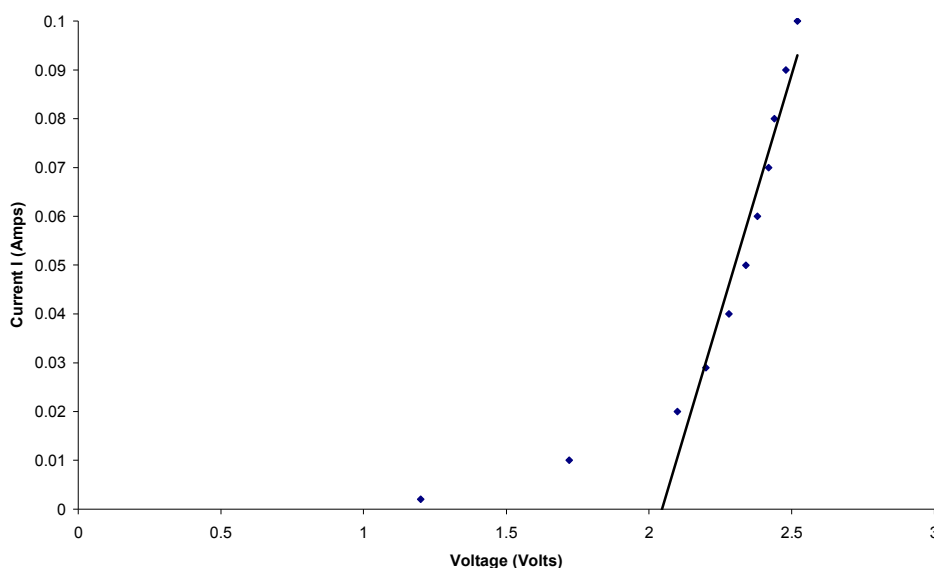


Figure 6.40: Current-voltage characteristic of electrolyser with material 06SJG044

Current did not begin to flow until approximately 1.2 V which is very close to the theoretical decomposition voltage of water (1.23 V)^[111]. The actual decomposition voltage however is given by the point of intersection of the steeper line and the abscissa, in this case approximately 2.1 V. Initial gassing on both sides of the membrane was observed at 2.4 V and 5 mA cm⁻², confirming the high decomposition voltage. This is much higher than

the theoretical decomposition of water and is most probably due to overvoltages at the electrodes and the resistance of the electrolyte^[112].

The electrolyser was left at 6.25 mA cm^{-2} for approximately 80 mins. As can be seen in figure 6.41 the working voltage of the electrolyser rose from 2.56 V to 2.60 V. The gases produced were collected and tested qualitatively, hydrogen giving a characteristic ‘pop’ with a lighted spill at the cathode, and the oxygen relighting a glowing splint at the anode. The amount of gas produced in at the cathode was $2.30 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1} \text{ mW}^{-1} \text{ cm}^{-2}$ (hydrogen) and at the anode $9.88 \times 10^{-4} \text{ cm}^3 \text{ s}^{-1} \text{ mW}^{-1} \text{ cm}^{-2}$ (oxygen), though quantitative analysis of the gases was not undertaken in these preliminary tests.

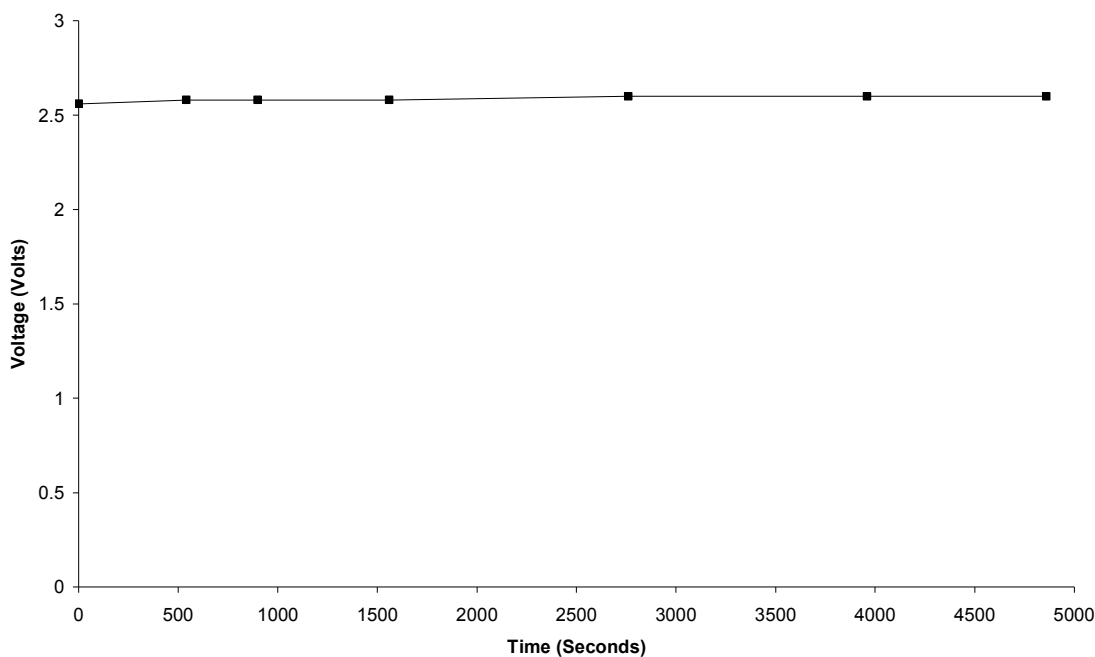


Figure 6.41: Voltage with time for material 06SJG044

Leaving the electrolyser for 24 hours to equilibrate reduced the decomposition voltage to approximately 1.99 V (see figure 6.42). An operating voltage of 2.62 V was stable for 35

minutes at 6.25 mA cm^{-2} , producing hydrogen at a rate of $2.29 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1} \text{ mW}^{-1} \text{ cm}^{-2}$ and oxygen $1.14 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1} \text{ mW}^{-1} \text{ cm}^{-2}$.

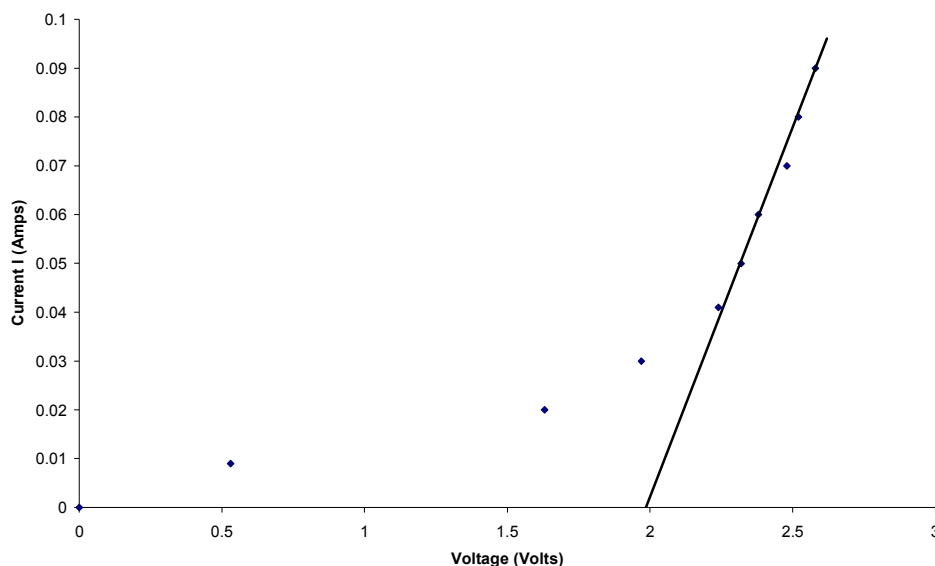


Figure 6.42: Current-voltage characteristic for electrolyser material 06SJG044 after equilibrating

The charge carrier in the anionic water electrolyser is the OH^- ion. Catalysis at the cathode produces hydrogen a hydroxyl ion^[113], as shown in equation 6.3



Prakash *et al*^[114] showed that four OH^- ions are catalysed at the anode to produce one oxygen molecule and two water molecules (eqn 6.4).



Giving a balanced equation of



The conductivity of the electrolyte was increased by replacing the demineralised water with 0.1 M sodium hydroxide (NaOH). Although higher conductivities could be achieved with higher concentrations of NaOH it was decided to proceed with a low concentration to minimise problems of membrane degradation seen in the fuel cell tests on similar materials.

The voltage at constant current (6.25 mA cm^{-2}) dropped over 30 mins from 2.54 V to 2.14 V and the characterisation of the cell was then taken, and a new decomposition voltage of 1.53 V was determined (see figure 6.43). Hydrogen production was at a rate of $2.67 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1} \text{ mW}^{-1} \text{ cm}^{-2}$ and oxygen at $1.33 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1} \text{ mW}^{-1} \text{ cm}^{-2}$, higher than the rates observed with demineralised water.

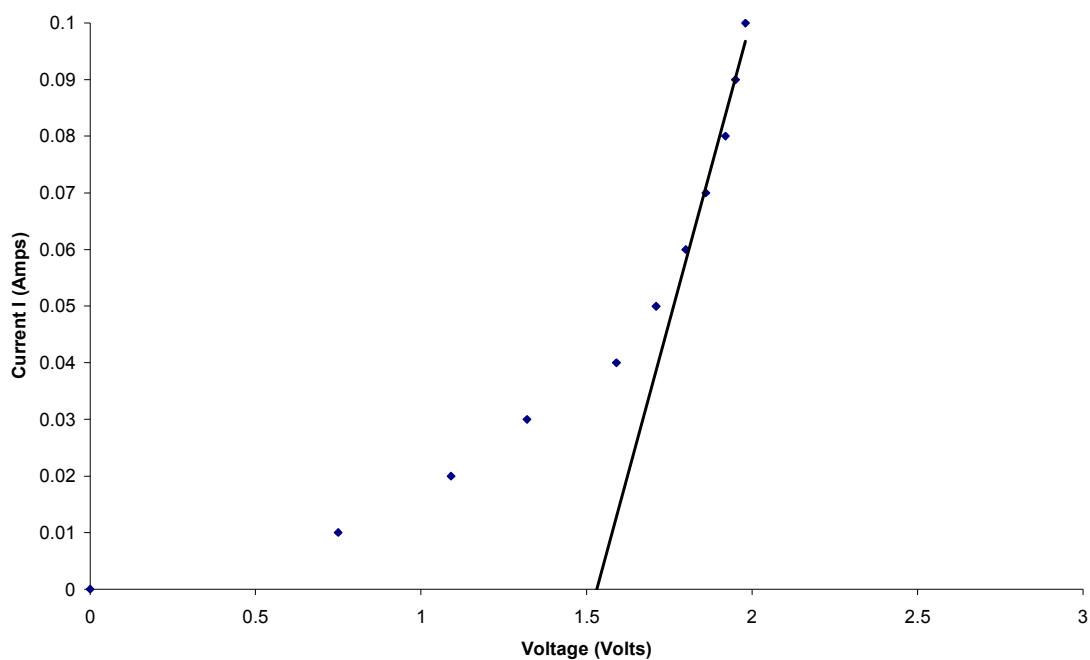


Figure 6.43: Current-voltage characteristic for material 06SJG044 with 0.1 M NaOH

The MeOX material 06SJG044 was shown to be capable of performance in an electrolyser cell, producing hydrogen and oxygen at rates of $2.29 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1} \text{ mW}^{-1} \text{ cm}^{-2}$ and $1.14 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1} \text{ mW}^{-1} \text{ cm}^{-2}$ respectively. Changing the electrolyte from deionised water to 0.1 M NaOH showed a reduction in decomposition voltage and an increase gas production rate for hydrogen and oxygen $2.67 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1} \text{ mW}^{-1} \text{ cm}^{-2}$ and $1.33 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1} \text{ mW}^{-1} \text{ cm}^{-2}$ respectively.

It was not possible to obtain long term stability data for the membrane as the electrolyser could not be run continuously unattended due to a lack of acceptable safety systems for the production of hydrogen and oxygen in the laboratory.

6.12 6.12 A Comment on Errors

The experimental errors in the study arise from all areas of the work, from membrane preparation, through characterisation and into fuel cell testing. Systematic errors such as those found in weighing and oven temperatures and timings are considered to be small (<1%). Errors in other material production techniques particularly the measurement of microwave power, are likely to be larger (~10%).

Random errors are also likely to have occurred in preparation of the MEAs and with clamping of the fuel cell. To some extent these errors were mitigated by practice and by repeat experimentation. The random (human) errors are likely to be larger and more influential than the systematic errors. They will manifest themselves in the total OCVs and power densities achievable in the fuel cell testing. Considering all causes the OCV error is

estimated to be approximately ± 0.1 V and this translates to a power density variation in the region of ± 2 mW cm⁻².

6.13 6.13 Results Summary

- Polymerisation of four materials by thermal radiation, gamma radiation and microwave radiation was undertaken. Of these two (MeOX and VPy) produced a solid copolymer systems suitable for characterisation.
- From the two hydrophilic systems chosen as the basis for further study a selection of materials were made and characterised and the effect of variation in each monomer assessed. These results were used to provide data for predicting a range of ideal materials with high water content, high dimensional stability and high conductivity. Characterisation of these ideal materials showed that other factors such as interaction within monomer compositions produced effects, which were equally important in determining the properties of the copolymers.
- The addition of hydrophilic monomers or ionic exchange moieties increased the amount of water absorbed within the samples but at the expense of their physical stability. This could be counter-acted by the addition of a crosslinking agent, such as AMX.
- The effect of different crosslinking agents was studied, with TT providing materials suitable for the alkaline DMFC which had zero methanol permeation over 6 hours. It was also noted that MeOX systems had lower methanol permeation than the VPy system.

- Production of copolymers using multi-mode microwaves produced materials with an inhomogeneous cure. The production of copolymers using a single-mode microwave cavity produced homogeneous materials, although the sample size was too small and further testing on the samples difficult.
- Materials containing MeOX had lower methanol permeations than copolymers with VPy. It was observed that copolymers with MeOX and TT had methanol permeation below the measurable limit over 3 hours. Materials thermally cured receiving 50 kGy of gamma radiation also produced copolymers with very low methanol permeation.
- Long term methanol permeation testing of materials over 24 hours proved showed that copolymers containing MeOX had a lower permeation than Nafion® 117. This led to the ability to use higher concentrations of methanol in the fuel for cell testing.
- The effect of radiation on thermally cured MeOX materials was studied and showed that zero methanol permeation over 6 hours could be obtained at total doses of 50 kGy. Analysis of the liquors from the radiation crosslinking experiments showed that the hydrophilic moiety NVP was extracted unpolymerised in the absence of radiation indicating that it did not fully polymerise in the thermal curing process alone.
- Increasing methanol concentration in fuel cell tests led to higher open circuit voltages (OCV) and higher max power density with MeOX copolymers. Increased

OCV and max p.d were also achieved by raising the operating temperature of the cell. The maximum power density achieved was twice that of the benchmark Nafion® 117 under the same conditions.

- An initial water electrolysis study showed that water electrolysis using an anionic solid polymer electrolysis was possible. The addition of NaOH to the electrolyte reduced the decomposition voltage from 2.60 V to 1.53 V, and increased the rate of production of hydrogen and oxygen gas to $2.67 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1} \text{ mW cm}^{-2}$ and $1.33 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1} \text{ mW cm}^{-2}$ respectively.

Chapter 7 . Conclusions

7.1 Introduction

This chapter identifies the conclusions drawn from the practical work undertaken during this project and suggests the effect of this work on the use of direct alkaline methanol fuel cells commercially.

7.2 Polymerisation

The copolymerisation of materials containing the monomer 4-vinyl pyridine (4-VPy) and 2-methyl-2-oxazoline (MeOX) was achieved by thermal, gamma radiation and microwave processes. Copolymerisation of anionic solid polymer electrolytes was not possible for materials containing the monomers 2-phenyl 2-oxazoline (PhOX) or aniline (AI) due to inconsistent polymerisation reactions.

The thermal copolymerisation of materials depended on type and concentration of free radical initiator used. Potassium persulphate was not soluble in the monomer matrices, and led to a poor heterogeneous cure. The use of ammonium persulphate led to membranes with varying thickness across the materials probably due to an unhomogenous distribution of the initiator in the sample solution. The use of azo-bis-isobutyronitrile (AIBN) led to a membrane with homogeneous thickness. However, the polymerisation using AIBN depended on the age of the thermal initiator, and towards the end of the project the initiator was withdrawn from commercial sale.

The small scale study using a single mode microwave proved that homogeneous polymerisation was possible at low power levels (5 W). The rate of polymerisation in both

single-mode and multi-mode microwave polymerisation was only possible in the presence of a known thermal initiator but was faster than thermal polymerisation in an oven. Faster polymerisation of materials may lead to cheaper production of membrane materials, hence reducing production costs of the membrane. This reduction in price is needed to achieve commercial viability.

Production of materials in a single-mode microwave is not limited to anionic exchange materials. Any materials which undergo polymerisation by thermal initiation, such as proprietary cationic exchange materials, could also be polymerised faster than existing methods.

7.3 Effect of Monomers and Crosslinkers

Hydrophilic monomers and ionic exchange moieties increased both the water content and the thickness of samples upon hydration. This could be counter-acted by the addition of a crosslinking agent such as allyl methacrylate (AMX). Increasing the AMX concentration led to improved dimensional stability but reduced conductivity. However above 5 % w/w this trend was reversed due to sections of homopolymer.

The absence of N-vinyl pyrrolidone (NVP) in the MeOX system caused the copolymer to be brittle and unmanageable. All useful MeOX systems contained NVP.

MeOX copolymers had much reduced methanol permeation rates compared to VPy system. It was observed that MeOX samples containing the crosslinking agent 2,4,6-triallyloxy-

1,3,5-triazine (TT) had low methanol permeation rates, whilst maintaining high water content.

A linear relationship between moles of active crosslinking sites and water content was observed in copolymers containing MeOX. This relationship was true up to a maximum of 0.02 M of active crosslinking site.

The materials produced containing 2-(dimethylamino)ethyl methacrylate (BE) were shown to have low conductivity and were therefore deemed unsuitable for use as solid polymer electrolytes, in both fuel cells and electrolyzers.

Large amounts of water within a polymer may cause a “dilution” effect, whereby layers of water surrounding an ion mask its ionic charge, and thus reduce the ionic conductivity of the system. A large thickness increase may also have an effect in reducing conductivity because the finite number of fixed ion groups are spread too far apart to facilitate the transfer of charge from one group to its nearest neighbour.

The theoretically “ideal” copolymer compositions chosen on the basis of the characterisation tests did not produce the predicted properties. This may be due to other factors in the interaction of the various monomers not being taken into account.

The MeOX thermally cured materials, which were subsequently subjected to 50 kGy of gamma radiation produced materials with zero methanol permeation over 6 hours. After this period the permeation to methanol was still lower than the benchmark Nafion® 117.

Materials with low methanol permeation are important as they permit the use of an increased methanol concentration in the fuel cell which in turn may lead to a longer time between refuelling or a higher power output from the cell.

7.4 Analysis

Analysis of extracted liquors confirmed the presence of unreacted NVP in the thermally cured samples. Subsequent irradiation with gamma radiation was shown to cause the NVP to be polymerised in the samples. However, extraction studies on these liquors provided information on materials with similar properties and functional groups to the monomer reagents used in the copolymers. This suggests that some degradation products exist, probably from chain scission caused by the gamma radiation.

7.5 Membrane Production

The production of membranes using the MeOX and the VPy system was possible. However, upon hydration they materials containing VPy became physically unstable and were not mechanically viable for use in a fuel cell environment.

7.6 Fuel Cell Testing

The peak p.d. was found to be 7.62 mW cm^{-2} at 80°C with 4 M MeOH/1 M NaOH and oxygen, this improved to 8.20 mW cm^{-2} with increased methanol concentration to 10 M. The membrane was 06SJG038O. This compared well with 4.08 mW cm^{-2} at 80°C for Nafion® 117 and 6.88 mW cm^{-2} at 80°C for ADP-100, both with 4 M MeOH/1 M NaOH and oxygen.

Cell temperature increased the open circuit voltage (OCV) and peak power density (p.d.) in all cell tests fuel cells with 4 M methanol.

Because membranes with very low methanol permeation rates were synthesised (e.g. MeOX/TT/50 kGy irradiated systems), high concentrations of methanol could be used as the fuel (up to 10 M). This resulted in higher power densities up to 8.20 mW cm^{-2} . However, very high methanol concentrations (24 M) which would lead to longer periods between refuelling or even higher p.d. could not be used due to the dehydration of the membranes.

A high concentration of sodium hydroxide in the fuel produced degradation in the membrane and this is considered to be by the Hoffman degradation process.

7.7 Electrolyser Testing

The use of an anionic solid polymer electrolyte, selected for its high water content and good anionic conductivity, was shown to be feasible in a water electrolyser. The addition of sodium hydroxide to the water decreased the water decomposition voltage in the cell to 1.53 V, and produced hydrogen and oxygen gas at a rate of $2.67 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1} \text{ mW cm}^{-2}$ and $1.33 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1} \text{ mW cm}^{-2}$ respectively.

7.8 Overall Conclusion

The use of 2-methyl-2-oxazoline (MeOX) produced copolymers with high water content, high conductivity and low methanol permeation. The addition of the crosslinking agent 2,4,6-triallyloxy-1,3,5-triazine (TT) and/or the subsequent crosslinking using gamma

radiation produced membranes with zero methanol permeation over 6 hours, leading to the ability to use a high concentration of methanol (10 M) in the fuel cell environment, achieving higher fuel cell performances in comparison to the more normal 4 M methanol concentrations.

Chapter 8 . Future Work

8.1 Introduction

This chapter considers what future work should be carried out to further the knowledge gained in this project.

8.2 Polymerisation

The polymerisation of materials in a single-mode microwave proved to be faster than thermal or gamma radiation polymerisation. However commercial single-mode microwaves are very expensive and have a small cavity size at the moment. Although a large single-mode microwave cavity was designed and produced, further testing and tuning of the cavity needs undertaken before meaningful polymerisation studies can proceed.

Studies into the effect of single-mode microwave power together with a comparison with materials produced by conventional thermal and gamma radiation methods would give a more detailed picture of the curing process under single-mode microwave conditions.

8.3 Radiation Crosslinking

High doses of gamma radiation can cause either chain scission or crosslinking effects depending on the total dose. Further experimentation on the effect of varying total doses of gamma radiation on the membrane systems and the resulting properties of methanol permeation, water content and thickness increase are needed. This would identify the doses required to provide the optimum characteristics of high water content, low thickness increase and low methanol permeation, whilst maintaining high ionic conductivity.

8.4 Ideal Material Model

The interactions of the hydrophilic and hydrophobic monomers in the preparation of some of the most interesting copolymers are thought to have caused unexpected effects. It was noted that hydrophilic monomers had more effect on the water content, thickness increase, and conductivity than hydrophobic monomers. Further studies into the interaction of these integral parts of the copolymer system are needed in order to obtain a greater understanding of the intrinsic properties of the copolymers, and to be able to more accurately predict the best material compositions for both fuel cell and electrolyser applications.

8.5 Long Term Fuel Cell Testing

Materials containing MeOX with low methanol permeation have been shown to produce power densities higher than benchmark standard materials under the same operating conditions. However, testing of these materials under load and OCV conditions beyond a few hours has not been possible. Long term testing is vital to be able to establish the stability of membranes in alkaline environment and their suitability in the alkaline direct methanol fuel cell in commercial use.

8.6 Optimisation of MEA Preparations

The MEAs used in this study were non-optimised and were based on commercially available precious metal catalysts and electrode materials. The ability to use non-platinum catalysts is a major advantage of the alkaline direct methanol fuel cell. Further research into the type and loadings of the catalyst in this cell are needed to make the most of this significant potential benefit. Faster catalysis would produce higher peak power densities and the ability to use lower loadings of catalyst. The lower cost of non-precious metal

catalysts would reduce its cost and since it is a major cost component of the cell would permit cost reduction and drive the application nearer to commercialisation.

The optimum preparation conditions of the MEA were considered to be outside the scope of this project. However it needs investigation. The role of Nafion® 117 interfacial solution on the catalyst cloth is unknown with these new material types. The most favourable conditions of preparation for maximum three-phase contact between, membrane, catalyst and fuel would improve the efficiency of the electrochemistry and permit greater power densities.

It has been widely reported that cell geometry plays an important part in its ultimate performance. Thus in order to integrate these new membrane materials into an optimum cell, attention will be needed in the areas of flow field plate design, catalyst support and membrane sealing in the cell.

8.7 Effect of Fuel Flow Rate on Power Density

Saarinen *et al*^[115] found that at high methanol concentrations the peak power density was produced at low fuel flow rates, and low concentrations of methanol required high flow rates to produce max p.d. This project has shown that materials containing MeOX can be utilised with a higher concentration of methanol than used by Saarinen and may lead to power densities even higher than those recorded by Saarinen ($\sim 6 \text{ mW cm}^{-2}$), a milestone not reported thus far.

8.8 Catalysis of Ethanol

This work only briefly touched on membranes for the alkaline direct ethanol fuel cell. The correct catalysis of ethanol may provide a route to a truly “green” carbon neutral fuel cell system. The nature of full catalysis of the ethanol and breakdown of the carbon-carbon bond in an alkaline media is potentially easier than in acidic media. To date no catalyst has been reported for the full breakdown of ethanol in either acidic or alkaline environment. Further, little work on the catalysis of ethanol in alkaline media has been reported, due to a lack of available anionic exchange membranes suitable for an alkaline direct ethanol fuel cell.

Further work in developing the anionic exchange membrane technologies required in this field, and produced by this project, may encourage research into ethanol catalysis in alkaline environments.

8.9 Alkaline Water Electrolysis

In order to satisfy the need for the hydrogen within the context of the well published “hydrogen economy” there has been a surge of interest in water electrolysis. The ability to electrolyse water in an alkaline environment may provide advantages over the more usual acidic environment. These include cheap catalysis and a less corrosive environment. Further research into the materials developed in this study in terms of their stability and suitability in alkaline solid polymer electrolyte water electrolyzers are needed to provide indications as to whether they have applications in this very important area.

References

-
- [1] Grove W. R. Philosophical magazine, 14, 127-130, 1839
- [2] World Energy Investment Outlook 2003 Insights International Energy Agency, France, 2003.
- [3] Onda K., Kyakuno, T., Hattori K., Ito K., **Prediction of production power for high-pressure hydrogen by high-pressure water electrolysis** Journal of Power Sources 132 (1-2), 64-70, 2004
- [4] Editors Vielstich W., Lamm A. and Gasteiger H. A. Handbook of Fuel Cells: Fundamentals, Technology and Applications, Volume 1 Fundamentals and Survey of Systems John Wiley and Sons Inc. New Jersey, 2003
- [5] Stojic D. L., Marceta M.P., Sovilj S.P., Miljanic S.S. **Hydrogen generation from water electrolysis—possibilities of energy saving** Journal of Power Sources 118 (1-2), 315-319, 2003
- [6] Rosa V.M., Santos M.B.F., da Silva E.P. **New materials for water electrolysis diaphragms** International Journal of Hydrogen Energy 20 (9) 697-700, 1995
- [7] Oi T., Sakaki Y. **Optimum hydrogen generation capacity and current density of the PEM-type water electrolyzer operated only during the off-peak period of electricity demand** Journal of Power Sources 129 (2), 229-237, 2004
- [8] Larminie J., Dicks A. Fuel Cells Systems Explained second edition, John Wiley and Sons, Chichester, 2003
- [9] Varkaraki E. Lymberopoulos N., Zachariou A. **Hydrogen based emergency back-up system for telecommunication applications** Journal of Power Sources, 118 (1-2): 14-22, 2003
- [10] Janssen H., Bringmann J.C., Emonts B., Schroeder V. **Safety-related studies on hydrogen production in high-pressure electrolyzers** International Journal of Hydrogen Energy, 29 (7): 759-770, 2004
- [11] Millet P., Andolfatto F., Durand R. **Design and performance of a solid polymer electrolyte water electrolyzer** International Journal of Hydrogen Energy 21 (2), 87-93, 1996
- [12] Page 421, Editors Vielstich W., Lamm A. and Gasteiger H. A. Handbook of Fuel Cells: Fundamentals, Technology and Applications, Volume 1 Fundamentals and Survey of Systems John Wiley and Sons Inc. New Jersey, 2003
- [13] Tanaka Y., Uchinashi S., Saihara Y., Kikuchi K., Okaya T., Ogumi Z. **Dissolution of hydrogen and the ratio of the dissolved hydrogen content to the produced hydrogen in electrolyzed water using SPE water electrolyzer** Electrochimica Acta 48 (27), 4013-4019, 2003
- [14] Carrette L., Friedrich K.A., Stimming U. **Fuel cells – fundamentals and applications** Fuel Cells, 1 (1) 5-39, 2001
- [15] Editors Blomen L. J. M., Mugerwa M.N. Fuel Cell Systems Plenum Press, New York, 1993
- [16] Housecroft C. E., Constable E. Chemistry: An Integrated Approach Longman Publishers, London, 1997
- [17] Kordesh K., Simader G. Fuel Cells and Their Applications, VCH, Weinheim, 1996
- [18] Ed. Mitchel W. Jr. Fuel Cells Academic Press, New York, 1st Edition, 1963
- [19] Crockett R. G. M. Newborough M., Highgate D.J., Probert S.D. **Electrolyser-based electricity management** Applied Energy, 51, 249-263, 1995
- [20] Agmon N., **The Grotthuss Mechanism** Chemical Physics Letters 244, 456-462, 1995

-
- [21] Zuettel A. **Hydrogen storage methods** Naturwissenschaften 91 (4), 157-172, 2004
- [22] Ghosh P. C., Emonts B., Stolten D. **Comparison of hydrogen storage with diesel-generator system in a PV-WEC hybrid system** Solar Energy 75 (3): 187-198 2003
- [23] Dillon R., Srinivasan S., Arico A.S., Antonucci V. **International activities in DMFC R&D: status of technologies and potential applications** Journal of Power Sources 12, 112-126, 2004
- [24] Apanel G., Johnson E. **Direct methanol fuel cells – ready to go commercial?** Fuel Cells Bulletin 11, 12-17, Nov 2004
- [25] Yamada K. Yasuda K., Fujiwara N., Siroma Z., Tanaka H., Miyazaki Y. Kobayashi T. **Potential application of anion-exchange membrane for hydrazine fuel cell electrolyte** Electrochemistry Communications 5, 892-896, 2003
- [26] de Lima R. B., Paganin V., Iwasita T., Vielstich W. **On the electrocatalysis of ethylene glycol** Electrochimica Acta 49, 85-91, 2003
- [27] Moisson F. J. M. Revue de l'Institut Francais du Petrole et Annales des Combustibles Liquides, 24 (6) 724-758, 1969
- [28] Ewe H., Justi E., Pesditschek M. **Ethylene-glycol as fuel for alkaline fuel-cells** Energy Conservation 15 (1-2) 9-14, 1975
- [29] Davis T. A., Genders J.D., Pletcher D. A First Course in Ion Permeable Membranes, Printed by Alresford Press, Alresford, 1st Edition, 1997
- [30] Ed. Stone F. G. A. Inorganic Polymers Academic Press, New York, 1st Edition., 1962
- [31] Sun J., MacFarlane D.R., Forsyth M. **Novel alkaline polymer electrolytes based on tetramethyl ammonium hydroxide** Electrochimica Acta 48, 1971-1976, 2003
- [32] Smitha B., Sridhar S., Khan A.A. **Synthesis and characterization of proton conducting polymer membranes for fuel cells** Journal of Membrane Science 225, 63-76, 2003
- [33] Poppe D., Frey H., Kreuer K.D., Heinzl A., Mulhaupt R. **Carboxylated and sulfonated poly(arylene-co-arylene sulfones)s: Thermostable polyelectrolytes for fuel cell applications** Macromolecules 35, 7936-7941, 2002
- [34] Bauer B., Strathmann H., Effenberger F. **Anion-exchange membranes with improved alkaline stability** Desalination 79, 125-144, 1990
- [35] Moor W. R. An Introduction to Polymer Chemistry University of London Press, London, 1963
- [36] Milinchuk V.K., Tupikov V. I. Organic Radiation Chemistry Handbook Ellis Horwood Limited, Chichester, 1989
- [37] O'Donnel J. H. Principles of Radiation Chemistry Sangster Edward Arnold Publishers, London. 1970
- [38] Porto A. F., Sadicoff B.L., Amorim M.C.V., de Mattos M.C.S. **Microwave assisted free radical bulk-polyaddition reactions in a domestic microwave oven** Polymer Testing 21, 145-148, 2002
- [39] Wang T., Liu J. **A Review of Microwave Curing of Polymeric Materials** Journal of Electronics Manufacturing 10 (3) 181-189, 2000
- [40] Perreux L., Loupy A. **A tentative rationalization of microwave effects in organic synthesis according to the reaction medium, and mechanistic considerations** Tetrahedron, 57, 9199-9223, 2001

-
- [41] Lidstron P., Tierney J., Wathey B., Westman J. **Microwave assisted organic synthesis-a review** Tetrahedron, 57, 9225-9283, 2001
- [42] Kabanov V. Y. **Preparation of polymer membranes for fuel cells by radiation graft polymerization** High Energy Chemistry 38 (2) 57-65, 2004
- [43] Dhathathreya K.S., Sridhar P., Sasikumar G., Ghosh K.K., Velayutham G., Rajalakshmi N., Subramaniam C.K. Raja M., Ramya K. **Development of polymer electrolyte membrane fuel cell stack** International Journal of Hydrogen Energy, 24, 1107-1115, 1999
- [44] Stuki S., Schlagowski S., Fischer E. **PEM water electrolyzers: evidence for membrane failure in 100 kW demonstration plants** Journal of Applied Electrochemistry 28, 1041-1049, 2003
- [45] http://www.gore.com/en_xx/ viewed 24/02/2005
- [46] Qiao J., Hamaya T. and Okada T. **Poly(vinyl alcohol)-poly(2-acrylamido-2-methyl-1-propanesulfonic acid) as a novel proton-conducting fuel cell membrane** American Chemical Society published on web site, received 17.02.05
- [47] Horsfall J. A, Lovell K.V. **Synthesis and characterization of acrylic acid-grafted hydrocarbon and fluorocarbon polymers with the simultaneous or mutual grafting technique** Journal of Applied Polymer Science 87, 230-243, 2003
- [48] Horsfall J.A., Lovell K.V. **Fuel cell performance of radiation grafted sulphonic acid membranes** Fuel Cells 1 (3-4) 186-191, 2001
- [49] Danks T. N., Slade R. C. T., Varcoe J. R. **Comparison of PVDF- and FEP-based radiation-grafted alkaline anion-exchange membranes for use in low temperature portable DMFCs** Journal of Materials Chemistry 12, 3371-3373, 2002
- [50] Legras M., Hirata Y., Nguyen Q.T., Langevin D., Metayer M. **Sorption and diffusion behaviours of water in Nafion 117 membranes with different counter ions** Desalination 147, 351-357, 2002
- [51] Scott K., Taama W. M., Argyropoulos P., Sundmacher K. **The impact of mass transport and methanol crossover on the direct methanol fuel cell** Journal of Power Sources 83 (1-2) 204-216, 1999
- [52] Wang Y, Li L., Hu L., Zhang L., Lu J., Xu B. **A feasibility analysis for alkaline membrane direct methanol fuel cell: thermodynamic disadvantages versus kinetic advantages** Electrochemistry Communications 5, 662-666, 2003
- [53] Every H. A., Hickner M.A., McGrath J.E., Zawodzinski, Jr. T.A. **An NMR study of methanol diffusion in polymer electrolyte fuel cell membranes** Journal of Membrane Science 250 (1-2) 183-188, 2005
- [54] Yang B., Manthiram A. **Multilayered membranes with suppressed fuel crossover for direct methanol fuel cells** Electrochemistry Communications 6 (3) 231-236, 2004
- [55] Si Y. C. Journal of the Electrochemistry Society 151 (3) A463-A469, 2004
- [56] Yu E. H., Scott K. **Development of direct alkaline fuel cells using anion exchange membranes** Journal of Power Sources 137, 248-256, 2004
- [57] Sata T., Tsujimoto M., Yamaguchi T., Matsusaki K. **Change of anion exchange membranes in an aqueous sodium hydroxide solution at high temperature** Journal of Membrane Science 112 (2) 161-170, 1996

-
- [58] Baden Fuller A. J. Microwaves, An introduction to microwave theory and techniques Pergammon Press, Oxford, Third Edition, 1990
- [59] Ku H. **Curing vinyl ester particle-reinforced composites using microwaves** Journal of Composite Materials 37 (22) 2027-2042, 2003
- [60] Gilmour Jr., A. S. Microwave Tubes Artech House, Dedham, USA, First Edition, 1986
- [61] Ed Tierney J. P., Lidstrom P. Microwave Assisted Organic Synthesis Publisher Blackwell Press, first edition, 2005
- [62] Wiesbrock F. Hoogenboom R., Schubert U. S. **Microwave-Assisted Polymer Synthesis: State-of-the-Art and Future Perspectives** Macromolecular Rapid Communications, 1739-1764, 25, 2004
- [63] Lidstrom P., Tierney J., Wathey B., Westman J. **Microwave Assisted Organic Synthesis-A Review** Tetrahedron, 9225-9283, 57, 2001
- [64] Barlow S., Marder S. R. **Single-Mode Microwave Synthesis in Organic Materials Chemistry** Advanced Functional Materials 13 (7) 517-518, 2003
- [65] Solomons T. W. G. Fundamentals of Organic Chemistry Fifth Edition, John Wiley and Sons, London 5th Edition 1997.
- [66] <http://www.chem.arizona.edu/kukolich/research/mwspec/spectra/spectra.htm> viewed 28/06/07
- [67] Degamber B., Fernando G. F. *et al* **Microwave processing of thermosets: non-contact cure monitoring and fibre optic temperature sensors** Plastics Rubber and Composites 32 (8-9) 327-333, 2003
- [68] Zhou J., Shi C., Mei B. C., Yuan R. Z., Fu Z. Y. **Research on the technology and the mechanical properties of the microwave processing of polymer** Journal of Materials Processing Technology 137 (1-3) 156-158, 2003
- [69] Chia H. L., Jacob J., Boey F. Y. C. **The microwave radiation effect on the polymerization of styrene** Journal of Polymer Science Part A-Polymer Chemistry 34 (11) 2087-2094, 1996
- [70] Li J., Zhu X., Zhu J., Cheng Z. **Microwave-assisted nitroxide-mediated radical polymerization of styrene** Radiation Physics and Chemistry 75, 253-258, 2006
- [71] Ng L. T., Chia L. H. L. **Practical microwave curing studies for undergraduates** Polymer International 48 (10) 952-955, 1999
- [72] Boey F. Y. C., Yap B. H., Chia L. **Microwave curing of epoxy-amine system - effect of curing agent on the rate enhancement** Polymer Testing 18 (2) 93-109, 1999
- [73] Cavusoglu I., Minbay F. Z., Temel S. G., Noyan S. **Rapid Polymerisation with Microwave Irradiation for Transmission Electron Microscopy** European Journal of Morphology, 5, 313-317, 2001
- [74] Sinnwell S., Ritter H. **Microwave accelerated polymerization of 2-phenyl-2-oxazoline** Macromolecular Rapid Communications 26, 160-163, 2005
- [75] Wiesbrock F., Hoogenboom R., Leenen M. A. M., Meier M. A. R., Schubert U. S. **Investigation of the living cationic ring-opening polymerization of 2-methyl, 2-ethyl, 2-nonyl, and 2-phenyl-2-oxazoline in a single-mode microwave reactor** Macromolecules 38, 5025-5024, 2005
- [76] Zhou S. J., Hawley M. C. **A study of microwave reaction rate enhancement effect in adhesive bonding of polymers and composites** Composite Structures 61 (4) 303-309, 2003

-
- [77] Biotage 2005 Catalogue, www.biotagedcg.com page 18, viewed 01/07/05
- [78] Wiesbrock F., Hoogenboom R., Abeln C. H., Schubert U. S. **Single-Mode Microwave Ovens as New Reaction Devices: Accelerating the Living Polymerisation of 2-Ethyl-2-Oxazoline** Macromolecular Rapid Communications 25, 1895-1899, 2004
- [79] Asmussen J., Lin H. H., Manring B., Fritz R. **Single-mode or controlled multimode cavity applicators for precision materials processing** Review Scientific Instruments 58 (8) 1477-1486 1987
- [80] Jacob J., Chia L. H. L., Boey F. Y. C. **Comparative study of methyl methacrylate cure by microwave radiation versus thermal energy** Polymer Testing 14, 343-354, 1995
- [81] David G., Alupe V., Simionescu B.C. **End-capping of living poly(2-methyl-2-oxazoline) with maleic acid** European Polymer Journal 37 (7) 1353-1358, 2001
- [82] Aoi K., Okada M. **Polymerization of oxazolines** Progress of Polymer Science 21 (1) 151-208, 1996
- [83] Galkowski M. T., Kulesza P.J., Miecznikowski K., Chojak M., Bala H. **Protective properties of redox polymer film deposited on stainless steel** Journal of Solid State Electrochemistry 8 (6) 430-434, 2004
- [84] Xin Y., Hu Y., Zeldin M., Fife W.K. **Copolymerization of hydrophilic and hydrophobic 1-alkyl-4-vinylpyridinium monomers** Macromolecules 26 (17) 4670-4674, 1993
- [85] Moulick M., Dutta A. **Measurement of ionic conductivity of poly-(4-vinyl pyridine) and its salt in solid state** Journal of Polymer Materials 19 (3) 253-257, 2002
- [86] Oikawa E., Ohsakiet T. **Properties of reverse osmosis membranes prepared from poly(4-vinyl pyridine)-acrylonitrile copolymer and the partially quaternized copolymer** Desalination 25 (2) 187-206, 1978
- [87] Wang J. G. **Anion exchange nature of emeraldine base (EB) polyaniline (PAn) and a revisit of the EB formula** Synthetic Metals 132 (1) 49-52, 2002
- [88] Wang J. G. **Polyaniline coatings: anionic membrane nature and bipolar structures for anticorrosion** Synthetic Metals 132 (1) 53-56, 2002
- [89] Sahiner N., Saraydin D., Karadağ E., Güven O. **Swelling and dye adsorption properties of radiation induced N-vinyl-2-pyrrolidone/acrylonitrile hydrogels** Polymer Bulletin 41 (3) 371-387, 1998
- [90] Brar A. S., Kumaret R. **Sequence determination of N-vinyl-2-pyrrolidone/acrylonitrile copolymers by NMR spectroscopy** European Polymer Journal 37 (9) 1827-1835, 2001
- [91] Ray S. K., Sawant S.B., Joshi J.B. Pangarkaret V.G. **Methanol selective membranes for separation of methanol-ethylene glycol mixtures by pervaporation** Journal of Membrane Science 154 (1) 1-13, 1999
- [92] de Campos E. A., Alfaya A. A.D., Ferrari R.T., Costa C.M.M. **Quaternary ammonium salts immobilized on silica gel: Exchange properties and application as potentiometric sensor for perchlorate ions** Journal of Colloid and Interface Science 240, 97-104, 2001
- [93] Liu Z., Xiao H., Wiseman N. **Emulsifier-free emulsion copolymerization of styrene with quaternary ammonium cationic monomers** Journal of Applied Polymer Science 76 (7) 1129-1140, 2000
- [94] Yeon K-H., Song J-H., Kim J.B., Moon S-H. **Preparation and characterization of UV-grafted ion-exchange textiles in continuous electrodeionization** Journal of Chemical Technology and Biotechnology 79 (12) 1395-1404, 2004

-
- [95] Yamada L., Sato K., Hirata M. **Uphill transport of organic electrolytes using polyethylene films photografted with 2-(dimethylamino)ethyl methacrylate** et al Journal of Materials Science 34, 1081-1091, 1999
- [96] Zeng F., Shen Y., Zhu S. **Synthesis of comb-branched polyacrylamide with cationic poly[(2-dimethylamino)ethyl methacrylate dimethylsulfate] quat** Journal of Polymer Science: Part A: Polymer Chemistry 40 (14) 2394-2405, 2002
- [97] Aziz M. S., Aggour Y.A. **Electrical conduction of polymer complexes of 2-(dimethylamino)ethyl acrylate with cobalt chloride** Polymer Testing 18 (7) 511-521, 1999
- [98] Rabek J.F. Experimental methods in polymer chemistry Wiley Interscience Publications, Chichester, 1983
- [99] Qiao J., Hamaya T., Okada T. **New highly proton-conducting membrane poly(vinylpyrrolidone)(PVP) modified poly(vinyl alcohol)/2-acrylamido-2-methyl-1-propanesulfonic acid (PVA-PAMPS) for low temperature direct methanol fuel cells (DMFCs)** Polymer 46 (24) 10809-10816, 2005
- [100] Liu Y., Mao R., Huglin M.B., Holmes P.A. **Reactivity ratios in copolymerizations involving allyl methacrylate** Polymer 37 (8), 1437-1441, 1996
- [101] Mennicken M., Nagelsdiek R., Keul H., Höcker H. **ATRP of Allyl Methacrylate with Alkyl Methacrylates - Crosslinking of Poly(methacrylate)s with Allyl Ester Side Groups** Macromolecular Chemistry and Physics 205 (18) 2429-2437, 2004
- [102] Yin X., Stöver H.D.H. **Temperature-sensitive hydrogel microspheres formed by liquid-liquid phase transitions of aqueous solutions of poly(N,N-dimethylacrylamide-co-allyl methacrylate)** Journal of Polymer Science: Part A: Polymer Chemistry 43 (8) 1641-1648, 2005
- [103] Housecroft C. E., Constable E. C. Chemistry An Integrated Approach second edition, pg 231, Longman, Harlow, 1997
- [104] Watkins K. W. **Heating in microwave ovens: An example of dipole moments in action** Journal of Chemical Education 60, (12) 1043-1044, 1983
- [105] Hovorka S., Roux A. H., Roux-Desgranges G. and Dohnal V. **Limiting partial molar excess heat capacities and volumes of selected organic compounds in water at 25°C** Journal of Solution of Chemistry 28 (12) 1289-1305, 1999
- [106] Jellinek H. H. G. Aspects of Degradation and Stabilization of Polymers Elsevier, Oxford, 1978
- [107] Wan Y., Creber K. A. M., Peppley B., Bui V. T., Halliop E. **New solid polymer electrolyte membranes for alkaline fuel cells** Polymer International 51, 5-10, 2005
- [108] Commer P., Cherstvy A. G., Spohr E. and Kornyshev A. A. **The effect of water content on proton transport in polymer electrolyte membranes** Fuel Cells 2 (3-4) 127-136, 2002
- [109] Paris R., De La Fuente J. L. **Synthesis and characterization of functional gradient copolymers of allyl methacrylate and butyl acrylate** Journal of Polymer Science Part A-Polymer Chemistry 44 (18) 5304-5315, 2006
- [110] Prabhuram J., Manoharan R. **Investigation of methanol oxidation on unsupported platinum electrodes in strong alkali and strong acid** Journal of Power Sources 74 (1) 54-61, 1998
- [111] Ed Linden D., Handbook of Fuel Cells Pg 1-8, McGraw-Hill Book Company, New York 1984

-
- [112] Matsushima H., Fukunaka Y., Kuribayashi K. **Water electrolysis under microgravity Part II. Description of gas bubble evolution phenomena** Electrochimica Acta 51, 4190-4198, 2006
- [113] Rosabino F., Maccio D., Angelini E., Saccone A., Delfino S. **Electrocatalytic properties of Fe-R (R= rare earth metal) crystalline alloys as hydrogen electrodes in alkaline water electrolysis** Journal of Alloys and Compounds 403, 275-282, 2005
- [114] Prakash J., Tryk D., Yeager E. **Electrocatalysis for oxygen electrodes in fuel cells and water electrolyzers for space applications** Journal of Power Sources 29, 413-422, 1990
- [115] Saarinen V; Himanen, O; Kallio, T; et al. **Current distribution measurements with a free-breathing direct methanol fuel cell using PVDF-g-PSSA and Nafion (R) 117 membranes** Journal of Power Sources, 163 (2) 768-776, 2007

Appendix A: Single-Mode Microwave Programme Setting

CEM Discovery model single-mode microwave with 5 mL cavity, programme:

WATER SOLVENT

MODE - POWER TIME

x. WATTS

x. MINUTE RUN TIME

MAX T = 100°C

MAX PRESSURE = 10 PSI

STIR OFF

COOLING OFF

CLOSED CAP VESSEL

LOAD LOWER SPECTRUM (1-3CM)

5ML SAMPLE

Where x was variable. During operation the pressure and temperature of the vessel was measured.

Figure B.1: Single-Mode cavity body as designed and tested in this project



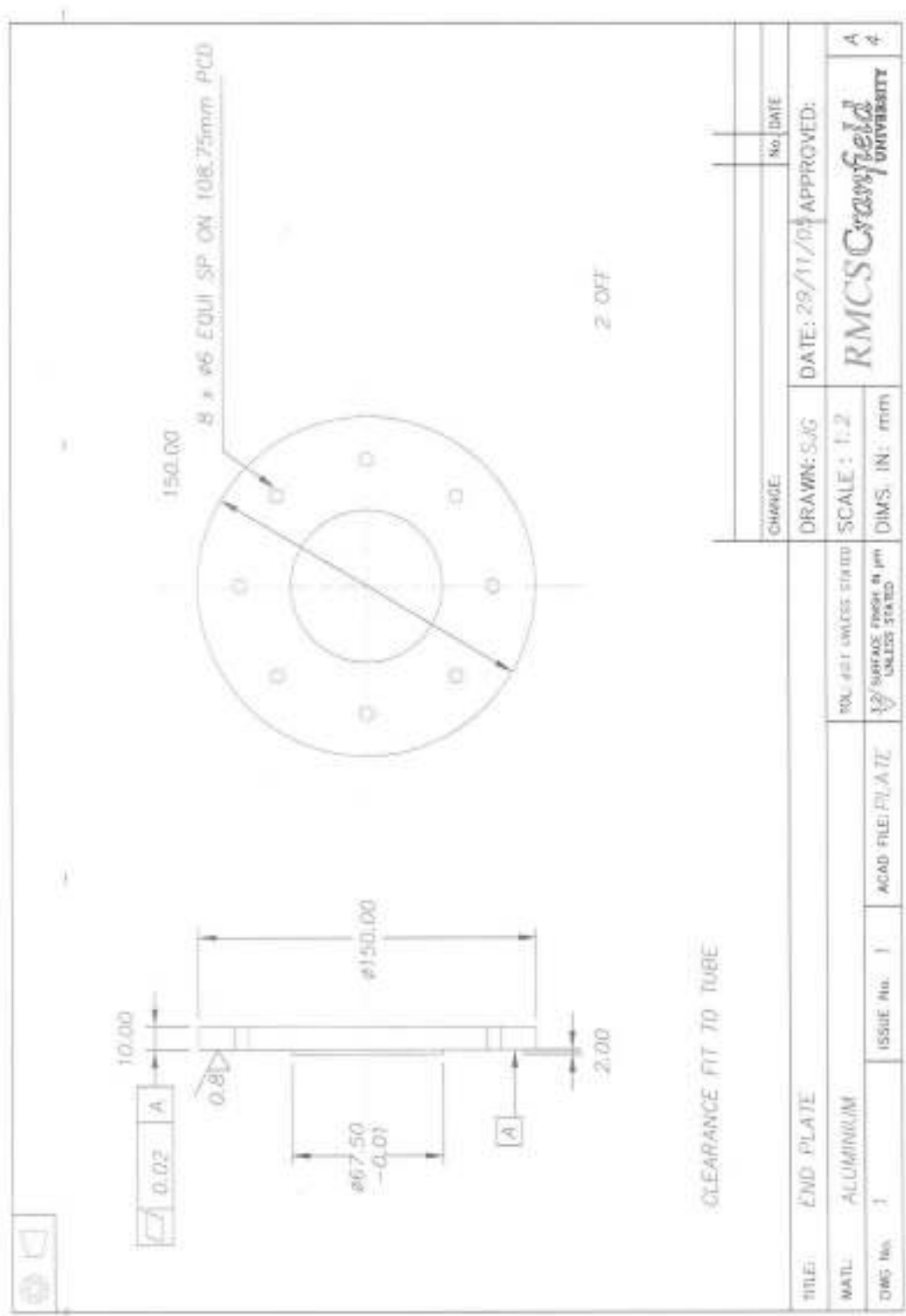


Figure B.2: Single-Mode cavity end plate

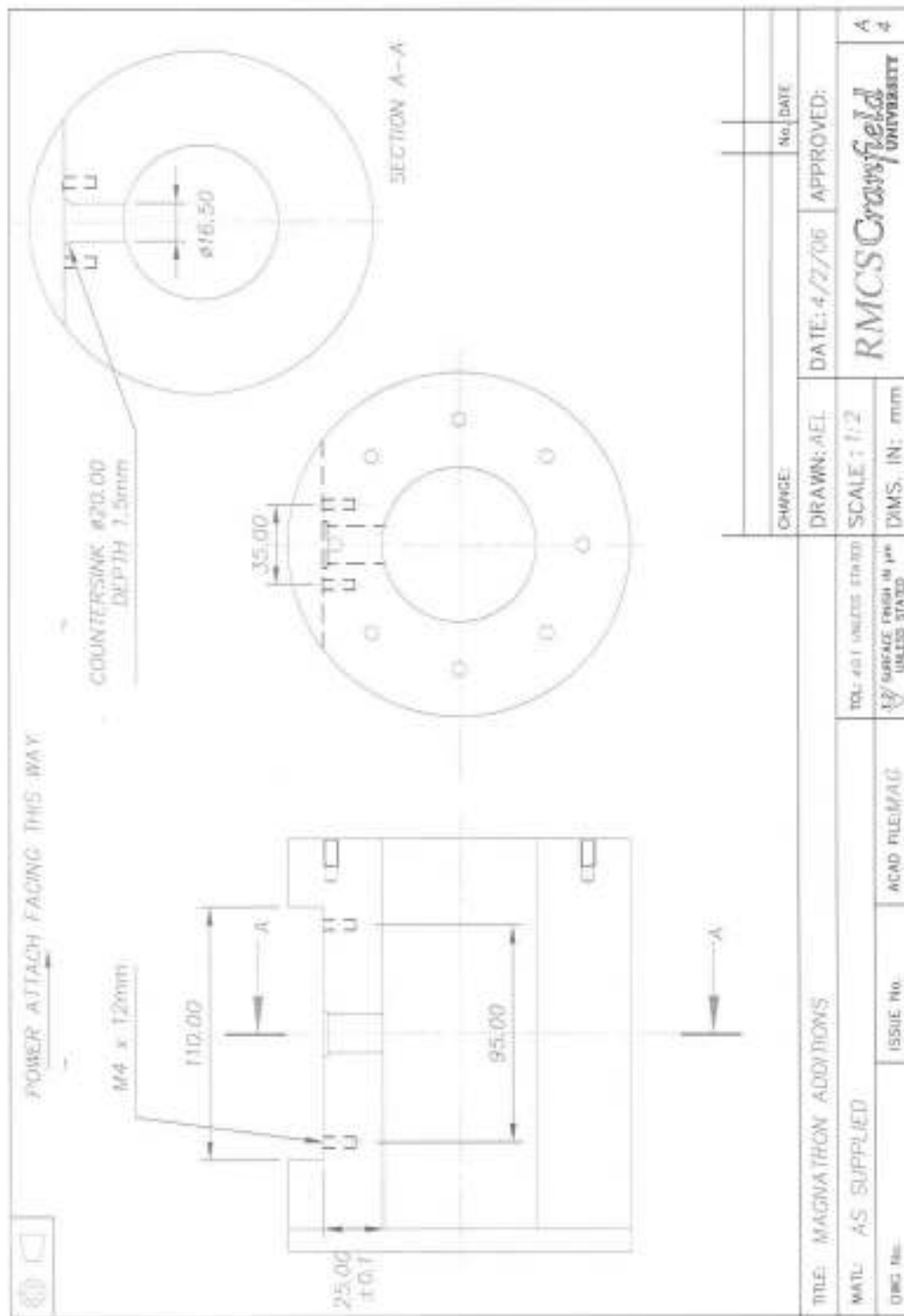


Figure B.3: Design showing the addition of the magnetron to single-mode cavity



Figure B.4: Photograph of the finished single-mode cavity with magnetron fitted (cavity size; radius 3.375 cm, length 17.00 cm).

Appendix C: Refractive Index

A calibration curve of refractive index at 25°C versus moles per litre was constructed from experimental measurements as shown in figure C.1 below.

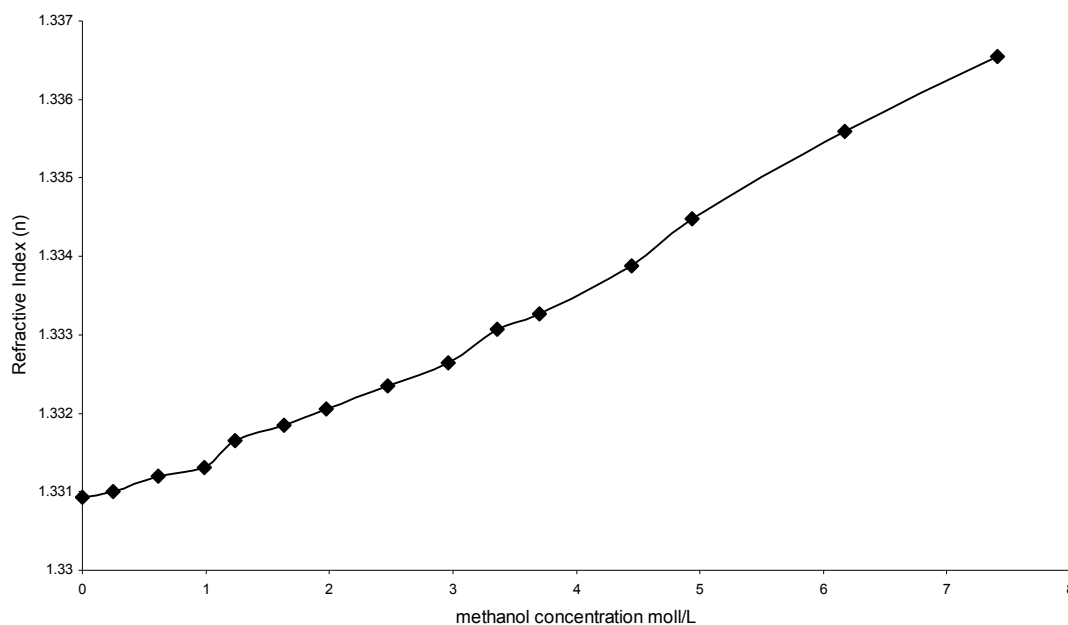


Figure C.1: Calibration curve for methanol permeation measurements

This curve can be approximated to a number of straight lines, which are converted into ‘macros’ running in MS Excel to be able to directly obtain the concentration value from refractive index number.

The straight lines are as follows:

$$0.0001 \leq \Delta n \leq 0.0007 \quad \text{conc} = \Delta n * 1547$$

$$0.0007 < \Delta n < 0.0009 \quad \text{conc} = \Delta n * 770 + 0.5454$$

$$0.0009 \leq \Delta n \leq 0.0013 \quad \text{conc} = \Delta n * 1532 - 0.14$$

$$0.0013 < \Delta n < 0.0015 \quad \text{conc} = \Delta n * 760 + 0.863$$

$$0.0015 \leq \Delta n \leq 0.0018 \quad \text{conc} = \Delta n * 1532 - 0.28$$

$$0.0018 < \Delta n < 0.002 \quad \text{conc} = \Delta n * 655 + 1.301$$

$$0.002 \leq \Delta n \leq 0.0022 \quad \text{conc} = \Delta n * 1650 - 0.69$$

$$0.0022 < \Delta n < 0.0024 \quad \text{conc} = \Delta n * 620 + 1.577$$

$$\begin{aligned}
0.0024 \leq \Delta n \leq 0.0026 & \quad \text{conc} = \Delta n * 1505 - 0.547 \\
0.0026 < \Delta n < 0.0035 & \quad \text{conc} = \Delta n * 998 + 0.77 \\
0.0035 \leq \Delta n \leq 0.0037 & \quad \text{conc} = \Delta n * 1485 - 0.934 \\
0.0037 < \Delta n < 0.0049 & \quad \text{conc} = \Delta n * 984 + 0.92 \\
0.0049 \leq \Delta n \leq 0.0051 & \quad \text{conc} = \Delta n * 1465 - 1.4365 \\
0.0051 < \Delta n < 0.0057 & \quad \text{conc} = \Delta n * 971 + 1.08 \\
0.0057 \leq \Delta n \leq 0.0077 & \quad \text{conc} = \Delta n * 1146 - 0.088
\end{aligned}$$

The MeOH concentration is then plotted against time as shown in figure C.2, and the diffusion coefficient (DK) can be calculated from the slope of the graph (G):

$$DK = \frac{GVT}{24.7A}$$

Where V is volume of water, T is the thickness of the test material and A is the area of material exposed to methanol.

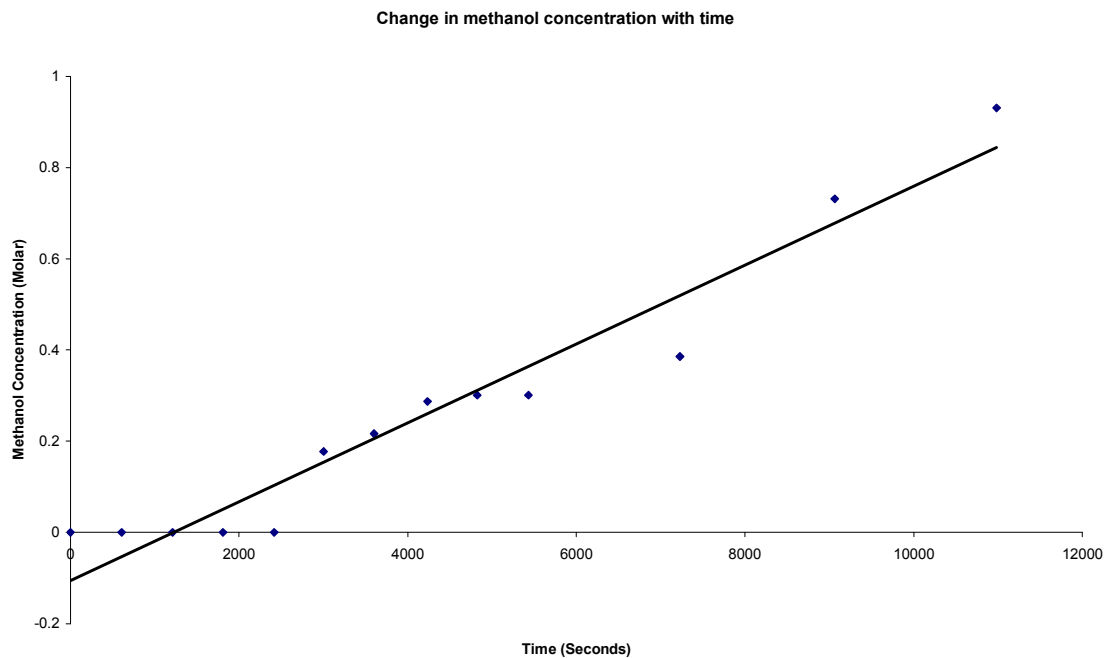


Figure C.2: Change in methanol concentration with time

Appendix D: Typical Chromatograms

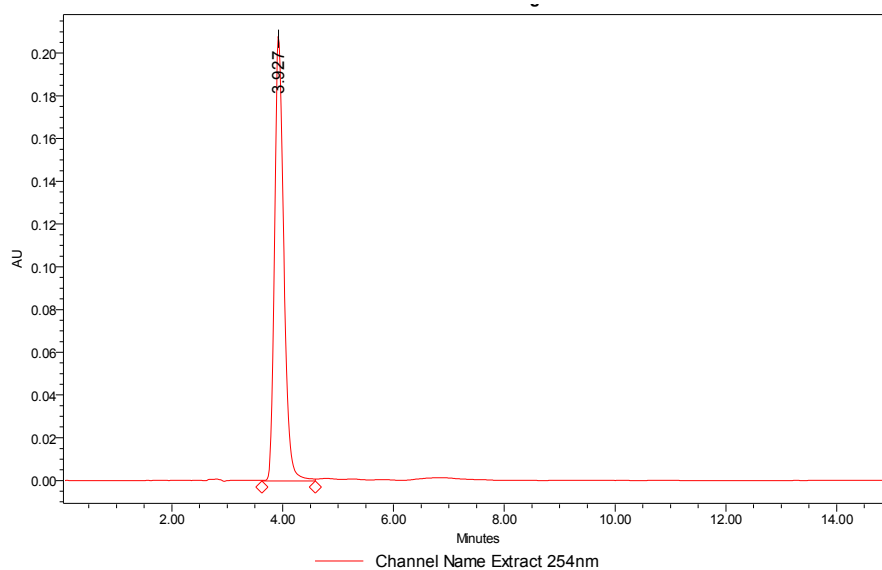


Figure D.1: HPLC Chromatogram showing N-vinyl pyrrolidone (VNP) standard

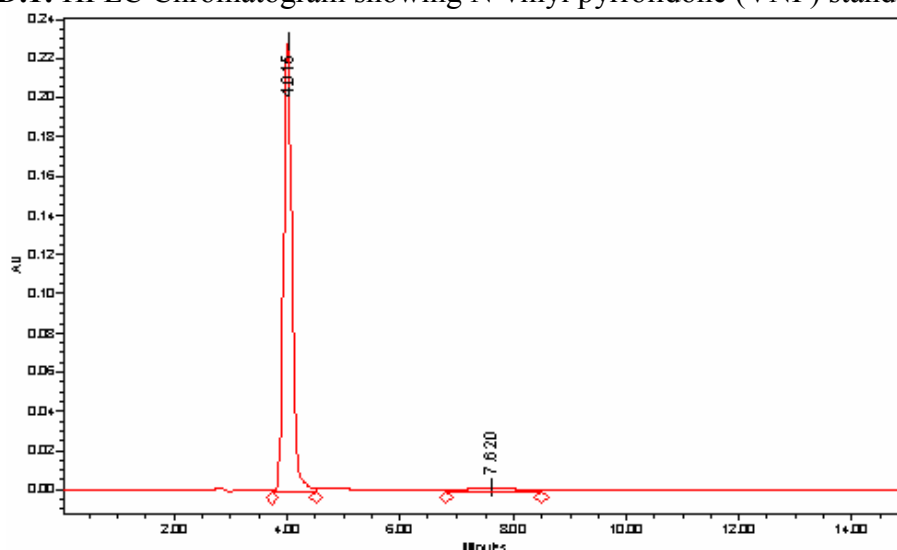


Figure D.2: HPLC chromatogram of liquors from sample 06SJG044 showing peak with retention time at similar time to standard NVP peak, as above. This confirms the presence of NVP in the liquors of sample 06SJG044.

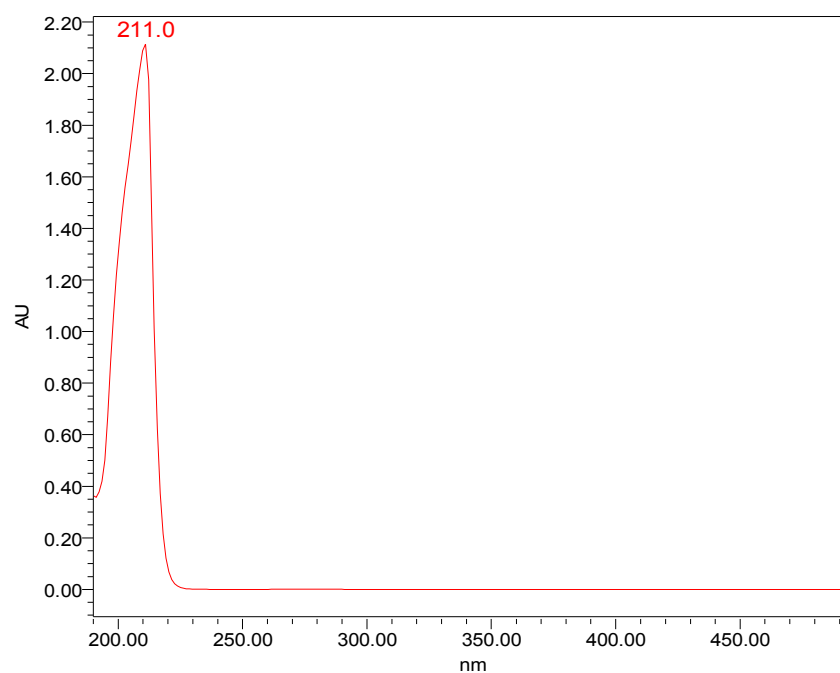


Figure D.3: Typical UV profile showing acrylonitrile (AN) standard

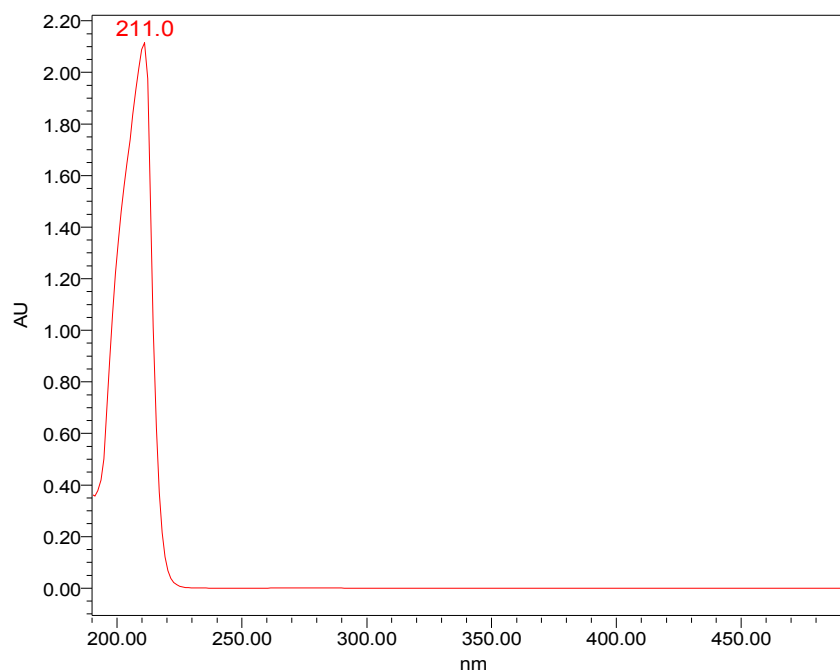


Figure D.4: Showing UV profile of sample with material similar to UV profile of AN.

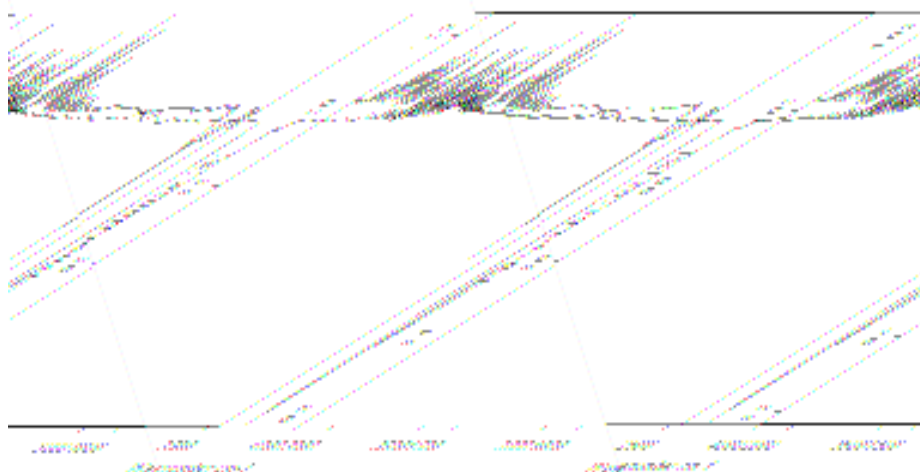


Figure D.5: Typical FT-IR spectra, showing N-vinyl pyrrolidone (NVP) standard with C=O peak shown at approx 2400 cm⁻¹

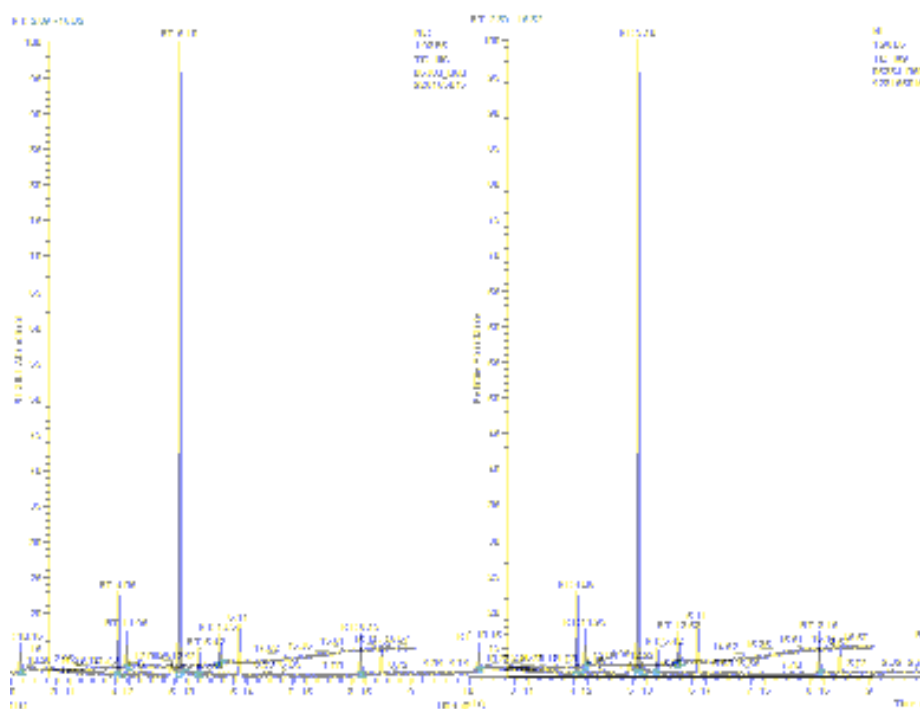


Figure D.6: Typical GC-MS chromatogram, showing sample 06SJG038K with NVP peak at retention time 5.10 mins. Mass of peak was 111, and daughter ion analysis of peak verifies NVP in liquors.
